Steel Pickling for Hot-Dip Galvanizing: Effects of Zinc and Iron on Pickling Rates for Hydrochloric and Sulfuric Acids

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ABSTRACT

Hot-dip galvanizing (HDG) is an industrial process that provides corrosion resistance to steel members by dipping and coating them in liquid zinc. In the preparation of the steel members for HDG, diluted strong acids are used to remove surface level imperfections to ensure the zinc coating adheres to the base metal of the steel in a process known as pickling. These acid solutions containing metal are commonly referred to as pickling liquors. Improvements in the longevity of the acid solutions can be achieved through a practice referred to as acid regeneration, for which guidance exists in the context of hydrochloric acid pickling, but less so for sulfuric acid pickling. The purpose of this study was three-fold: first to validate the process and methods found in existing literature describing regeneration for hydrochloric acid solutions; second to characterize regeneration behavior for sulfuric acid solutions; and third to explore the effects of zinc on the efficacy and efficiency of both acid solutions. The study was conducted using small-scale tests via benchtop experimentation utilizing both hydrochloric and sulfuric acid, elemental iron and zinc powders, and steel coupons with mill scale to determine the pickling rates for the acid solutions. Through testing, the existing procedure for hydrochloric acid regeneration was recreated, a regeneration procedure was developed for sulfuric acid, and the effect of zinc on the pickling reaction was characterized for both acids. It was found that the regeneration process was able to reduce pickling times up to 50%. The presence of zinc was found to impede pickling at low acid concentrations.

KEY WORDS: hot-dip galvanizing, pickling, pickling liquor, acid regeneration

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1.1 – THESIS ORGANIZATION

This thesis is divided into four distinct chapters with additional appendices for data and photos. Overall, Chapter 1 provides an introduction of the research. Chapter 1.2 introduces the topic of study and the motivation for the research, including an explanation of the approach commonly used for hydrochloric acid pickling solution regeneration by the galvanizing industry and the need for regeneration guidance for use with sulfuric acid pickling. Chapter 1.3 presents the primary objectives, split into three separate tasks, as well as their importance to the future efficiency and sustainability of pickling practices in the galvanizing industry. Chapter 2 includes descriptions of the methods and materials used to conduct tests of the various pickling solutions found in each task. Additionally, Chapter 2 describes how pickling for a given coupon was assessed and relevant background information. Chapter 3 presents the results of each task and examines the significance of the findings. Finally, Chapter 4 presents conclusions from the results of the experimental testing and suggestions for further study. All experimental data are provided in Appendices A-F. Appendices A and B contain the full data for the first task and the photos taken during the first task. Appendices C and D contain the full data for the second task and the photos taken during the second task. Appendices E and F contain the full data for the third task and the photos taken during the third task.

1.2 - INTRODUCTION

1.2.1 – Galvanizing and Pickling Overview

Hot-dip galvanizing (HDG) is the process of submerging a steel part into molten zinc to provide a metallurgically bonded zinc layer to protect against corrosion. For hot-dip galvanizing, the molten zinc is at a temperature of about 450° C (840° F) (Sa-nguanmoo et al. 2011). This elevated temperature allows for the zinc to coat and react with the outer layer of the steel to form a protective alloy layer. The zinc coating provides corrosion resistance in two ways: barrier protection and galvanic protection (Marder 2000).

To ensure that the zinc coating adheres evenly and thoroughly to the base metal of the steel being dipped, steel requires cleaning and surface preparation before immersion in the zinc (Marder 2000). Surface preparation for HDG encompasses three steps, with rinsing of the steel part between each step. To ensure a prepared surface, the steel must be treated with a degreaser to remove any organic components, a dilute strong acid solution to remove any mill scale and/or corrosion products, and a fluxing agent to prevent the formation of iron oxides prior to immersion in the zinc and to encourage even wetting of the part with liquid zinc (American Galvanizers Association n.d.). One of the main steps in this process is removing surface-level oxides formed on the steel during production, milling, and transportation to the galvanizing plant. These oxides include surface rust, also known as Hematite – Fe_2O_3, and mill scale, which is comprised of multiple iron oxides: Wüstite – FeO, Magnetite – Fe_3O_4, and Hematite. The iron oxides are dissolvable in strong acids such as hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). Surface cleaning of the steel prior to galvanization is commonly referred to as industrial pickling, or just pickling (Barlow 2015), and is commonly conducted using either hydrochloric or sulfuric acid in the United States.

In the United States, approximately half of the industrial pickling performed uses hydrochloric acid, while the other half uses sulfuric acid (Philipp 2007). The entire HDG process produces environmentally harmful wastes, in the forms of solid, liquid, and gaseous byproducts or emissions. However, the pickling process contributes the most waste, by mass, due to the creation and subsequent disposal of spent pickling acids (Stocks et al. 2005).

Pickling acids incorporate more iron into solution with each steel part put through the solution. After continuous use, a pickling solution, or liquor, will become spent. A spent solution is characterized by containing high levels of iron in solution and by having pickling times above 15-20 minutes. For hydrochloric acid batch pickling operations, the typical immersion types are 5-15 minutes (Hudson 1994). In industry, the practical lower limit of acid concentrations is in the range of 5-9% for hydrochloric acid (Stocks et al. 2005).

A pickling solution can also become impeded due to the presence of high concentrations of dissolved iron compounds, such as ferrous or ferric chlorides ($FeCl_2$ and $FeCl_3$, respectively) in the case of hydrochloric acid (Campano 2012). For sulfuric acid, these dissolved iron compounds are ferrous or ferric sulfates ($FeSO_4$ and $Fe_2(SO_4)_3$, respectively). In both acids, these compounds remained dissolved in the pickling solution until their respective solubility limits are reached.

A solubility limit characterizes the maximum amount of a given compound an aqueous solution can contain. In terms of the pickling process, through repeated removal of mill scale and rust, the pickling liquor can reach a point where no further steel can be pickled; the further addition of iron compounds results in solid crystals being formed within the acid solution. These crystalline solids tend to collect at the bottom of the pickling vat (Campano 2012), and also cling to the side walls of the vat and/or to the part being pickled, causing the pickling reaction to cease.

1.2.2 – The Kleingarn Curve and its Applications

Kleingarn (1988) conducted an important study pertaining to the hydrochloric acid pickling process that provided a framework for acid regeneration. Kleingarn's work brought about a broader understanding of this process still utilized in the galvanizing industry (Campano 2012). While Kleingarn reported several factors that can be used to describe and define the pickling reaction for hydrochloric acid, two of the most impactful aspects of his work are the concept of spent acid regeneration and the figure he derived to illustrate the usefulness of such regeneration, often referred to as the Kleingarn Curve. When used in tandem, these two concepts can aid galvanizers in predicting the rate of pickling for a given solution and how to extend the usable life of a given solution.

Spent acid regeneration describes the process of adding a volume of either fresh, diluted, or comparably less spent acid solution into a previously spent pickling solution. Acid regeneration results in an extension of usability of what would otherwise be a fully spent pickling liquor by increasing the acid concentration and reducing the iron concentration of the newly-regenerated solution, as compared to the initial spent solution (Campano 2012).

The regeneration equations for spent acid require knowledge of the volumes and concentrations of the spent solution, the acid solution used to regenerate the initial spent solution, and the desired acid strength of the regenerated solution. By manipulating these values, two equations are derived that can inform a galvanizer of two important metrics: (1) the amount of spent acid to be removed and replaced with stock or less spent acid solution to create the desired regenerated solution, and (2) the iron concentration of the newly regenerated solution.

Using these principles, Kleingarn constructed a curve providing guidance on how regeneration can be used to improve the lifespan and pickling rates of otherwise spent hydrochloric

acid solutions. Kleingarn's research presents three main relationships: a curve representing solutions that have yet to be regenerated, with slow pickling rates; an optimal solution curve representing possible improvements to pickling reaction rates achievable through regeneration; and a saturation curve representing solubility limits for iron in hydrochloric acid. The curves are defined in terms of the acid and iron concentrations of the hydrochloric acid pickling solution, expressed in units of grams per liter.

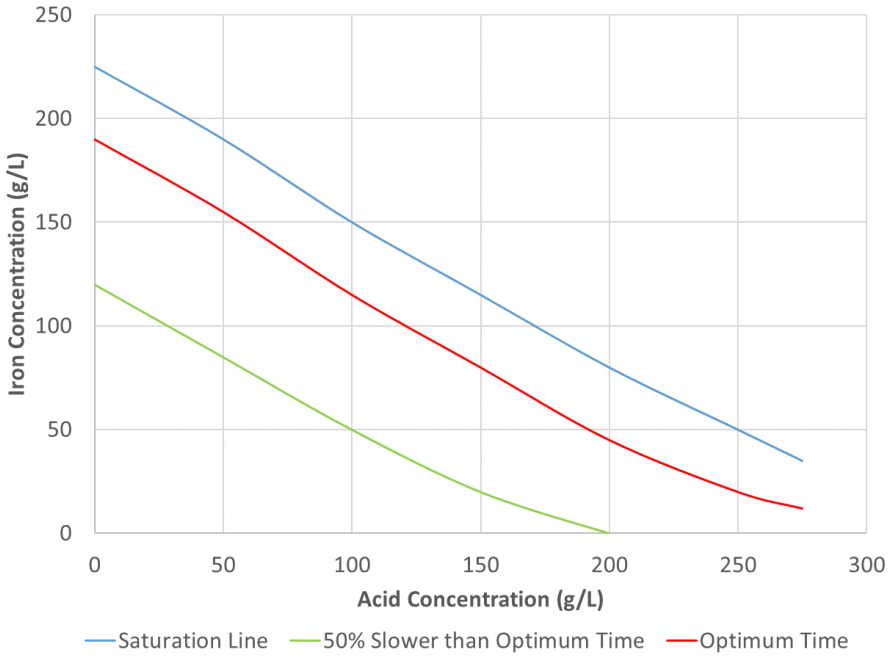

Figure 1: The Kleingarn Curve (adapted from American Galvanizers Association 2019; Kleingarn 1988)

To illustrate the use of the Kleingarn Curve, consider the following example. A galvanizer begins with a fresh pickling solution by filling a tank of a known volume with a solution of 14% hydrochloric acid (acid concentration = 150 g/L; iron concentration = 0 g/L). At this concentration, pickling should occur in approximately 5-10 minutes (Campano 2012). After continued operation, the galvanizer determines that the pickling liquor has degraded to 4.5% hydrochloric acid (46 g/L)

and 82 g/L of iron. At this point, the time to achieve pickling is approximately 20-25 minutes (Campano 2012), a noticeable slowdown in the reaction rate.

Utilizing the regeneration equations described by Kleingarn (1988), the galvanizer can regenerate the solution using stock 36% hydrochloric acid and attempt to regenerate the pickling solution very close to the curve indicating optimum pickling times. The regeneration equations allow creation of a new solution at a given acid concentration through the mixing of two existing solutions of different concentrations. By removing approximately half of the existing solution's volume and replacing it with the stock acid, the newly regenerated solution will have an acid concentration of 18.5% (202 g/L) and an iron concentration of 46 g/L. The regenerated solution will now be able to pickle in approximately 10 minutes, a pickling time 50% of that required prior to regeneration. This example is plotted in Figure 2.

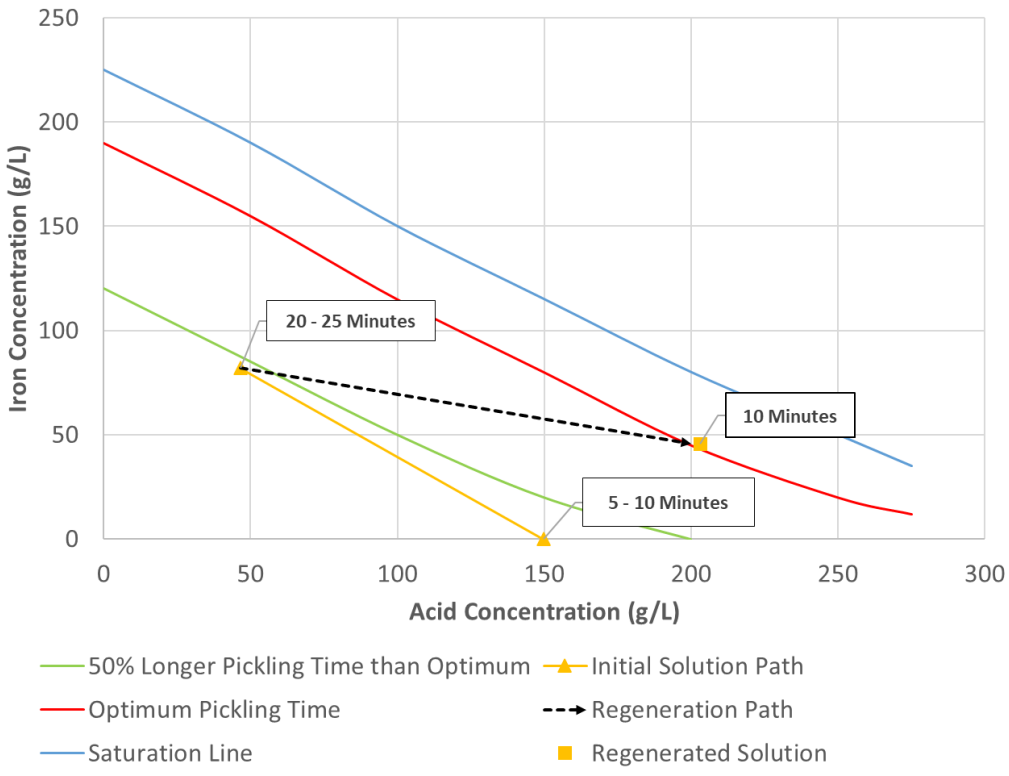

Figure 2: The Kleingarn Curve – Example regeneration for illustrative purposes

The Kleingarn Curve tracks a solution across a span of concentrations it may reach throughout its use. Considering the variability in starting acid concentration, iron concentrations, and the acid concentration of the fresher solution used for regeneration, pickling solutions and their concentrations can plot widely across the curve. With higher starting acid concentrations, the pickling reaction will occur more rapidly (Barlow 2015). By starting with a higher starting acid concentration, more iron can be incorporated into the solution compared to a lower acid solution. Figure 3 illustrates an example showing this variability by having three initial solutions, at 8%, 12%, and 15% acid concentration, all degrade down to 5% acidity with various concentrations of iron.

The fresh solution used for regeneration can also impact the location of a regenerated solution on the Kleingarn Curve. Using a fresher solution with a very high acid concentration will result in a regenerated solution with a similar iron concentration to the spent solution. This is because a high acidity fresh solution will require little spent solution to be removed to achieve the desired regenerated solution acid strength. Regenerating a spent solution with a fresh solution containing some iron is also a possibility. This still achieves the desired increase in acid strength, but the iron concentration will be higher than if regenerated with a fresh solution without iron. Figure 4 provides an example that illustrates the change in regenerated solution location on the Kleingarn Curve due to changes in fresher solution acid concentration. To regenerate the spent solution to 10% acidity, three different fresh solutions, with acid concentrations of 15%, 20%, and 30%, are in consideration. This results in three different possible regenerated solutions with varying iron concentrations.

The Kleingarn Curve has made possible significant reductions in total acid used and spent acid waste (Stocks et al. 2005). A pilot study was conducted with Spanish and French galvanizing

plants to examine the potential benefits of utilizing the practices proposed by Kleingarn; the study found that total hydrochloric acid consumption was reduced by 10-15% and spent pickling solution volume was reduced by 40-50% (Stocks et al. 2005). These reductions in required fresh acid and spent acid waste underscore the utility of Kleingarn's work.

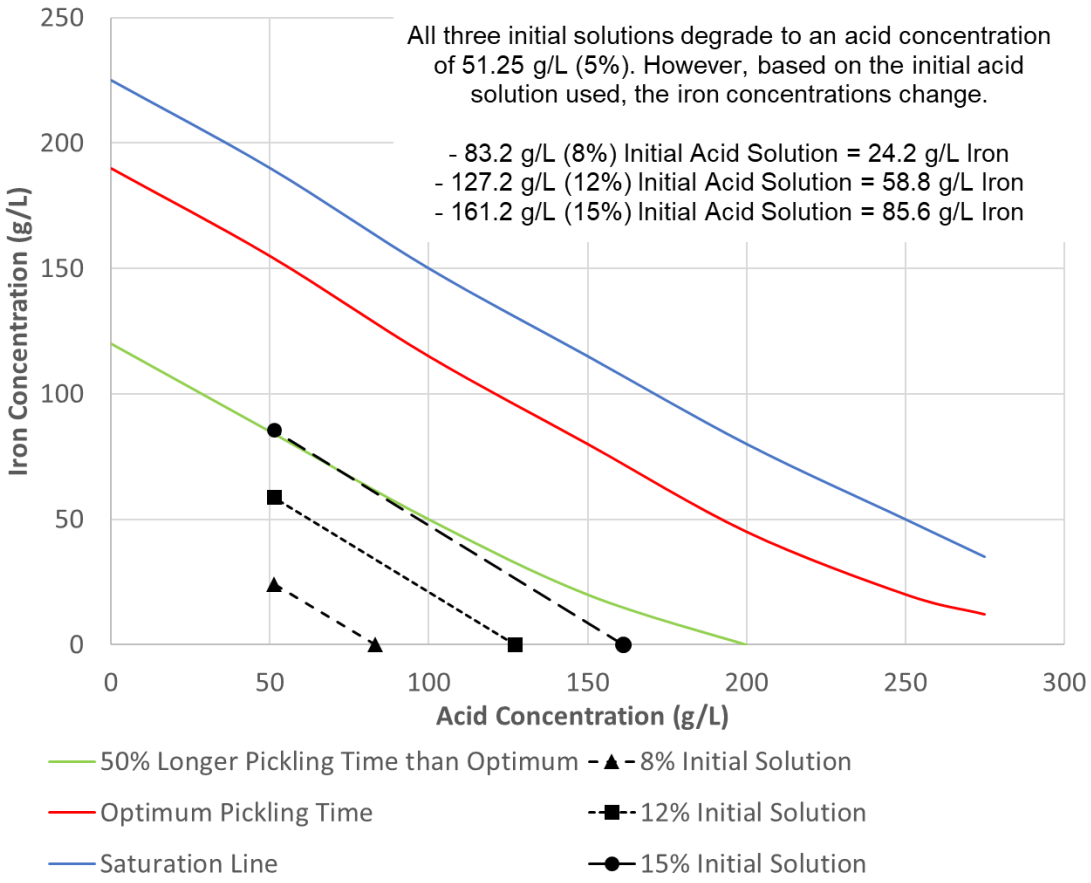

Figure 3: Example of initial acid strength changes to path of solutions on the Kleingarn Curve

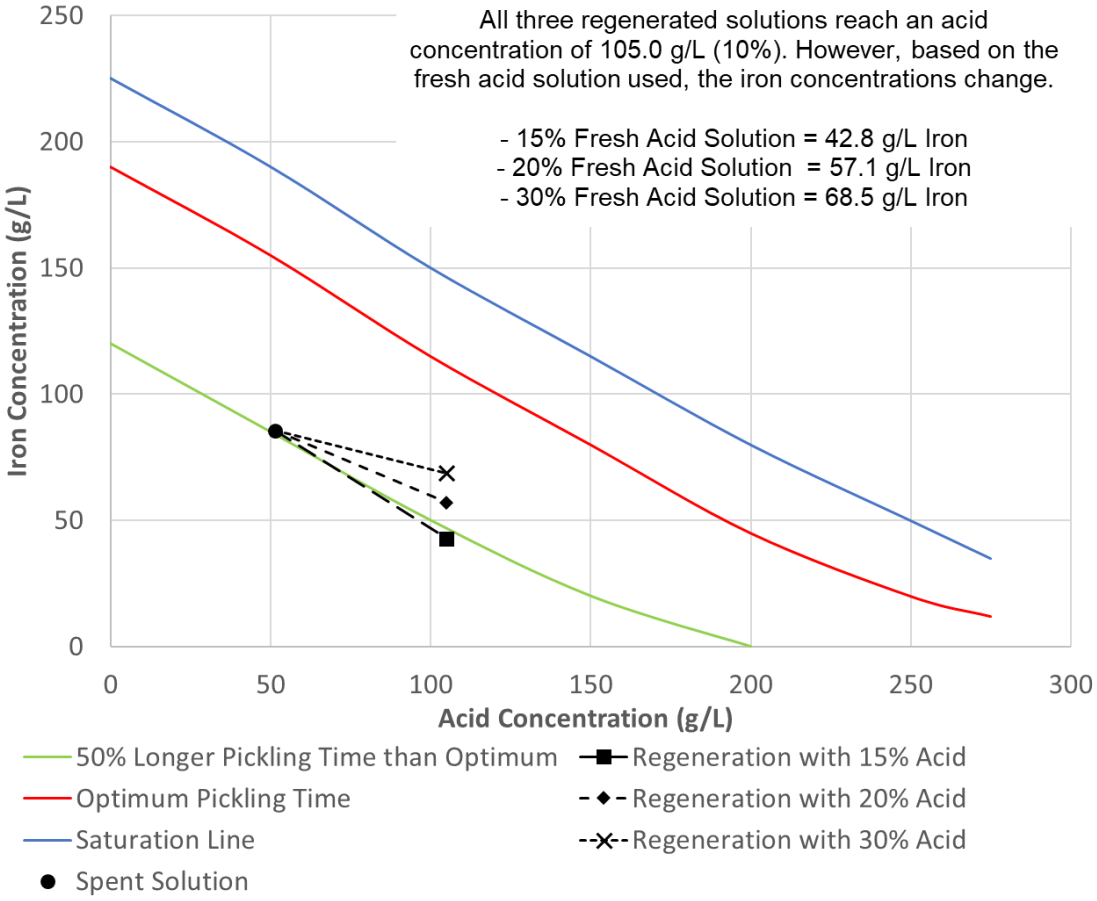

Figure 4: Example of fresh acid strength in regeneration impact on solution path on the Kleingarn Curve

1.3 – OBJECTIVES AND SIGNIFICANCE

The main goals of this research were to develop a framework for regenerating sulfuric acid pickling solutions, and to evaluate the influence of zinc on pickling in hydrochloric and sulfuric acid solutions.

The first task (Task 1) was aimed at replicating the Kleingarn Curve via benchtop experimental testing. This first task contained a total of 15 tests. The second task (Task 2) was focused on developing a regeneration curve for sulfuric acid pickling solutions, tying together acid and iron concentrations. This second task was comprised of 51 total tests. The third task (Task 3)

was to evaluate the influence of zinc on the pickling reaction for both hydrochloric and sulfuric acids. This task was comprised of 20 total tests. Across all three tasks, a total of 86 tests were performed. Each test generated two data points, as each test was carried out simultaneously on two steel coupons with similar levels of mill-scale and rust. The results reported in this paper are averages of the results recorded from the two data points.

This research aims to aid galvanizers in predicting and extending use of their pickling solutions, to support waste reductions. Currently, no analogous curve to the Kleingarn Curve exists for sulfuric acid pickling, presenting an opportunity to improve industry understanding and practices for sulfuric acid pickling. Additionally, the influence of zinc on the effectiveness of the pickling process is currently not well understood. Since galvanizers may need to strip zinc coatings, it is possible for zinc to build up in a pickling liquor much like iron. As galvanizing is a common practice for providing corrosion resistance, advancements in understanding and sustainability of the process may provide benefits for years to come.

2 – MATERIALS & METHODS

All three tasks were conducted using small-scale benchtop tests in the Environmental Engineering Laboratory at the University of Kansas. The standard volume of pickling solutions used to determine the rate of pickling across all three tasks was 50 milliliters (3.05 cubic inches). To gauge the rate of pickling reaction, small A572-50 steel coupons with two exposed faces covered in mill scale and surface rust were used. The surface area of each face containing the relevant iron oxides was 1.27 centimeters by 1.27 centimeters (½ inch by ½ inch). Coupons were allowed to reside in pickling solutions until the full extent of the pickling reaction had occurred, revealing a shiny grey metallic surface of steel base metal underneath.

Visual observation was used to assess completion of the pickling reaction. Throughout the pickling process, iron oxides present in mill scale and surface rust dissolve away until the visual appearance of the steel is uniform, without pits or oxides. Time was recorded for each test to determine the time required for the reaction to occur within a given acid solution. Additionally, coupons were weighed before and after the pickling reaction to estimate the amount of scale and corrosion product removed during the process. The visual changes that occurred during the pickling reaction are evident in Figure 5.

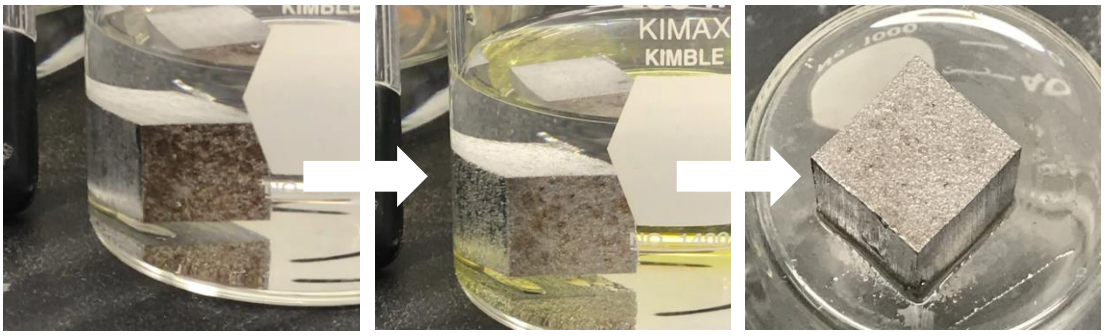

Figure 5: Visual changes to typical steel coupon pickled in a solution of 14% hydrochloric acid

All testing was performed inside a chemical fume hood, as sulfuric and hydrochloric acids can release harmful gasses during the pickling process (Hudson 1994). To simulate accumulation of metal due to repeated pickling of steel and/or zinc within the same acid solution, elemental iron powder (Fe) was used as a proxy. Although iron oxides and elemental iron are fundamentally different in their composition, they yield roughly the same products when reacting with each acid, with the only notable difference being the production of water with the oxides and hydrogen gas with the elemental form (Hudson 1994). In preliminary testing, iron oxides were found to dilute the pickling solutions in ways that were difficult to predict and control, which led to the decision to utilize the elemental form of iron.

Since the Kleingarn Curve was calibrated to the concentration of iron in solution and not mass, and since both elemental iron and iron oxide produce the same iron (II) chlorides through reaction with the acid, no significant changes to pickling solution composition occurred because of this decision. The only noticeable impact was that a greater mass of elemental iron was required to reach a similar level of iron concentration and reduction in acid concentration as compared to the use of iron oxides.

2.1 – Task 1 Testing

The 15 tests conducted for Task 1 can be broken into four groups. Six initial tests were performed to confirm the pickling times at various acid concentrations reported in existing literature (Campano 2012). From these six tests, three solutions were then regenerated to the optimum line shown in the Kleingarn Curve, resulting in an additional three tests to record the effects of regeneration on pickling times. To explore the saturation line shown in the Kleingarn Curve, three tests were performed along the far-left portion of the optimum line. Solutions along this portion of the optimum line are characterized by high concentrations of iron (150+ g/L),

making them likely to reach the solubility limits for iron in hydrochloric acid. These three solutions were then regenerated to concentrations that plotted them above the saturation line. This developed three further solutions that were tested with the intention of reaching and exceeding the solubility limits shown in the Kleingarn Curve.

The Kleingarn Curve is a helpful tool for predicting pickling solution behavior, but it does not quantify pickling time for given solution concentrations (Kleingarn 1988). It presents the possible changes to pickling time in terms of an optimum pickling time (Figure 1), relative to a lower curve that represents 50% slower pickling rates than optimal. This is the only relationship between iron and acid concentrations and pickling time in the Kleingarn Curve. To derive some points of comparison between pickling times and solution concentrations, Campano's (2012) work provides insight into the expected pickling times at various acid and iron concentration.

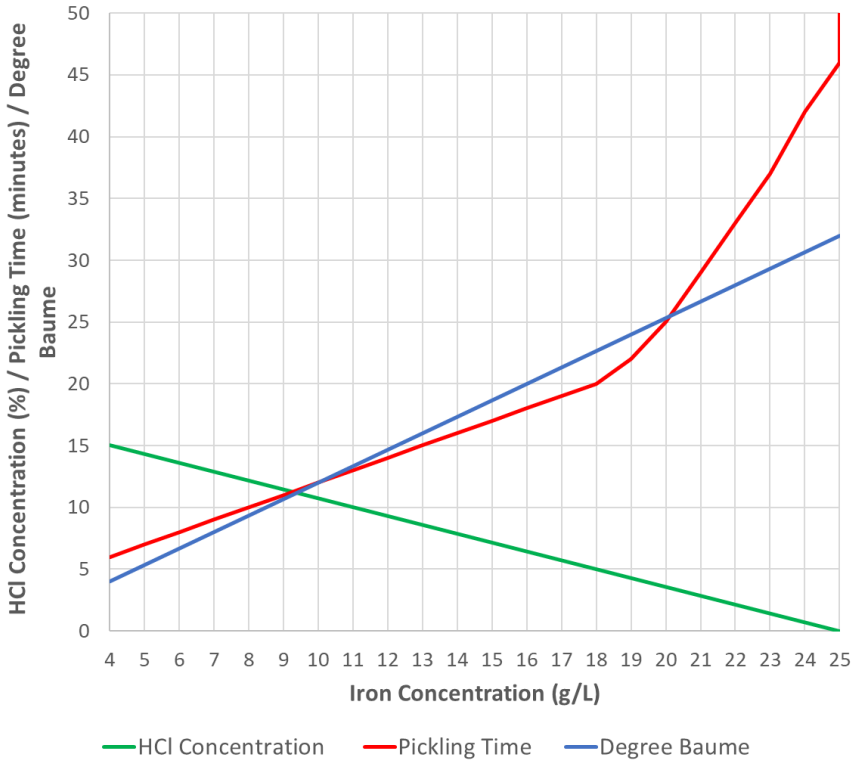

Figure 6: Hydrochloric acid pickling chart (adapted from Campano 2012)

The pickling chart shown in Figure 6 relates multiple variables that can describe a hydrochloric acid pickling solution. The vertical axis describes both the concentration of the acid solution and pickling time for a given solution. The horizontal axis describes the iron concentration in a given solution. The values shown for the iron concentrations in Figure 6 vary significantly from the allowable iron concentrations shown in the Kleingarn Curve; Campano (2012) notes that the probable cause of this discrepancy is likely the difference in methods used to analyze iron content in a solution between his work and Kleingarn's work.

The line labelled HCL Concentration illustrates how acid concentration decreases as iron concentration increases for a fresh hydrochloric acid solution that has been diluted to a starting acid concentration of ~15%. The curve labelled Pickling Time illustrates how pickling time increases as the solution becomes increasingly laden with iron and decreases in acidity. For hydrochloric acid concentrations at or below 3%, pickling times have been observed to dramatically increase and resemble asymptotic behavior (Barlow 2015). Similarly, as hydrochloric acid concentrations increase beyond ~8%, asymptotic behavior can be seen; this indicates that there is a practical limit of the strength of hydrochloric acids used in the pickling application, as further increases in acid concentration do not translate to significant reductions in pickling time (Barlow 2015).

The line labelled Degree Baumé illustrates how the density of pickling solutions changes using a scale known as the Baumé Scale. The Baumé Scale is one of many ways a scientist can calibrate a hydrometer to determine the density of an aqueous solution and properties of that solution tied to its density (Wright et al. 2020). The degree Baumé line reveals the increasing density of a given volume of hydrochloric acid as more iron is incorporated into the pickling solution.

With Campano's (2012) chart providing a basis for expected pickling times of hydrochloric acid pickling solutions, the remaining nine tests in Task 1 incorporate the effects of regeneration to characterize the curves shown in the Kleingarn Curve. Initially, this process of regeneration was explained with a figure known as a mixing cross (Kleingarn 1988). Over time, this mixing cross was simplified into two equations for easier use in industry and academia: one to determine the amount of removed spent acid to achieve a desired level of acid regeneration - Equation 1 - and one to determine the new iron concentration contained within the regenerated solution – Equation 2 (DEFRA 2006; Campano 2012). The original mixing cross, as well as the two equations derived from it, are presented in Figure 7 and Equations 1 and 2.

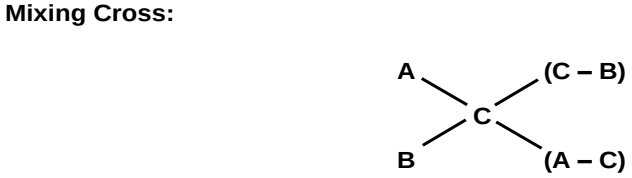

Figure 7: Initial regeneration guidance as a mixing cross (adapted from Kleingarn 1988)

$$y = \frac{(\text{Conc.}_{\text{Regen Solution}} * \text{Vol.}_{\text{Regen Solution}}) - (\text{Conc.}_{\text{Spent Solution}} * \text{Vol.}_{\text{Spent Solution}})}{(\text{Conc.}_{\text{Fresh Solution}} - \text{Conc.}_{\text{Spent Solution}})} \quad \textit{(1)}$$

$$z = \frac{(\text{Iron Conc.}_{\text{Spent Solution}} * \text{Vol.}_{\text{Remaining Spent}}) - (\text{Iron Conc.}_{\text{Fresh Solution}} * \text{Vol.}_{\text{Fresh Solution}})}{(\text{Vol.}_{\text{Regen.Solution}})} \quad \textit{(2)}$$

2.2 – Task 2 Testing

Of the 51 tests contained in the second task, 41 were performed to understand the effects of regeneration on sulfuric acid solutions to develop an optimum line, much like the one in the Kleingarn Curve (Kleingarn 1988). Since the regeneration equations shown in Equations 1 and 2 are based upon the general concepts of solution concentration and volume, they are not tethered to use exclusively with hydrochloric acid. These regeneration equations were applied to the sulfuric

acid tests carried out in Task 2, in the same way that they were applied to hydrochloric acid solutions. The remaining 10 tests were performed to confirm solution saturation, as described in existing literature for the solubility limits of iron in sulfuric acid (Bullough et.al 1952; Kobe and Frederickson 1956).

Sulfuric acid pickling has some key differences from hydrochloric acid pickling, including the need for sulfuric acid pickling to be performed at an elevated temperature, ranging from 50°C to 80°C (110°F to 180°F) (Barlow 2015). By heating the sulfuric acid, pickling times can be reduced compared to pickling at ambient temperatures. In contrast, hydrochloric acid pickling is often carried out in ambient operating temperatures as it is highly volatile. Heating such a volatile solution would increase the production of hazardous fumes (Barlow 2015).

For this research, all sulfuric acid pickling tests in Task 2 and Task 3 were conducted at a temperature of 60°C (140°F). While the temperature of the pickling solution influences required pickling times (Campano 2012; Barlow 2015), the decision to use 60°C (140°F) as the test temperature for sulfuric acid tests was made to represent the approximate midrange of common temperatures seen in industrial applications. The sulfuric acid pickling solutions used in Tasks 2 and 3 were held at 60°C (140°F) using a circulating hot water bath. When testing was performed for a given solution, the solution was transferred to a large glass dish containing a water bath kept at 60°C (140°F), allowing for easy addition of the steel coupons and for unobstructed observation of the coupons as they pickled. Photos of the hot water baths used for testing can be seen in Figure 8.

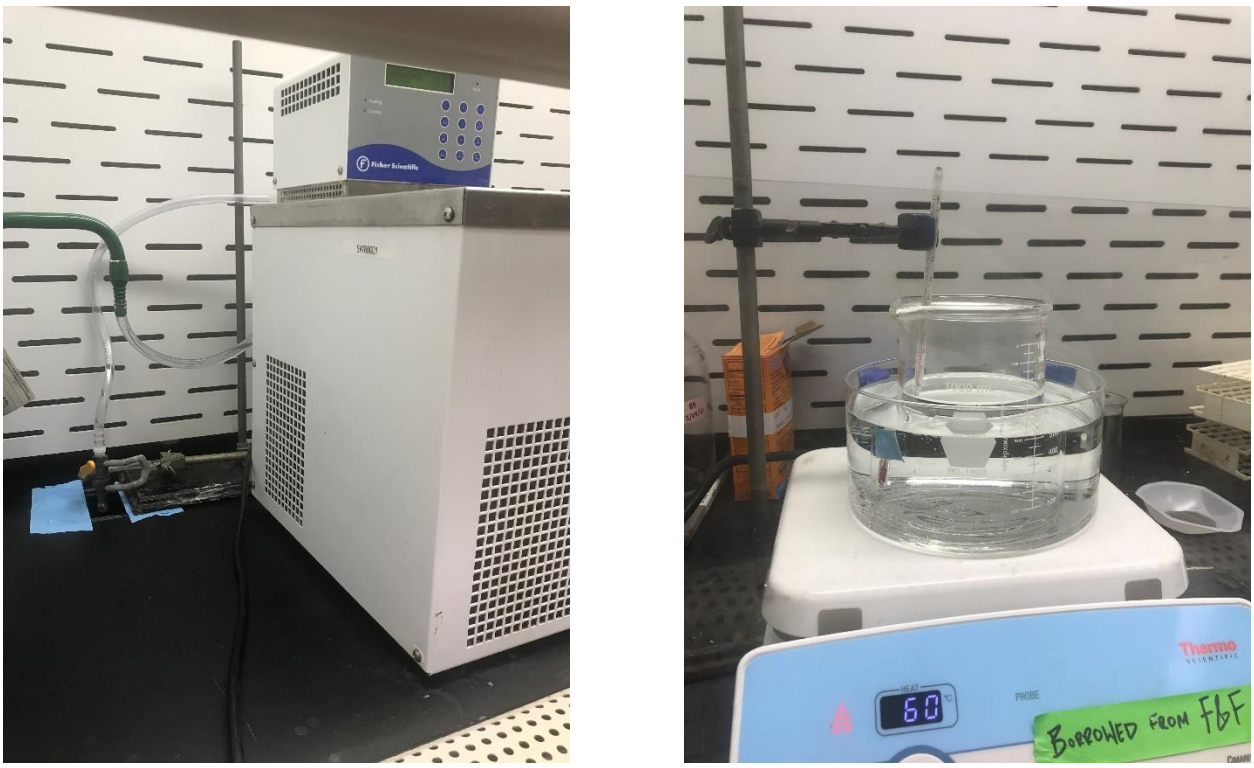

Figure 8: Test set-up for sulfuric acid tests: circulating hot water bath on left, glass dish water bath on right

2.3 – Task 3 Testing

Of the 20 tests conducted in Task 3, there were 10 tests for hydrochloric acid, five of which captured relatively low zinc concentrations (6-19 g/L) and five for relatively high zinc concentrations (30-94 g/L). There were also 10 tests for sulfuric acid: five tests for low zinc concentrations (5-13 g/L) and five for high zinc concentrations (27-67 g/L). For all sulfuric acid tests performed in Task 3, the test temperature of 60°C (140°F) was held constant. The solutions generated for this test had nearly identical acid concentrations to solutions used in Tasks 1 and 2. This allowed for comparison between solutions containing only iron and solutions containing both iron and zinc.

Existing literature on workable concentrations of zinc in pickling solutions is scarce, as the pickling reaction is primarily performed for the removal of iron oxides from steel parts. For hydrochloric acid pickling solutions, a practical limit of 5-12 g/L of zinc in pickling solutions is

suggested by Maass and Peissker (2011). No information regarding practical limits for zinc concentrations in sulfuric acid pickling solutions could be identified. Some pickling solutions are utilized for the purpose of zinc stripping, which can lead to relatively high zinc concentrations. A sampling of pickling solutions from UK galvanizing plants is shown in Figure 9, which illustrates the range of possible zinc concentrations (Stocks et al. 2005). Over 50% of the solutions in Figure 9 contained zinc concentrations below 20 g/L, which roughly corresponds with the practical limits referenced. The decision to examine two ranges of zinc concentrations in Task 3 is due to the possible zinc concentrations shown in Figure 9.

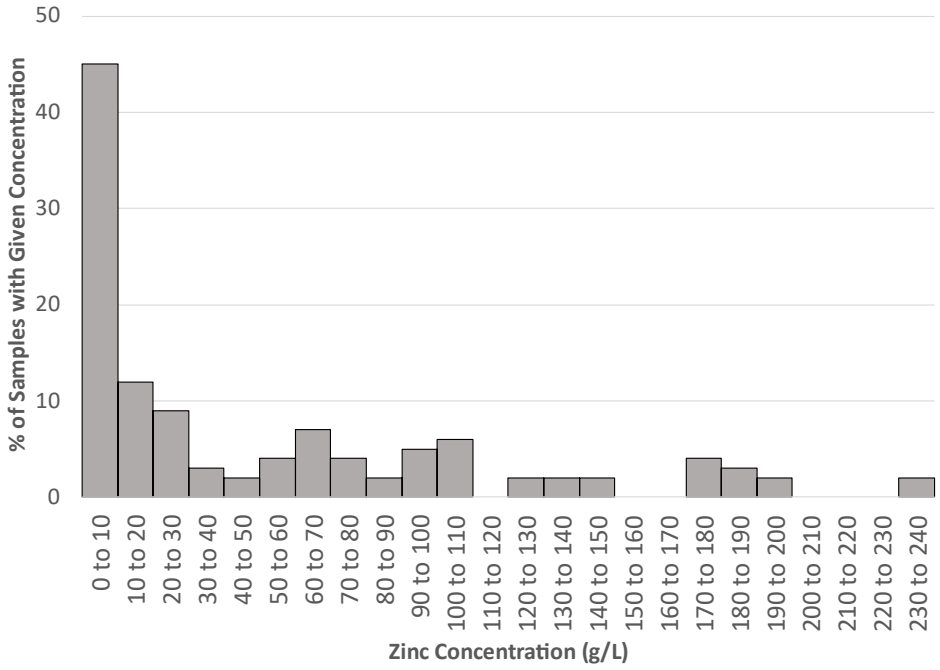

Figure 9: Range of zinc concentration in solution samples (adapted from Stocks et al. 2005)

3 – RESULTS & DISCUSSION

Across all three tasks, a similar convention was used to identify the concentrations of a pickling solution, the following format of "##A##F." The numbers preceding 'A' represent acid concentration expressed as a percentage, and the numbers preceding 'F' represent iron concentration expressed in grams/liter. A solution identified as 5A100F has an acid concentration of 5% and an iron concentration of 100 g/L. For Task 3, 'F' is replaced with the two letters 'FZ' indicating both iron and zinc in the solution. The number preceding these two letters is the combined concentrations of both the iron and zinc in solution. The full expressions of all concentrations can be found in the appendices corresponding to each task's results.

3.1 – Task 1 Results

The tests for Task 1 are presented in two sub-categories, to aid in the understanding of the results and conclusions. The first sub-category, Chapter 3.1.1, contains six tests calibrated with respect to the work done by Barlow Campano, as discussed in Chapter 2.1. The second sub-category, Chapter 3.1.2, contains nine tests that build off of the first six tests and further characterize the Kleingarn Curve, as discussed in Chapters 1.2.2 and 2.1.

3.1.1 – Tests Utilizing Campano's Work as a Comparison

The Kleingarn Curve explains the regeneration process in relative terms, presenting an optimum pickling time curve and a curve representative of solutions that are 50% slower than this optimum pickling time (1988). To establish reference pickling times for various concentrations of hydrochloric acid and iron, research conducted by Campano (2012) informed the initial starting point for Task 1.

A stoichiometric approach utilizing the chemical equations governing the reaction between elemental iron and hydrochloric acid was used to determine the iron concentrations. The

stoichiometric approach compared the known molar masses of reactants and products from the hydrochloric acid pickling reaction. The ratios of these molar masses were then used to determine the iron (II) chloride ($FeCl_2$) generated per gram of hydrochloric acid. Using the molar mass ratio of elemental iron per gram of iron (II) chloride, the iron concentration can be calculated for the 50 mL test volume of the pickling solution. The chemical equation and resulting mass ratios are shown in Equations 3-6.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \quad \textbf{(3)}$$

$$55.85 + 72.92 \rightarrow 126.75 + 2.016 \quad \textbf{(4)}$$

$$\frac{126.75 \text{ g } FeCl_2}{72.92 \text{ g HCl}} = 1.738 \frac{\text{g } FeCl_2}{\text{g HCl}} \quad \textbf{(5)}$$

$$\frac{55.85 \text{ g Fe}}{126.75 \text{ g } FeCl_2} = 0.4406 \frac{\text{g Fe}}{\text{g } FeCl_2} \quad \textbf{(6)}$$

This approach was similar to the approach utilized by Kleingarn (1988). The ratio of elemental iron to iron (II) chlorides was found in both the approach for this research, as well as in Kleingarn's work, to be 0.44 or 44%. Kleingarn's approach rounds the atomic masses for iron to 56 and for iron (II) chlorides to 127. Dividing 56 by 127 results in a ratio of 0.44 or 44%, which is the same ratio shown in Equation 6.

Acid and iron concentrations were calculated for six hydrochloric pickling solutions. These solutions were pinned to locations on the chart shown in Figure 6 according to their acid concentrations. Coupons were tested in each of the six solutions to determine pickling times. The pickling times observed were very similar to the times reported by Campano (2012); four had differences less than 10% relative to pickling times reported by Campano.

The two solutions that had differences in average pickling times greater than 10% did not exceed more than 22% difference from Campano's reported pickling times. The solution with the greatest percentage of difference in pickling time was the solution with the fastest pickling time, and the experimental solution yielded an average pickling time (8.5 minutes) that exceeded Campano's reported pickling time by 90 seconds. Campano (2012) reported that the given pickling time at this solution concentration should be seven minutes. When comparing the relative amount of difference between the experimentally found and the reported pickling times, having a reported time of relatively small magnitude will make even small differences appear large, when reported as a percent difference.

The other solution that exhibited a difference of more than 10% of the reported value was a solution characterized by a relatively long pickling time. Campano (2012) reported that the pickling time for this solution should be around 35 minutes, while the experimentally found average pickling time was 41.5 minutes. The discrepancy here can be explained by the asymptotic behavior of pickling times for hydrochloric acid solutions with low acid concentrations as described in Chapter 2.1. The solution in question was a solution with an acid concentration of 2%, which is below the noted acid concentration of 3% (Barlow 2015), at which this asymptotic behavior of pickling times can be seen. With pickling times increasing dramatically for low acid concentrations, scatter in results can be expected. The results of these initial six tests are presented in Table 1, and the solutions are plotted over the curve shown in Campano's (2012) work in Figure 10.

Table 1: Summary of results from six Task 1 tests – Campano comparison

Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)	Predicted Pickling Time (minutes)	Actual Pickling Time 1 (minutes)	Actual Pickling Time 2 (minutes)	Pickling Time Average (minutes)
2A103F	2	16.9	103	35	42	41	41.5
3A96F	3	28.1	96	28	27	25	26
4.5A82F	4.5	44.1	82	22	23	23	23
6A68F	6	64.3	68	18	18	17	17.5
8A51F	8	82.6	51	15	15	15	15
14A0F	14	149.5	0	7	9	8	8.5

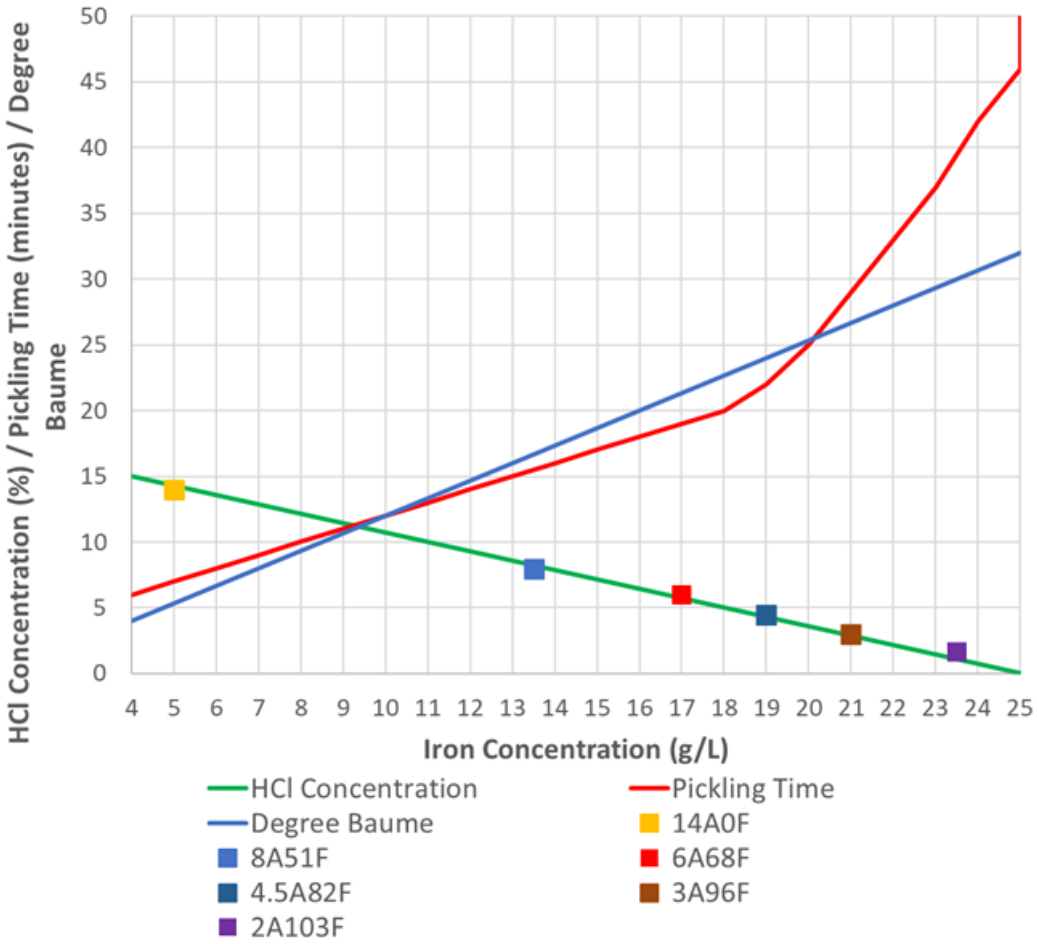

Figure 10: Task 1 solutions – overlaid on chart (adapted from Campano 2012)

3.1.2 – Tests Utilizing Kleingarn's Work as a Comparison

After confirming the reported pickling times from Campano (2012), the solutions generated for those tests were plotted onto the Kleingarn Curve, as shown in Figure 11. From these solutions, the regeneration equations were applied to three of the six solutions. The regeneration equations were applied iteratively until the regenerated solutions had acid and iron concentrations that plotted them in proximity to the optimum pickling time curve outlined by Kleingarn (1988). Then, steel coupons were submerged in the regenerated solutions to determine average pickling times. The paths of these three regenerated solutions, and their pickling times, are shown in Appendix A – Figure A-1.

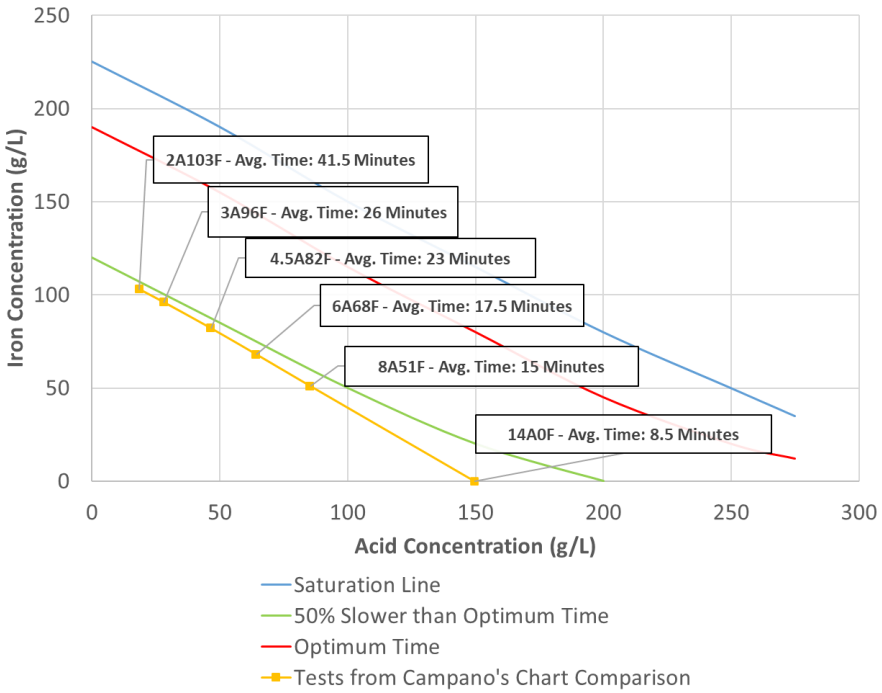

Figure 11: Six solutions from Campano comparison tests plotted on the Kleingarn Curve

The pickling times observed for the three regenerated solutions were all approximately half that of the pickling times for the respective solutions before regeneration. When the reductions in pickling times were averaged across the three solutions that underwent regeneration, the regenerated solutions showed pickling times that were on average 50.8% of the pickling times of

their respective pre-regeneration solutions. It is believed that this is what Kleingarn (1988) was describing with the curve labelled as having 50% slower than optimum pickling times.

With the relationship between the first curves on the Kleingarn Curve characterized with quantitative experimental values for the average pickling times, the remaining portion of the curve to be tested was the saturation line. Three solutions were generated with relatively high iron concentrations. These solutions were then regenerated until the regenerated solutions fell above/outside of the saturation line shown on the Kleingarn Curve. As predicted by Kleingarn (1988), when the three solutions were regenerated to concentrations that would plot them above this line, all three solutions reached their solubility limits. Precipitation of iron (II) chlorides was observed in the form of solid salt crystals. An illustrative photo of the iron (II) chloride solid precipitate that occurred in hydrochloric acid is shown in Figure 12. These solutions are presented on the Kleingarn Curve in Appendix A – Figure A-2.

All three curves proposed by Kleingarn (1988) were shown to exhibit the behavior he described. Additionally, the ability to recreate his results through small-scale benchtop testing was achieved. Table 2 contains a summary of the results of the 12 solutions from Task 1. Figure 13 shows all the solutions in Table 2 plotted on the Kleingarn Curve.

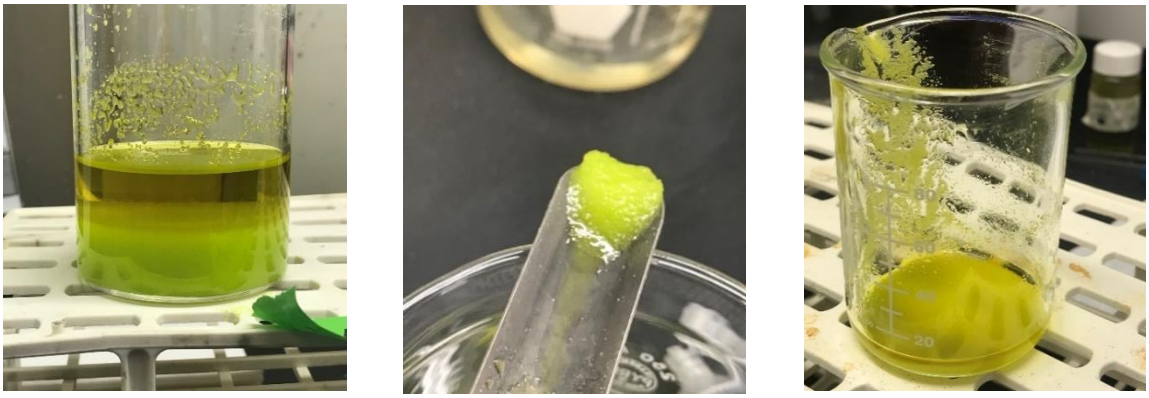

Figure 12: Iron (II) chloride solids formed from exceeding solubility limits in hydrochloric acid

Table 2: Summary of solutions and results for Kleingarn Curve tests

50% Slower than Optimum to Optimum Line Testing

Pre-Regeneration Process				Post-Regeneration Process			
Solution	Acid Conc. (g/L)	Iron Conc. (g/L)	Avg. Pickling Time (Minutes)	Solution	Regen Acid Conc. (g/L)	Regen Iron Conc. (g/L)	Avg. Pickling Time (Minutes)
2A103F	16.9	102.7	41.5	16A60F	172.4	60.2	19.5
4.5A82F	44.1	82.1	23	19A46F	203.0	45.6	10
8A51F	82.6	51.3	15	22A25F	245.0	25.1	8.5

Optimum Line to Solubility Limit Testing

Pre-Regeneration Process				Post-Regeneration Process			
Solution	Acid Conc. (g/L)	Iron Conc. (g/L)	Avg. Pickling Time (Minutes)	Solution	Regen Acid Conc. (g/L)	Regen Iron Conc. (g/L)	Avg. Pickling Time (Minutes)
3A163F	33.0	162.6	43	17A94F	181.8	94.5	Saturated
4A156F	43.4	156.1	43.5	18A89F	193.5	88.6	Saturated
5A149F	54.4	149.2	39	19A83F	205.3	82.9	Saturated

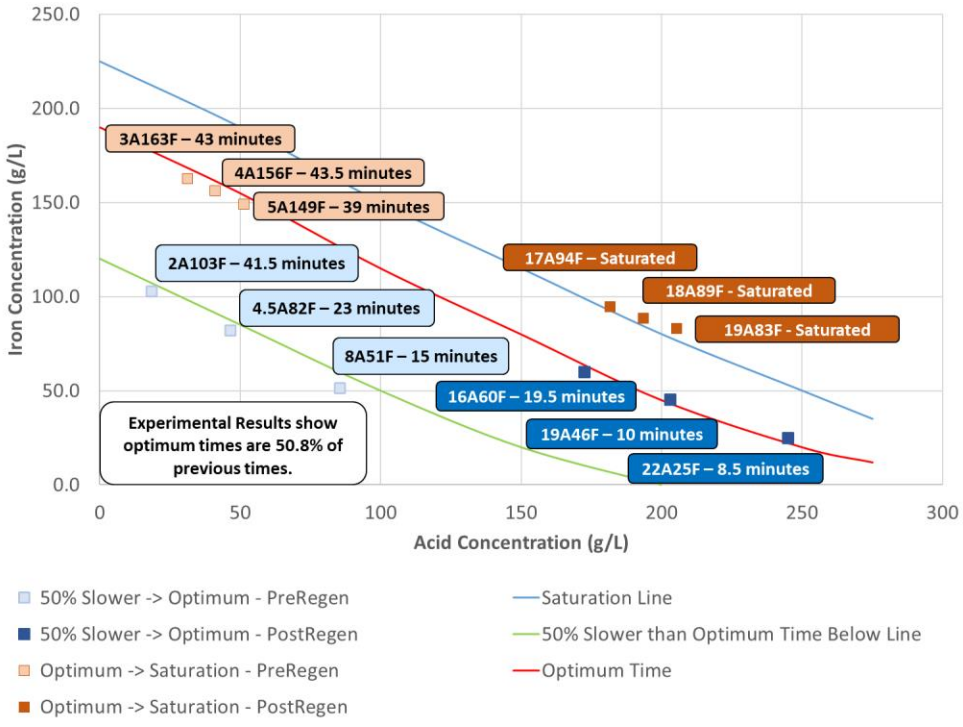

Figure 13: Summary of Task 1 results used to characterize the Kleingarn Curve

3.2 – Task 2 Results

The tests for Task 2 were conducted in two sub-categories to aid in the understanding of the results and conclusions. The first sub-category, Chapter 3.2.1, contains 41 tests that were used to derive an optimum pickling time curve, as described in Chapter 2.2. The second sub-category, Chapter 3.2.2, contains 10 tests used to characterize the saturation curve, indicative of the solubility limits of iron in sulfuric acid, as described in Chapter 2.2.

3.2.1 – Tests for Determination of Optimum Line

To quantify the effects of regeneration for sulfuric acid pickling solutions, an initial acid concentration representative of typical industrial use was needed. While the strength varies based on the application of the pickling bath, 7-18% sulfuric acid is representative of pickling of low-carbon bar steel (Hudson 1994). Based on this, an initial acid concentration of 15% was chosen. Using an initial 15% acid concentration, five pickling solutions with acid concentrations ranging from 2.5%-13% and iron concentrations ranging from 10-80 g/L were created. These solutions can be seen plotted by their concentrations in Figure 14. This step is like the step taken in Task 1, shown in Figure 11.

This approach captured a variety of pickling solutions, from those that are barely spent to those that are almost entirely spent, providing a broad range of possible pickling times. Calculation of the impact of added iron on reducing the acid concentration, as well as the overall iron concentration contained within the solution, was performed similarly to the method described in Chapter 3.1.1. The one notable difference between the two methods comes from the difference in molar masses between hydrochloric acid and sulfuric acid, and the resulting iron compounds formed from the pickling reaction. The chemical reaction and molar mass ratios are shown in Equations 7-10.

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \quad \textbf{(7)}$$

$$55.85 + 98.08 \rightarrow 151.91 + 2.016 \quad \textbf{(8)}$$

$$\frac{151.91 \text{ g } FeSO_4}{98.08 \text{ g } H_2SO_4} = 1.550 \frac{\text{g } FeSO_4}{\text{g } H_2SO_4} \quad \textbf{(9)}$$

$$\frac{55.85 \text{ g Fe}}{151.91 \text{ g } FeSO_4} = 0.3676 \frac{\text{g Fe}}{\text{g } FeSO_4} \quad \textbf{(10)}$$

Steel coupons were submerged in five initial sulfuric acid pickling solutions, and pickling time for each initial solution was recorded. Then, all five solutions were regenerated in 5% increments, from their initial acid concentrations to a maximum acid concentration of 30%. The pickling times for each initial solution's set of incremental regenerations was recorded at these 5% increments, providing an understanding of the effects of regeneration on pickling time across a variety of initial pickling solutions. A visual representation of this process and the accompanying changes in pickling times, shown as data tags, is shown in Figure 15.

This process is like the one illustrated in Figure A-1 that was used for Task 1. However, with Task 2, there was no known curve to identify an optimum point of regeneration for a sulfuric acid solution. Incremental regenerations were performed to capture the change in pickling rate across multiple concentration changes for one initial solution due to regenerations of varying strengths. In Task 1, the optimum pickling time curve found on the Kleingarn Curve allowed for easy prediction of required regeneration. Table 3 shows the initial solution concentrations from which the incremental regenerations were performed. The data containing the acid and iron concentrations found at each incremental regeneration is provided in Appendix C Tables C-1 through C-3.

After recording the pickling times shown for the solutions in Figure 15, some of the data revealed little to no significant improvements to pickling times through regeneration. Across all five initial solutions, pickling times showed little practical improvement for regenerations above 20%. Each solution had incremental regenerations to 25% and 30% acid concentration. These acid strengths exceed the 18% maximum concentration reported for low-carbon bar steel by Hudson (1994). These data points were considered outside of the range of practical use, and they were subsequently removed from the data considered in development of an optimum pickling time curve. Two of the five initial solutions had moderately high acid concentrations (10% and 13%), and regenerations of these two solutions showed little change in pickling times (less than 5 minutes in reduction from their initial acid concentrations to their maximum regenerated concentrations of 30%). Data for these two solutions was also removed from the dataset considered for determination of an optimum pickling time curve. The optimum pickling time curve describes reductions in pickling time due to regeneration, and initial solutions that pickle steel relatively fast with no significant benefit from regeneration do not provide insightful data for this curve. All data points removed from further analysis are shown with crosses in Figure 15.

Table 3: Initial sulfuric acid pickling solution concentrations

Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)
2.5A80F	2.46	25.90	79.71
5A63F	5.22	55.90	62.63
8A46F	7.88	85.90	45.55
10.5A29F	10.46	115.90	28.47
13A11F	12.97	145.90	11.39

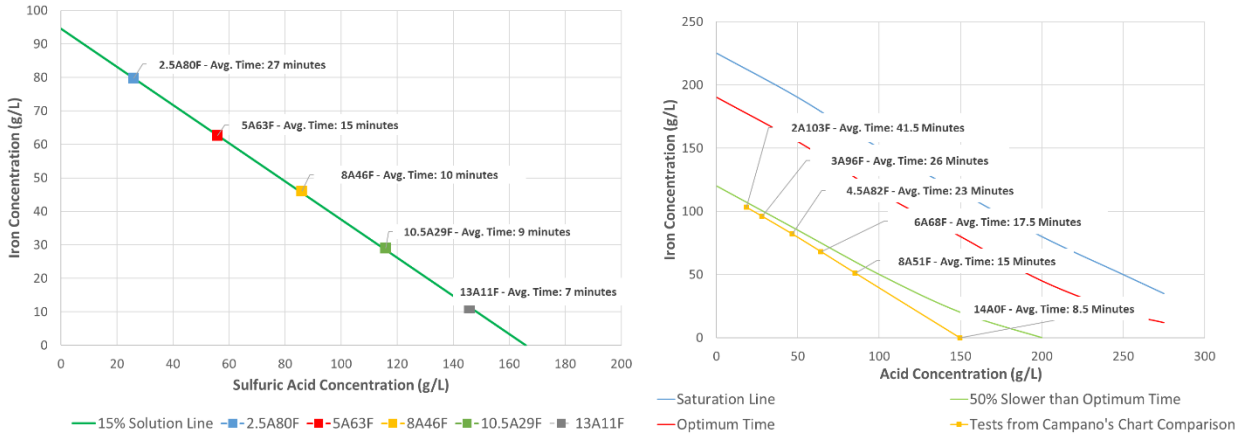

Figure 14: Initial solutions tested for Task 2 creation of an optimum curve – the Burnett Curve for the relationship between acid and iron concentrations and pickling rate of sulfuric acid raised to 60°C. Figure 11 shown on right to illustrate similarities between steps taken in Tasks 1 and 2.

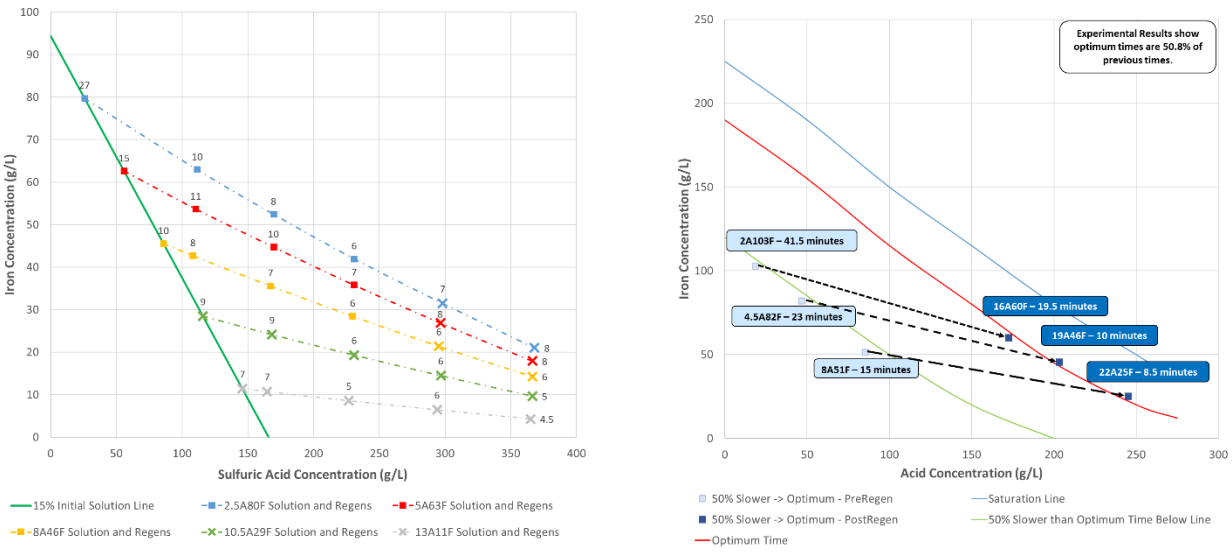

Figure 15: Initial solutions & regenerations tested for Task 2 – the Burnett Curve. Figure A-1 shown on the right to illustrate similarities between steps taken in Tasks 1 and 2.

After re-focusing on a more practical range of acid concentration, the need for more data points to fully develop the optimum pickling time curve arose. To capture the effects of solutions that have already been regenerated once, thus allowing them to contain more iron, three more initial solutions were developed. The three solutions had initial sulfuric acid concentrations of 0.7%, 2.6%, and 4.5%. These solutions were regenerated in approximately 3% increments, as the

initially low acid concentrations would begin showing much faster pickling times through incrementally less regeneration than the previously described solutions. The data from the tests of these solutions and their regenerations, including their acid and iron concentrations, can be found in Appendix C Tables C-1 and C-2. The results of these solutions, along with the prior solutions that fell within a practical range, are shown in Figure 16. Each plotted point is sized relative to its pickling time, and pickling times are shown as data tags.

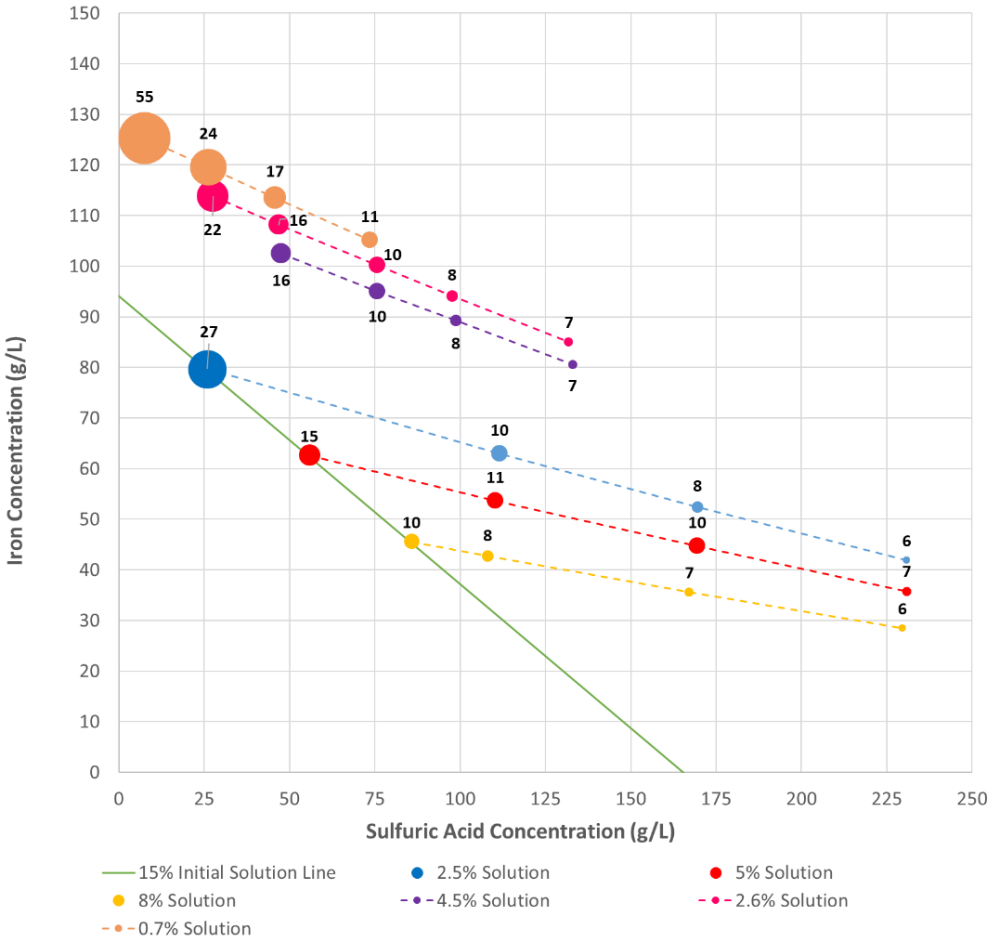

Figure 16: All solutions considered for the development of optimum curve – The Burnett Curve

To develop the optimum pickling time curve for these data points, the relationship between the two relevant regions of the Kleingarn Curve - an optimum solution having half the pickling time of its pre-regenerated solution - was used. To determine the regenerated acid and iron concentrations that would represent half of the pickling time for each initial solution tested, a general relationship between sulfuric acid concentration and pickling time was needed. With this connection, the acid concentration corresponding to half of each initial solution's pickling time could be determined. Then, the second regeneration equation (Equation 2) could be applied, using the known values for the solution's initial and desired regenerated acid concentrations, resulting in the iron concentration at this half-time regenerated solution. The American Galvanizers Association has a figure illustrating the relationship between sulfuric acid concentration and pickling times (Barlow 2015), shown in Figure 17.

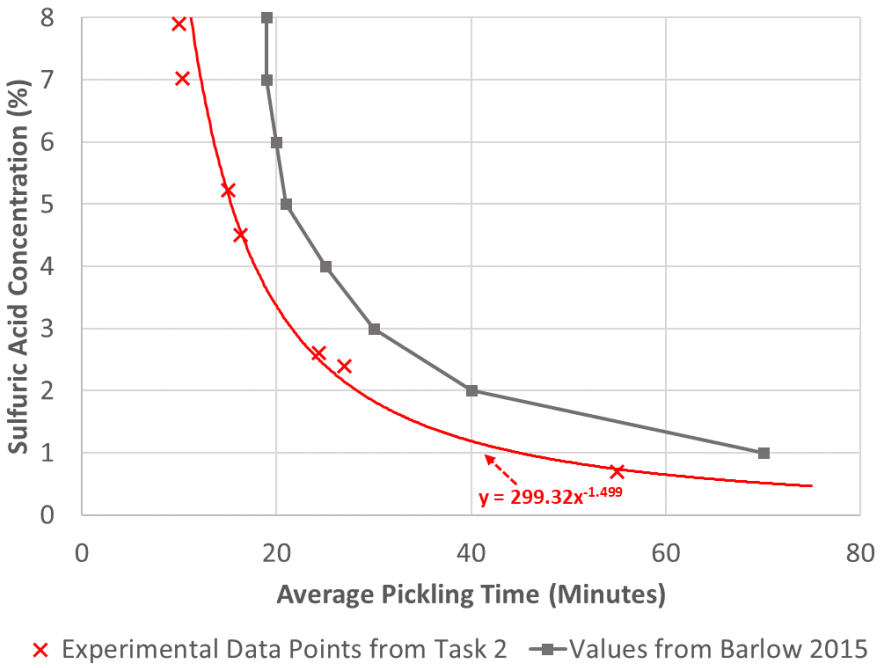

Figure 17: Sulfuric acid concentration vs. pickling times at 60°C (adapted from Barlow 2015)

Using data gathered from Task 2, a curve like Barlow's (2015) was created to ensure validity between his curve and the experimental results. The experimentally derived curve showed a similar appearance to the one in Barlow (2015), with the notable difference of faster pickling times at higher concentrations of acid. This can be explained by Barlow's curve considering sulfuric acid concentrations up to 8%. The experimental data considered regenerated solutions. above this 8% threshold, resulting in generally faster pickling times. The two curves are shown in Figure 17.

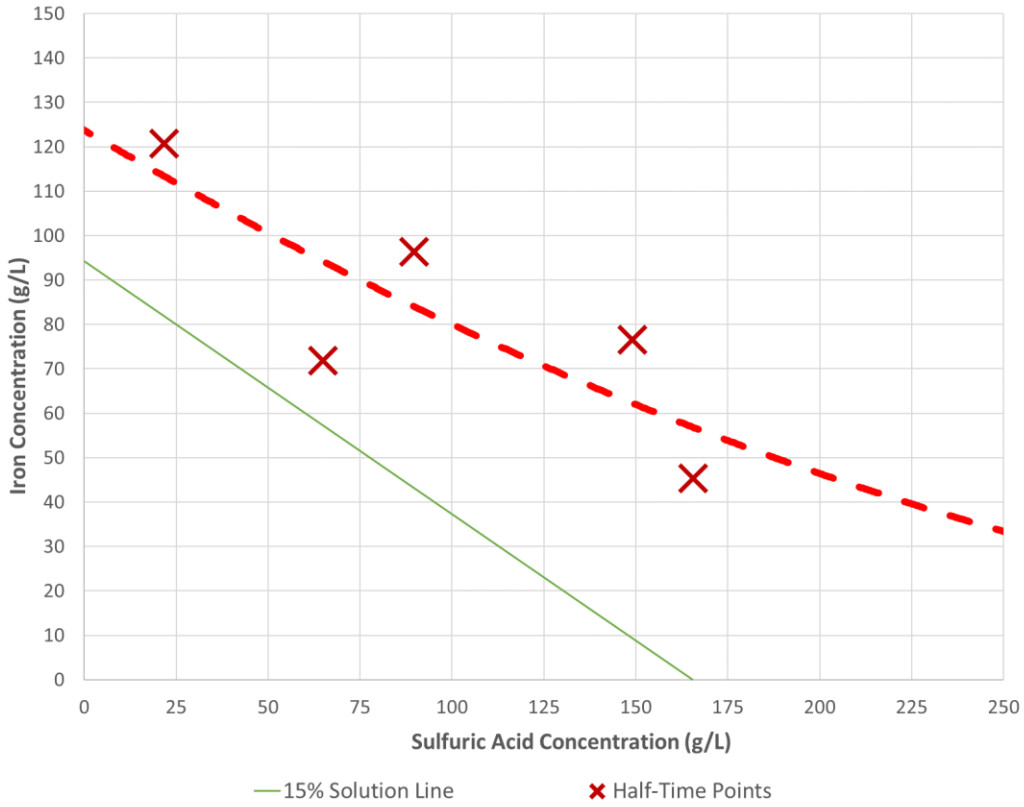

Figure 18: Plotting of points for the determination of the optimum curve – The Burnett Curve

From the experimental curve shown on the left in Figure 17, a relationship between sulfuric acid content and expected pickling time was generated by fitting a curve to the data and the equation describing this curve, (Equation 11). Using this equation, in conjunction with the

regeneration equations, points that were representative of the necessary regeneration of the initial solutions to produce an optimum pickling time - a pickling time equivalent to half of a pre regenerated solution's pickling time – were found and plotted with the sulfuric acid regeneration curve. The resulting best fit curve is shown in Figure 18.

$$\text{Sulfuric Acid Concentration } (\%) = 299 * (\text{Pickling Time})^{-1.5} \qquad \textbf{(11)}$$

3.2.2 – Tests for Determination of Saturation Line/Solubility Limits

To determine the region of the Burnett Curve that would illustrate solubility limits of iron in sulfuric acid, an existing solubility curve for these two materials was examined (Cullivan n.d.). Figure 19 shows the existing curve for iron solubility in sulfuric acid. The existing curve was created from findings across multiple bodies of work: Belopolskly and Shpunt (1941), Bullough et.al (1952), and Kobe and Frederickson (1956). The figure illustrating the existing understanding of the solubility limits for iron in sulfuric acid presents the data in format that was not readily comparable to the format used in this research. The existing relationships show solubility of iron, presented as % weight/volume, for different acid concentrations, also presented as % weight/volume, across a range of possible temperatures. However, the Burnett Curve finds its basis using a similar format as the Kleingarn Curve, with iron and acid concentrations presented in grams/liter.

The process used to convert the solubility limits presented in existing literature into a format that could be incorporated with the Burnett Curve is outlined in the following. Multiple known values of the solutions considered are required, including density of the iron compound formed from reaching the solubility limit, density of sulfuric acid solutions across a range of

concentrations, and solution temperature. The process is a series of conversions between various ways to describe the amount of iron required to reach saturation within a sulfuric acid solution.

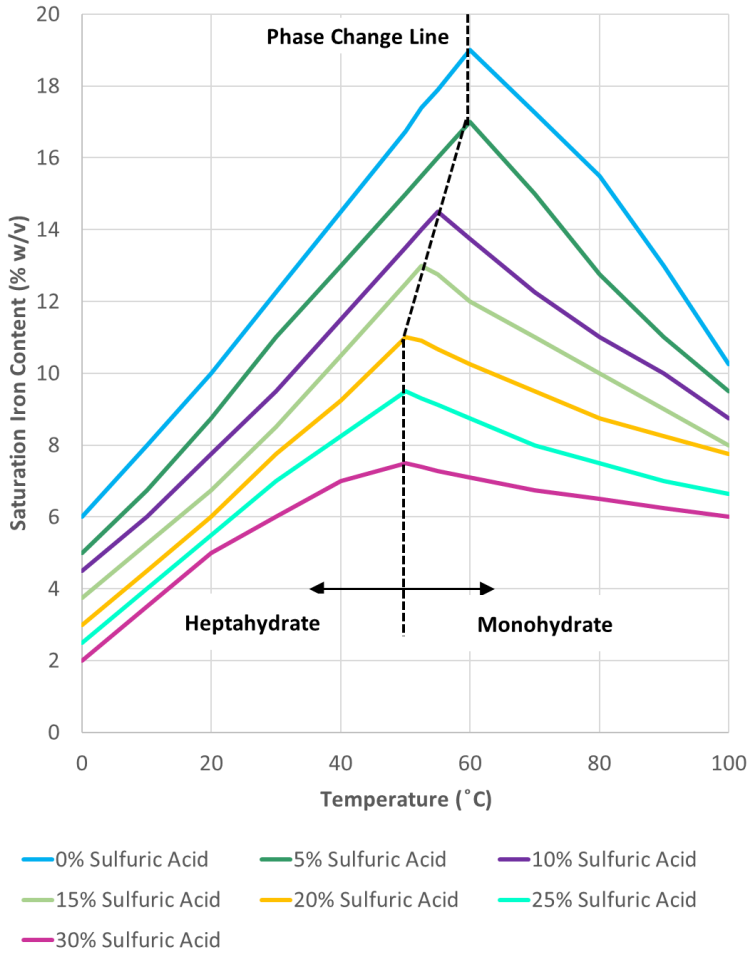

Figure 19: Solubility of iron in sulfuric acid solutions (adapted from Cullivan (n.d.) – from Belopolskly and Shpunt (1941), Bullough et.al (1952), and Kobe and Frederickson (1956))

First, the concentration of iron required to reach the solubility limits for a sulfuric acid solution must be converted into a mass of iron that corresponds to reaching these limits in an acid solution containing 100 milliliters (6.10 cubic inches) of water. This conversion must be performed according to the density of the iron compound predicted to form from the conditions considered. For solutions with sulfuric acid concentrations ranging from 0-5%, the density used was that of the heptahydrate (1.895 g/mL), assuming that the temperature would be slightly lower than 60°C

(140° F) due to transferring solutions in-and-out of hot water baths. For sulfuric acid solutions above this concentration range, the monohydrate was the precipitate expected based on the existing figure, and the accompanying density (3 g/mL) was used.

The mass of iron must be adjusted for the actual amount of water present in a sulfuric acid solution of a given acid concentration. This adjustment can be performed by manipulating the density of a sulfuric acid solution at a given concentration, providing the volume of acid contained within 100 mL (6.10 $in.^3$) of that acid solution. The remaining volume of the 100 mL (6.10 $in.^3$) solution comes from water used to dilute the acid to the considered acid concentration. With the mass of iron in grams correctly attuned for the volume of water present in the acid solution, the mass considered for a volume of 100 mL (6.10 $in.^3$) can be multiplied by ten to produce a mass of iron needed to reach the solubility limit in 1000 mL, or 1 liter (61.0 $in.^3$), of the sulfuric acid.

To illustrate this process, a series of tables, equations and figures are shown. Table 4 presents the iron concentrations, as % weight/volume or w/v, that correspond to various sulfuric acid concentrations, also as % w/v, found from the existing solubility curve. Equation 12 shows the formula for converting an iron concentration, as % w/v, into a mass of iron required to reach saturation for 100 mL (6.10 $in.^3$) of water. Table 5 presents the remaining steps and values used in those steps. This table shows the mass of iron found (using Equation 12) divided by the 100 mL of water used as a standardized volume. The following column in Table 5 contains the volume of sulfuric acid contained in 100 mL (6.10 $in.^3$) of solution for each listed acid concentration. From this volume value, a mass of iron required for reaching saturation for each sulfuric acid solution is shown in the next column of Table 5. Equation 13 shows the method for converting mass of iron per 100 mL (6.10 $in.^3$) water to a representative mass required to reach saturation for a given sulfuric acid concentration. Finally, the last column of Table 5 presents the concentration of iron

(g/L) indicative of reaching the solubility limits for each sulfuric acid solution, which is found by taking the value of the previous column and multiplying by ten. Figure 20 presents these theoretically derived solubility limits for iron in sulfuric acid overlaid on the Burnett Curve.

Table 4: Sulfuric acid concentrations and corresponding iron required for saturation

Acid Conc. (% w/v)	Required Iron (% w/v)	Acid Conc. (% w/v)	Required Iron (% w/v)
0	19.1	15	11.9
1	18.5	18	11
3	17.6	20	10.2
5	16.7	23	9.4
8	14.9	25	8.7
10	13.8	28	7.7
12	12.7	30	7

$$\text{Iron}_{\text{Sat.}}\,(\text{g}) = \frac{\text{Iron}_{\text{Sat.}}\,(\%\frac{\text{w}}{\text{v}})}{[\,1-\left(\frac{\text{Iron}_{\text{Sat.}}\left(\%\frac{\text{w}}{\text{v}}\right)}{100\text{ mL}}*\frac{1}{\text{Density of Iron Sulfate form}\left(\frac{\text{g}}{\text{mL}}\right)}\right)]} \qquad \textit{(12)}$$

$$\text{Iron}_{\text{Sat.in Solution}}\,(\text{g}) = (100\text{ mL water} - \text{Volume of Acid}_{100\text{ mL Solution}}) * \text{ Iron}_{\text{Sat.}}\,(\text{g}) \qquad \textit{(13)}$$

Table 5: Conversion from iron mass (g) for 100 mL water to iron concentration (g/L)

Acid Conc. (%)	Iron to Reach Saturation (g/100 mL water)	Volume of Acid in 100 mL of Given % Solution (mL)	Iron Adjusted for 100 mL of solution (g)	Saturation Iron Conc. (g/L)
0	0.212	0.00	21.24	212.4
1	0.205	0.57	20.38	203.8
3	0.194	1.72	19.07	190.7
5	0.183	2.91	17.77	177.7
8	0.157	4.74	14.96	149.6
10	0.145	6.00	13.63	136.3
12	0.133	7.29	12.33	123.3
15	0.124	9.29	11.25	112.5
18	0.114	11.35	10.11	101.1
20	0.106	12.76	9.25	92.5
23	0.097	14.99	8.25	82.5
25	0.090	16.52	7.51	75.1
28	0.079	18.88	6.41	64.1
30	0.072	20.50	5.72	57.2

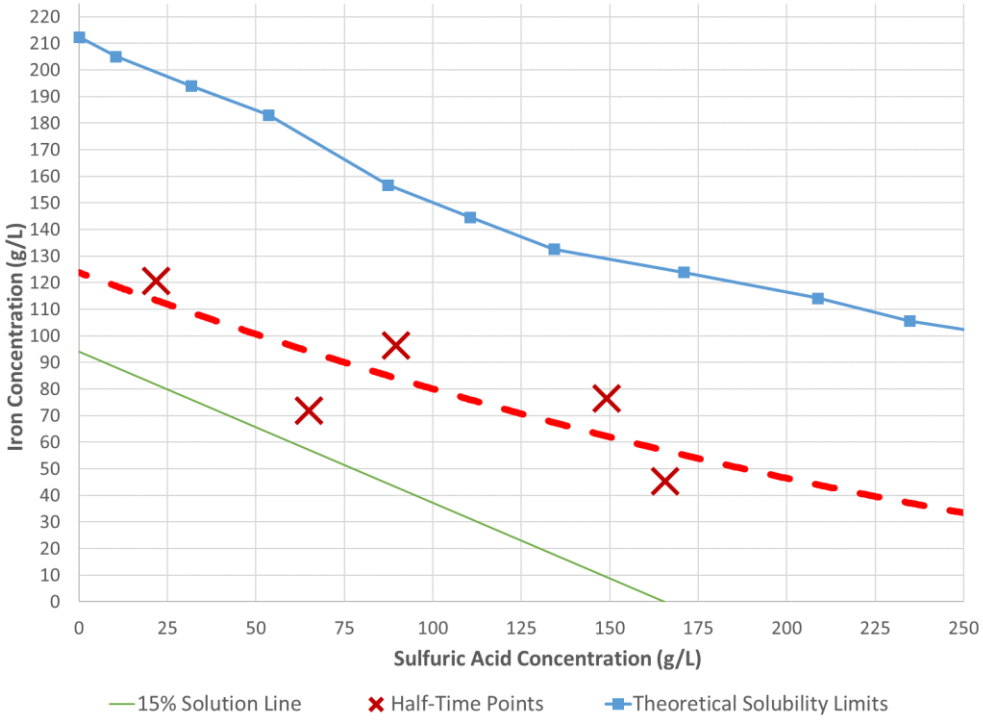

Figure 20: The Burnett Curve – Theoretical solubility limits added

To confirm the solubility limits determined through stoichiometry, a group of three solutions were tested. The approach for the creation and testing of these solutions was like that used to confirm the solubility limits of the Kleingarn Curve. These three solutions had high initial iron concentrations, causing them to be plotted just below the line representative of the derived solubility limits. These three initial solutions were then regenerated incrementally until the effects of saturation were observed, with the sulfuric acid and iron concentrations recorded at each point saturation occurred. These three solutions and their incremental regenerations are shown in Figure 21. Shown next to this is Figure A-2, which is meant to highlight the similarity in the approach taken between Tasks 1 and 2. The crosses on these solution paths shown in Figure 22 indicate the solution with the lowest iron concentration where saturation was observed.

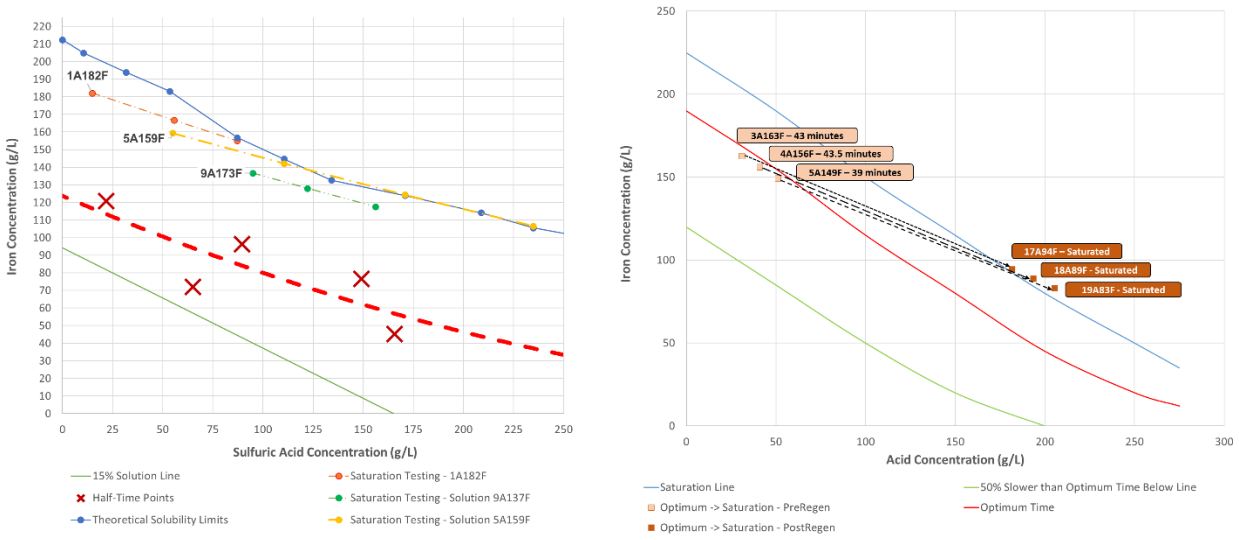

Figure 21: Saturation line solutions & regenerations tested for Task 2 – the Burnett Curve. Figure A-2 shown on the right to illustrate similarities between steps taken in Tasks 1 and 2.

Figure 23 adds a second-order polynomial relationship fit to describe the experimentally observed solubility limits. Figure 23 represents the finalized version of the Burnett Curve. It contains a curve illustrating an initial sulfuric acid solution with a concentration of 15% or less, an optimal pickling time curve illustrating the acid and iron concentrations of regenerated solutions that would halve the pickling time of a solution prior to regeneration, and a curve illustrating the solubility limits for iron in sulfuric acid determined through existing literature and experimental testing. Figure 24 shows photographs of the solid iron (II) sulfate precipitates formed from saturation.

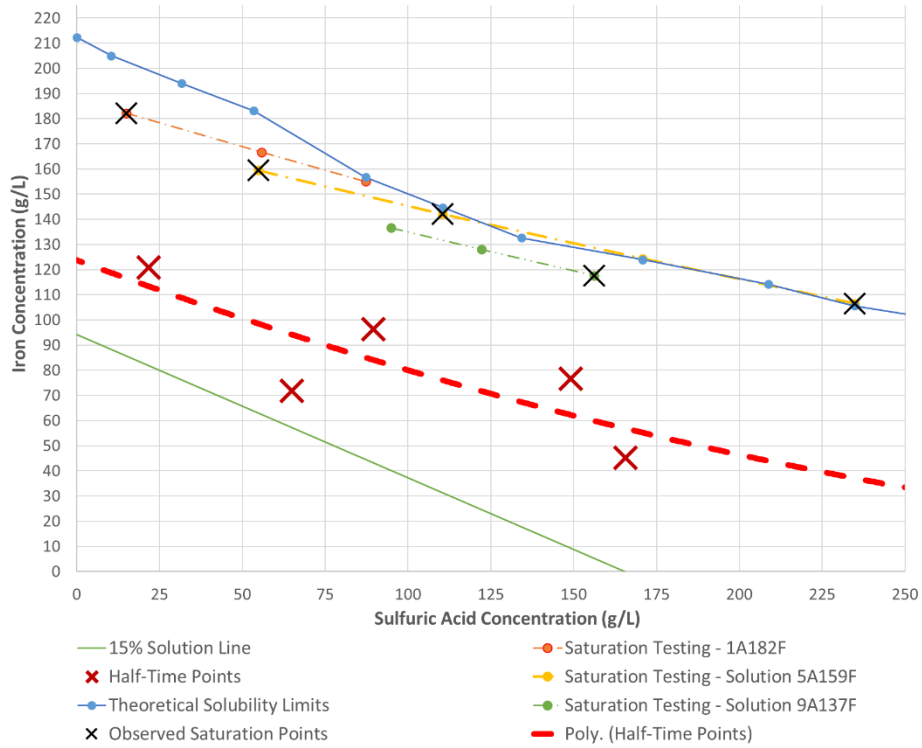

Figure 22: The Burnett Curve – Saturation test solutions and locations of observed saturation

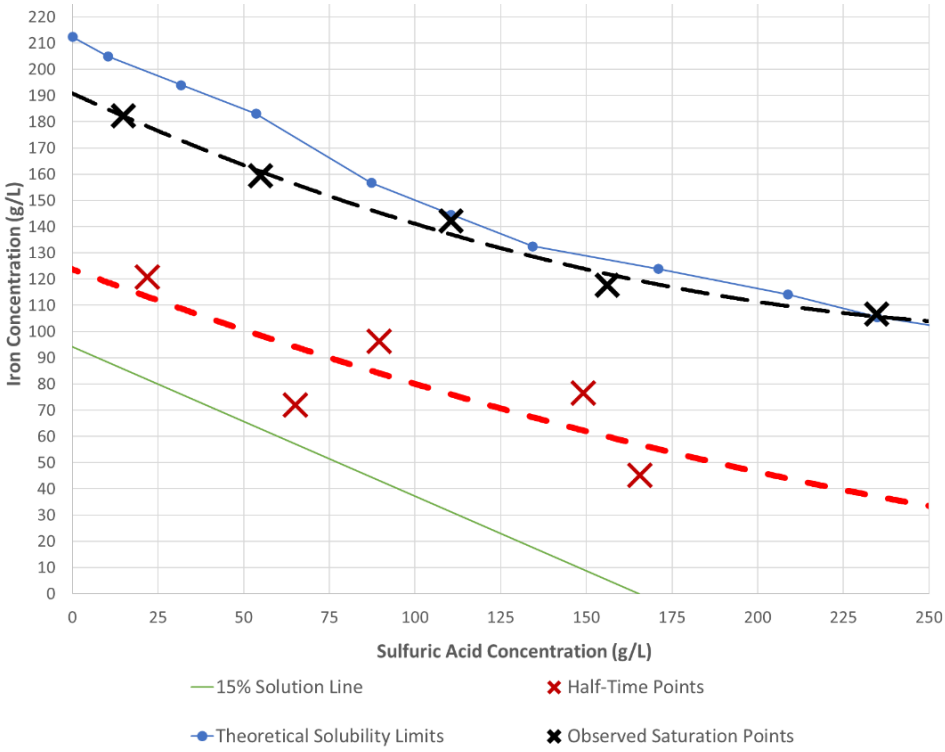

Figure 23: The Burnett Curve – Finalized version

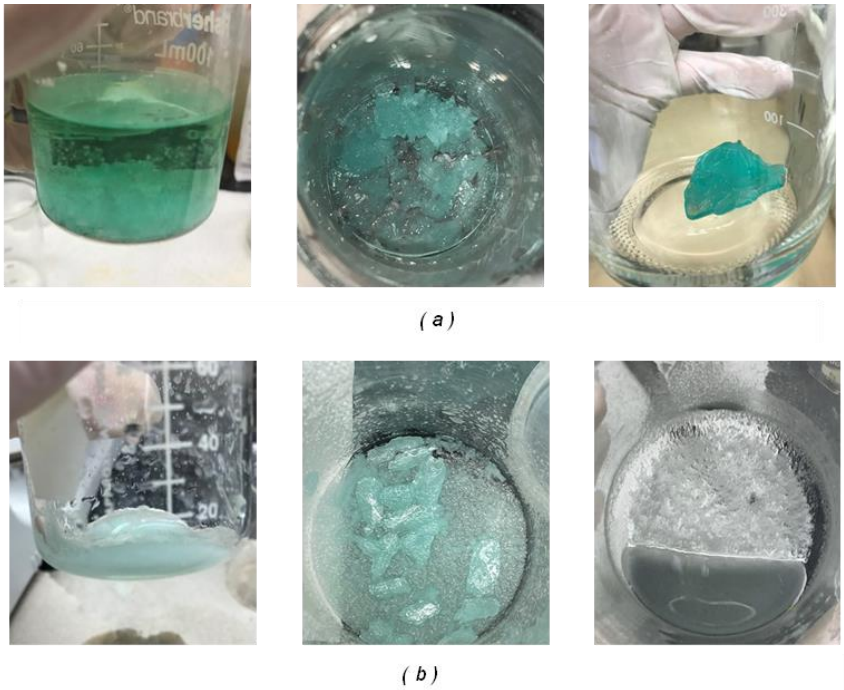

Figure 24: Iron (II) sulfate solids from exceeding saturation**:** (a) – Iron (II) sulfate heptahydrate form – characterized by blue-green crystals (b) – Iron (II) sulfate monohydrate form – characterized by a lighter, often white color

To illustrate the potential use of the Burnett Curve, an example like the one provided for the Kleingarn Curve will be explored. Figure 25 plots the solution in this example onto the Burnett Curve, and the solutions considered have their pickling times displayed as data tags. In this scenario, a galvanizer begins their sulfuric acid pickling bath, set at 60°C (140°F), with an initial acid concentration of 15% and a pickling time of seven minutes (Barlow 2015). After repeated pickling the galvanizer determines the sulfuric pickling liquor to have an acid concentration of 4%, an iron concentration of 71 g/L, and a pickling time of 18 minutes.

The galvanizer wants to regenerate the solution, and a regenerated acid strength of 12% would provide a pickling time of 9 minutes (Barlow 2015), half of the spent liquor's pickling time. To regenerate this spent liquor, the galvanizer has 45% sulfuric acid ready to use for regeneration. With a 12% desired acid concentration, a 45% acid concentration for the fresh solution, and an assumed tank volume of 132.1 gallons (500 liters), the regenerated solution will require 25.78

gallons (97.6 liters) of the spent liquor to be removed and replaced with the same volume of the 45% fresh sulfuric acid solution. From the initial spent liquor iron concentration of 71g/L, the regeneration will decrease the resulting solution iron concentration to 57 g/L. Both the volume of spent liquor to be removed and the resulting solution iron concentration were found using the equations 1 and 2 respectively, the acid regeneration equations. After performing this regeneration, the resulting solution's acid and iron concentrations will be plotted near the optimum pickling time curve, indicating the solution reaching a pickling time through regeneration that is half of the previously spent solution's pickling time.

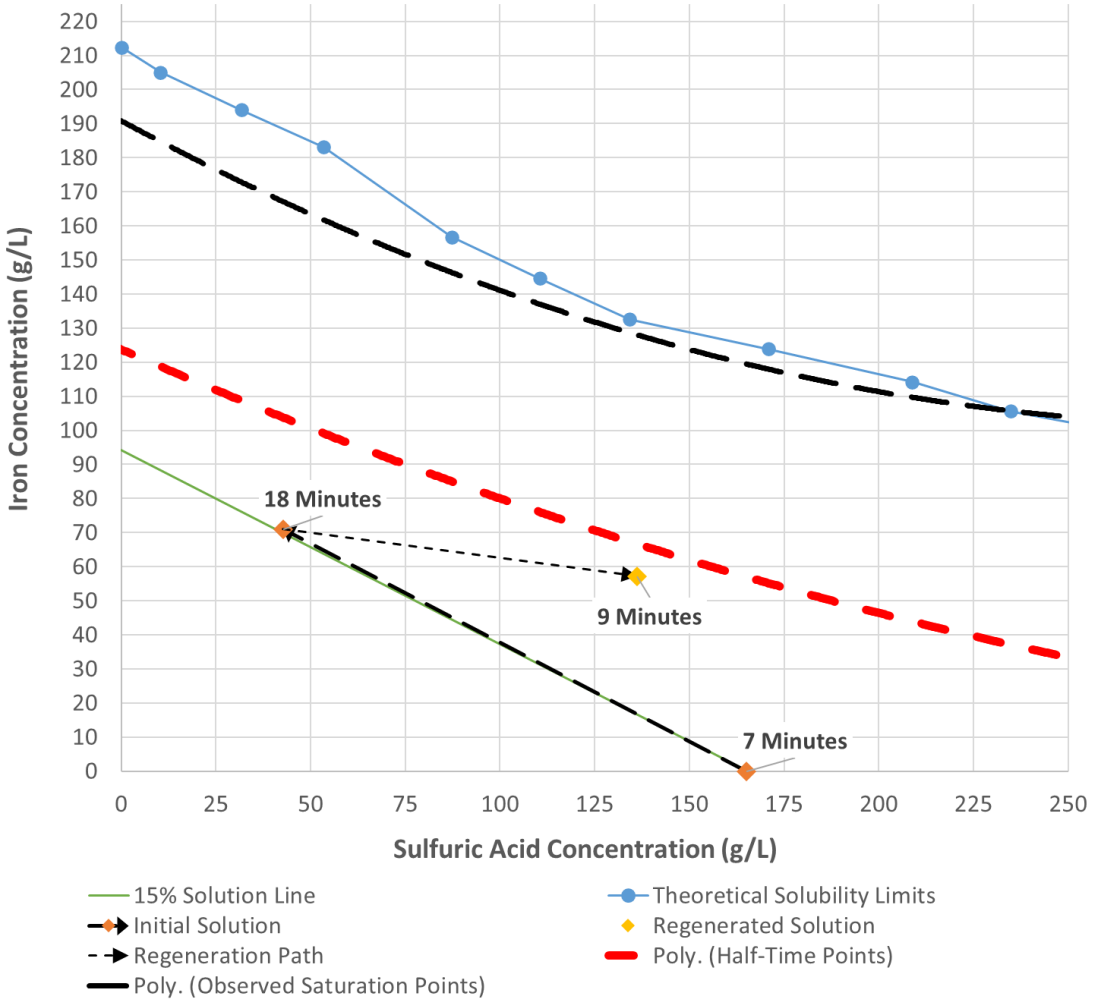

Figure 25: Example for the use of the Burnett Curve for regeneration of a sulfuric acid solution

3.3 – Task 3 Results

The tests performed for Task 3 are described in two subcategories to aid in understanding of the results. The first 10 tests, Chapter 3.3.1, were performed for relatively low zinc concentrations (5-20 g/L), with five tests for hydrochloric acid and five for sulfuric acid. The remaining 10 tests, Chapter 3.3.2, were performed for relatively high concentrations of zinc (25-95 g/L), split across five tests for hydrochloric acid and five for sulfuric acid.

To provide points of comparison, five hydrochloric acid solutions tested in Task 1 and five sulfuric acid solutions in Task 2 were used as benchmarks of expected pickling times without the influence of zinc. The solutions tested in Task 3 began and ended at the same acid concentrations as used in Tasks 1 and 2. The degradation of acid concentration through the addition of metals was held constant. For the low zinc concentrations, this decrease in acid concentration was calculated so that 90% of the decrease would come from the addition of iron, while the remaining 10% decrease in acid concentration would be due to zinc addition. For the high zinc concentrations, the decrease in acid concentration was split evenly between the iron and zinc, i.e., 50% of the decrease came from iron addition and 50% came from zinc addition.

To illustrate this, consider an initial solution starting with an acid concentration of 15%. The comparison point from the previous tasks' results is a solution that degraded to a 5% acid concentration solely from the addition of iron, meaning the decrease in acid concentration was a total of 10% (15% - 5% = 10% decrease). In the low zinc concentration solutions, 9% of this degradation would be from the addition of iron, while the remaining 1% would come from zinc. In the high zinc concentration solutions, the 10% degradation would be split evenly: 5% degradation of the acid concentration due to iron addition and 5% degradation of the acid concentration due to zinc addition.

3.3.1 – Tests for Low Zinc Concentrations

The basis for the low zinc concentration tests was found in existing literature from Maass and Peissker (2011), which listed the practical limits for zinc concentration in hydrochloric acid pickling solutions as 5-12 g/L. The solutions found in these ten tests were calculated to have a similar range of zinc concentrations. For the hydrochloric acid solutions, zinc concentrations ranged from 6-18 g/L. The sulfuric acid solutions contained zinc concentrations of 5-13 g/L.

In relation to the analogous solutions from the previous tasks (Task 1 for hydrochloric acid and Task 2 for sulfuric acid), the solutions with low concentrations of zinc showed little variation in the observed pickling times. Across both the hydrochloric and sulfuric acid results, the only difference observed for pickling times was a slight decrease in pickling times for the two hydrochloric acid solutions containing a large concentration of metal in solution. These decreases were less than 10 minutes in magnitude, and the pickling times observed in Task 1 were around 40 minutes for both solutions. In the operation of batch-pickling using hydrochloric acid, the typical immersion times are in the range of 5-15 minutes (Hudson 1994). As such, seeing changes in pickling times from around 40 minutes (Task 1) to around 32 minutes (Task 3) is outside of the relevant range considered for typical pickling times and does not indicate a change of major significance. The likely explanation for this decrease in observed pickling time is due to the Task 3 solutions containing a lower concentration of iron in solution, as the zinc added now contributes a small portion of the overall metal concentration. With a lower iron concentration in these Task 3 solutions, as compared to the analogous solutions from Task 1, the pickling process, i.e., the incorporation of more iron into the acid solution, is likely to be slightly more favorable.

While the observed pickling times showed little change, the behavior of the pickling reaction showed noticeable differences. For both hydrochloric and sulfuric acid pickling solutions,

the pickling reaction was observed to be uneven and spotty at low acid concentrations. For hydrochloric acid pickling solutions, uneven pickling was observed in a solution with an acid concentration of 1.68%, a zinc concentration of 11.65 g/L, and an iron concentration of 92.58 g/L. This solution was tested twice to confirm this observed behavior. The first test of this solution produced one coupon that had small spots of iron oxides on one face, while the other face was thoroughly pickled. The second coupon also contained one pickled face, but this coupon's other face was noticeably dotted with remaining iron oxides. While the second test produced more evenly pickled surfaces, the coupons tested also showed uneven surface appearances. The lack of predictable pickling behavior is shown in Appendix F - Figures F-1 through F-4 - which contains a total of four coupons from the two tests after being pickled in this hydrochloric acid pickling solution.

The sulfuric acid pickling solutions also produced spotty and uneven pickling at low acid concentrations. Two solutions showed this behavior. Both solutions had acid concentrations of roughly 2.5%. One solution had a zinc concentration of 9.31 g/L and an iron concentration of 71.48 g/L, while the second solution had a zinc concentration of 13.33g/L and an iron concentration of 102.48 g/L. The uneven appearance of the pickled surfaces was more noticeable in these solutions as compared to the hydrochloric acid pickling solutions. It should be noted that sulfuric acid pickling results in a generally darker surface appearance than hydrochloric acid pickling (Hudson 1994). Even with the understanding of a different visual appearance from sulfuric acid pickling, the observed surface appearance of the coupons showed signs of overpickling, appropriate levels of pickling, and remaining iron oxides. The four coupons from these two sulfuric acid tests, after being pickled, are shown in Appendix F – Figures F-13&14 and F-21&22.

It is believed that such behavior can be considered a practical limitation on zinc in pickling solutions. The presence of zinc at low acid concentrations caused the predictability of the pickling reaction to become unreliable. While pickling was still observed, it occurred with little consistency across the steel surface. The observed practical limits for zinc concentrations are shown in Table 6.

Table 6: Observed limits for uneven pickling for both acid solutions

HYDROCHLORIC ACID TESTS				
Observed Limits for Disruption of Even Pickling:	**12 - 20**	g/L	Zn	For high concentrations of Iron (90+ g/L)
SULFURIC ACID TESTS				
Observed Limits for Disruption of Even Pickling:	**10 - 20**	g/L	Zn	For all concentrations of Iron

3.3.2 – Tests for High Zinc Concentrations

Based on personal correspondence with the American Galvanizers Association (2022), pickling baths used for the removal of zinc can be sorted into two approaches found in industry. One approach is designating a single bath specifically for zinc removal, resulting in high zinc concentrations, represented by the tests performed in this Chapter. The other approach is using multiple pickling baths that are primarily used for iron oxide removal. The desired removal of zinc is spread across multiple baths to prevent an excess accumulation of zinc in a singular pickling solution. This approach is represented by the tests performed in the previous Chapter, as those tests contained mostly iron with a small concentration of zinc in solution.

Like the results found in the low zinc concentration tests, the hydrochloric acid pickling solutions showed less difficulty achieving pickling as compared to the sulfuric acid pickling

solutions. The hydrochloric acid pickling solutions produced uneven pickling behavior. However, the coupons pickled within the hydrochloric acid – high zinc concentration pickling solutions had an appearance that was less spotty than the comparable low zinc concentration tests. While this may seem counterintuitive, the results led to a likely conclusion. Since the low zinc concentration test solutions had higher iron concentrations than the high zinc concentration test solutions, it seemed the presence of zinc in hydrochloric acid solutions was not necessarily the sole impediment for consistent pickling behavior. As the pickling reaction is primarily the result of the acid reacting with the iron oxides found in the mill scale and surface rust on steel, the results from the zinc-addition tests indicated that the concentration of iron is a significant factor in determining the predictability of a hydrochloric acid pickling solution's behavior.

The sulfuric acid solutions with high concentrations of zinc showed one important difference. Like the low zinc concentration tests, difficulty in even pickling behavior was observed at acid concentrations of 2%. However, with the high zinc concentration tests, two of the solutions presented an inability to efficiently pickle iron oxides. These solutions consisted of sulfuric acid concentrations of 2.5% and 4%. These two solutions contained 66 g/L and 60 g/L of zinc, with 56.93 g/L and 51.24 g/L of iron, respectively. The analogous solutions from Task 2, with the same acid concentrations, were observed to have average pickling times of 22 minutes (for the 2.5% solution) and 16 minutes (for the 4% solution). The two comparable high zinc concentration solutions produced little to no removal of iron oxides from the submerged test coupons after both solutions were allowed to pickle for 30 minutes. While possible that pickling may have been achieved with greater durations of time, the level of oxide removal observed over 30 minutes presented doubt that pickling could be achieved in a timescale that was efficient for industrial use.

The cease of effective pickling within these sulfuric acid solutions with high concentrations of zinc presented an interesting difference between hydrochloric and sulfuric acid pickling behavior. While the hydrochloric acid solutions provided results that indicated iron concentrations were the primary impediment to consistent pickling behavior, the sulfuric acid solutions produced results that indicated zinc concentrations imparted a significant role in pickling behavior. It is likely that sulfuric acid pickling is more sensitive to the effects of metal salts (zinc or iron) in solution as compared to hydrochloric acid. Although not specified for zinc salts, existing literature does indicate that a known disadvantage to sulfuric acid pickling is a greater inhibiting effect on the acid due to the presence of iron salts (Hudson 1994). The coupons tested in the sulfuric acid solutions that showed an inability to pickle are shown in Appendix F – Figures F-39 through F-42. A comprehensive table of the effects of zinc concentrations and iron concentrations on both acid solutions and their ability to pickle is shown in Table 7.

Table 7: Observed impacts of zinc on pickling behavior for both acid solutions

HYDROCHLORIC ACID TESTS				
Observed Limits for Disruption of Even Pickling:	**12 - 20**	g/L	Zn	For high concentrations of Iron (90+ g/L)
	80 - 90	g/L	Zn	For low concentrations of Iron (50-90 g/L)
SULFURIC ACID TESTS				
Observed Limits for Disruption of Even Pickling:	**10 - 20**	g/L	Zn	For all concentrations of Iron
Observed Limits for Severe Disruption of Pickling:	**45 - 60**	g/L	Zn	For all concentrations of Iron

The results for all the tests conducted for Task 3 provide more understanding into interactions between zinc and both acid solutions and the effects on pickling. For hydrochloric acid, results showed that the iron concentration and the zinc concentration both impacted pickling behavior with iron concentration being of importance. The high zinc tests for hydrochloric acid showed more reliable and thorough pickling behavior when compared to the low zinc tests. The high zinc tests contained more zinc and less iron than the low zinc tests.

Results for sulfuric acid indicated that the zinc concentration impacted pickling behavior. For the low zinc tests, the two sulfuric acid solutions that unevenly pickled coupon surfaces were the two solutions with the lowest acidity and the highest amount of both zinc and iron. For the high zinc tests, the two sulfuric acid solutions that showed an end in effective pickling were the two solutions with the highest zinc concentrations. The two solutions that had pickling issues had zinc concentrations between 60-70 g/L, while the sulfuric acid solution containing the next highest amount of zinc has a zinc concentration of 46.5 g/L. Since the pickling reaction lost effectiveness with two solutions with zinc concentrations above 60+ g/L, the limits that identify this loss of pickling identify the range of concentrations between the last solution that could pickle and the first one that could not, concentrations of 46.5 and 60 g/L respectively.

4 – CONCLUSIONS & FUTURE STUDY

4.1 – Conclusions

An experimental study using benchtop testing methods was undertaken to reproduce results seen in the Kleingarn Curve, establishing a similar curve for the use of sulfuric acid pickling solutions, and for investigating the effects of zinc on both hydrochloric and sulfuric acid pickling solutions. Testing performed for this research confirmed the relationships described in the Kleingarn Curve. The testing reinforced the ability to reproduce the acid regeneration procedure described by Kleingarn and the procedure's ability to accurately predict a pickling solution's acid and iron concentrations after regeneration occurred. Furthermore, the testing performed provided understanding of the relationship between the optimum pickling time curve described and the slower pickling time curve. Testing was also performed to confirm the validity of the region indicative of reaching saturation for iron within hydrochloric acid. The tests to confirm this limit showed the precipitation of solids, as predicted by the Kleingarn Curve.

Based upon the principles that guided the Kleingarn Curve, it was hypothesized that a similar curve for sulfuric acid could be constructed at a given test temperature. Through the testing shown in this research, this hypothesis was found to be true. By defining an initial starting acid concentration and recording pickling times for solutions derived from this initial concentration, the effects of regeneration were able to be recorded and quantified in terms of reduction in pickling times. Through the relationship between a given sulfuric acid concentration and an observed pickling time at that concentration, an optimum pickling time curve was derived. The optimum pickling time curve represents the acid and iron concentrations of a regenerated solution with a pickling time of half of the pre-regenerated solution. Additionally, through interpretation of existing literature and corresponding experimental testing, the curve indicative of saturation for

iron in sulfuric acid was also derived. The concentrations of the solutions were similar between existing literature and the experimental results, providing validity to the constructed saturation curve.

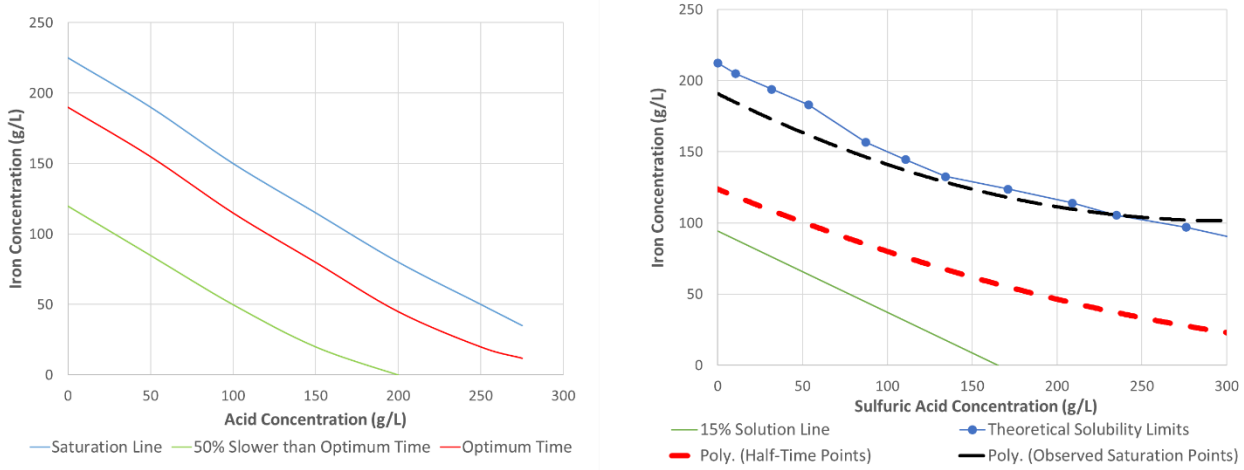

Figure 26: Side-by-side comparison of the Kleingarn Curve and the Burnett Curve

Figure 26 shows the Kleingarn Curve on the left and the Burnett Curve on the right. The two curves share similarities and differences worth noting. One important difference is the lower iron concentrations for the optimum pickling time line in the Burnett Curve when compared to the Kleingarn Curve. This difference does seem to agree with existing literature. Hudson (1994) lists a greater inhibiting effect of iron salts in solution as one of the disadvantages of sulfuric acid pickling. Since iron in sulfuric acid pickling solutions can cause inhibiting effects on the pickling reaction, maintaining relatively low iron concentrations is important when regenerating solutions. Another difference can be seen in the Burnett Curve extending to the right further than the Kleingarn Curve. Although the research used to create the Burnett Curve considered solutions with concentrations near these ranges, it is likely that solutions in industry will never be at such extremes. For industry use, it could be useful to reduce the bounds of consideration in the Burnett Curve in order to more closely examine a range of typical concentrations. It could be beneficial to

conduct a future test over a narrower range of sulfuric acid concentrations to further refine the shape of the Burnett Curve.

Both curves are similar in their aims. Both the Kleingarn Curve and the Burnett Curve describe pickling rates and solutions for two different acids, and both curves can be used to track these solutions throughout their usable lifetimes and regenerations. An optimum curve can be found in both curves, and this optimum curve is illustrative of the concentrations to be reached for a regenerated solution to have a pickling time that is half of the time prior to regeneration. Additionally, both curves have a curve representative of a solution that begins with an initial acid concentration of 15%. The purpose of this curve is to provide an initial basis for an average pickling solution, one that begins with 15% acid. Starting pickling solutions can be found in ranges above and below this 15% initial concentration point for both acids (Hudson 1994). Both curves can be used with a solution that begins with an acid concentration below 15%, using the regeneration equations to find solution concentrations after regeneration. However, starting with a weaker acid will cause the initial pickling time to be longer, so the solutions starting below the curve will be slower than those that start on or above it.

The effects of zinc on pickling solutions of both hydrochloric and sulfuric acids were also tested. While the effects observed were difficult to convey in precise values of solution concentrations, a range describing impacts on pickling behavior was created. It was observed that solutions with lower acid concentrations showed difficulty in predictable and even pickling behavior for both hydrochloric and sulfuric acid pickling solutions. Hydrochloric acid pickling solutions were observed to show more difficulty when iron concentrations were higher, with zinc also present in solution. On the other hand, sulfuric acid pickling solutions were observed to show more difficulty from higher concentrations of zinc in solution. This was likely due to sulfuric acid

having greater pickling inhibition effects from the presence of metal salts as compared to hydrochloric acid.

4.2 – Future Studies

The results of this research provide multiple opportunities for future study that could further investigate and expand upon the understanding of pickling solutions for hot-dip galvanizing. Existing literature for the pickling process notes the effects of increasing temperature on reducing pickling times for both hydrochloric and sulfuric acids (Barlow 2015; Campano 2012). While Task 2 was calibrated to a midrange temperature for sulfuric acid pickling, expanding the scope to include tests across the full range of commonly seen temperatures could provide further understanding into the pickling rates for sulfuric acid. The effects of temperature on pickling times for both hydrochloric and sulfuric acids is shown in Table 8.

Table 8: Predicted pickling times for 5% solutions of both acids (adapted from Barlow 2015)

Temperature (°C)	Pickling Time - 5% HCl Solution (minutes)	Pickling Time - 5% H_2SO_4 Solution (minutes)
25	38	160
35	20	70
50	10	37
60	8	22
80	6	6

The effects of temperature are more impactful for sulfuric acid than for hydrochloric acid, but both acids show reductions in pickling time as temperature increases. Due to the significant impacts on pickling time experienced by sulfuric acid across a range of elevated temperatures, along with the hazards of increased fume production of hydrochloric acid at elevated temperatures (Barlow 2015), it seems more reasonable to explore the sulfuric acid pickling solutions in this

context. By further expanding the investigation of sulfuric acid pickling rates to capture a range of temperatures, more specific guidance could be given to galvanizers.

While Task 3 explores the effects of zinc on the pickling reactions for both hydrochloric and sulfuric acids, it is possible to investigate further. In this research, both the iron and zinc concentrations are variable, while the initial and final acid concentrations are held constant. To further characterize the impact zinc can have on a pickling solution, it could be beneficial to examine the effects of holding constant the iron concentrations and the final acid concentrations, while varying the zinc concentrations and initial acid concentrations. This would provide a comparison of solutions that isolates the effect of increasing amounts of zinc for pickling solutions with similar acid concentrations and iron concentrations at the point of pickling steel. Doing so would characterize the effects zinc alone can have on directly comparable pickling solutions.

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APPENDIX A – TASK 1 TEST RESULTS

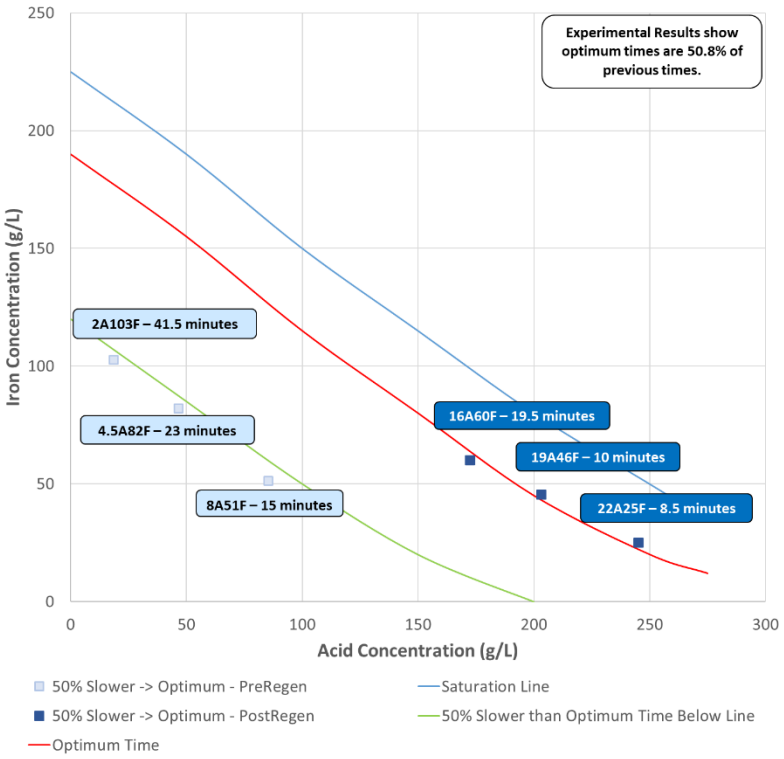


Figure A-1: Regeneration of solutions tested for the optimum pickling time curve

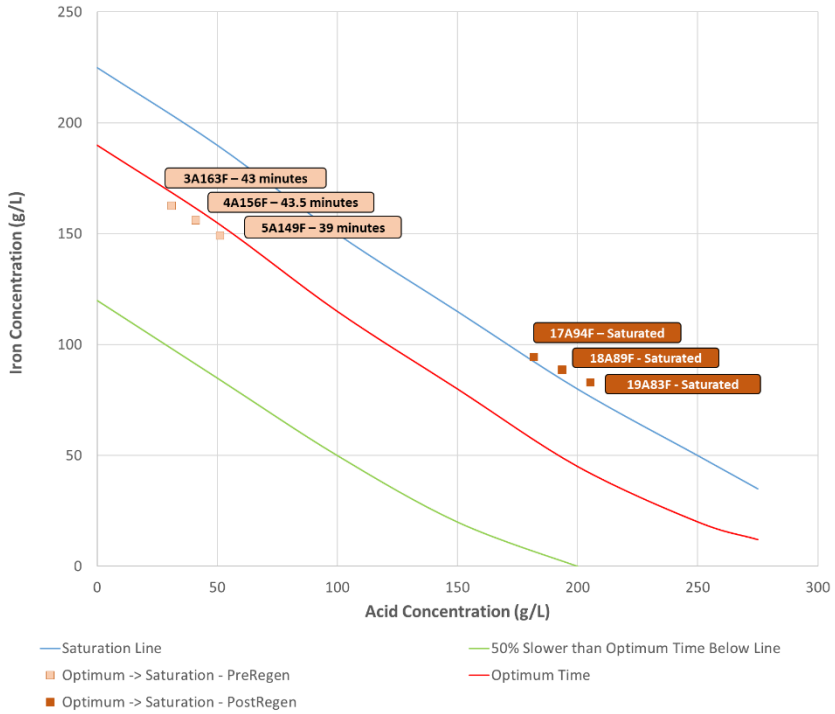


Figure A-2: Regenerations of Task 1 solutions for confirmation of saturation

Table A-1: Solution data and results from initial six tests based on Campano (2012)

Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)	Predicted Pickling Time (minutes)	Actual Pickling Time 1 (minutes)	Actual Pickling Time 2 (minutes)	Pickling Time Average (minutes)
2A103F	2	16.9	103	35	42	41	41.5
3A96F	3	28.1	96	28	27	25	26
4.5A82F	4.5	44.1	82	22	23	23	23
6A68F	6	64.3	68	18	18	17	17.5
8A51F	8	82.6	51	15	15	15	15
14A0F	14	149.5	0	7	9	8	8.5

Table A-2: Coupon mass changes from pickling for solutions in Table A-1

2A103F Coupon 1		**2A103F Coupon 2**		**3A96F Coupon 1**		**3A96F Coupon 2**		**4.5A82F Coupon 1**		**4.5A82F Coupon 2**	
Mass Before (g)	31.73	Mass Before (g)	31.67	Mass Before (g)	32.91	Mass Before (g)	32.93	Mass Before (g)	35.35	Mass Before (g)	35.15
Mass After (g)	31.71	Mass After (g)	31.64	Mass After (g)	32.89	Mass After (g)	32.91	Mass After (g)	35.33	Mass After (g)	35.12
Loss (g)	0.02	Loss (g)	0.03	Loss (g)	0.02	Loss (g)	0.02	Loss (g)	0.02	Loss (g)	0.03
6A68F Coupon 1		**6A68F Coupon 2**		**8A51F Coupon 1**		**8A51F Coupon 2**		**14A0F Coupon 1**		**14A0F Coupon 2**	
Mass Before (g)	35.71	Mass Before (g)	38.26	Mass Before (g)	35.95	Mass Before (g)	35.12	Mass Before (g)	31.5	Mass Before (g)	33.43
Mass After (g)	35.69	Mass After (g)	38.24	Mass After (g)	35.92	Mass After (g)	35.08	Mass After (g)	31.48	Mass After (g)	33.4
Loss (g)	0.02	Loss (g)	0.02	Loss (g)	0.03	Loss (g)	0.04	Loss (g)	0.02	Loss (g)	0.03

Table A-3: Solution data and results from regenerated solutions

Solution	Acid Conc. (g/L)	Iron Conc. (g/L)	Pickling Time Average (minutes)	Removed Spent Acid (mL)	Fresh Acid Conc. (g/L)	Fresh Acid Conc. (%)
2A103F	16.9	103	41.5	20.76	424.5	36
4.5A82F	28.05	82	23	22.22		
8A51F	82.65	51	15	25.36		

Solution	Acid Conc. (g/L)	Iron Conc. (g/L)	Pickling Time 1 (minutes)	Pickling Time 2 (minutes)	Pickling Time Average (minutes)
16A60F	172.4	60.23	19	20	19.5
19A46F	203	45.6	10	10	10.0
22A25F	245	25.1	8	9	8.5

Table A-4: Coupon mass changes from pickling for solutions in Table A-3

16A60F Coupon 1		16A60F Coupon 2		19A46F Coupon 1		19A46F Coupon 2		22A25F Coupon 1		22A25F Coupon 2	
Mass Before (g)	35.66	Mass Before (g)	34.32	Mass Before (g)	31.76	Mass Before (g)	35.27	Mass Before (g)	36.13	Mass Before (g)	32.15
Mass After (g)	35.59	Mass After (g)	34.28	Mass After (g)	31.74	Mass After (g)	35.24	Mass After (g)	36.1	Mass After (g)	32.11
Loss (g)	0.07	Loss (g)	0.04	Loss (g)	0.02	Loss (g)	0.03	Loss (g)	0.03	Loss (g)	0.04

Table A-5: Solution data and results for saturation solutions before regeneration

Solution	Acid Conc. (g/L)	Iron Conc. (g/L)	Pickling Time Average (minutes)	Pickling Time 1 (minutes)	Pickling Time 2 (minutes)
3A163F	28.9	162.6	43	43	43
4A156F	43.4	156.1	43.5	43	44
5A149F	47.4	149.2	39.25	39	39.5

Table A-6: Coupon mass changes from pickling for solutions in Table A-5

3A163F Coupon 1		3A163F Coupon 2		4A156F Coupon 1		4A156F Coupon 2		5A149F Coupon 1		5A149F Coupon 2	
Mass Before (g)	32.04	Mass Before (g)	36.28	Mass Before (g)	30.92	Mass Before (g)	36.29	Mass Before (g)	35.42	Mass Before (g)	35.59
Mass After (g)	32.02	Mass After (g)	36.25	Mass After (g)	30.9	Mass After (g)	36.26	Mass After (g)	35.39	Mass After (g)	35.56
Loss (g)	0.02	Loss (g)	0.03	Loss (g)	0.02	Loss (g)	0.03	Loss (g)	0.03	Loss (g)	0.03

APPENDIX B – TASK 1 TEST PHOTOS

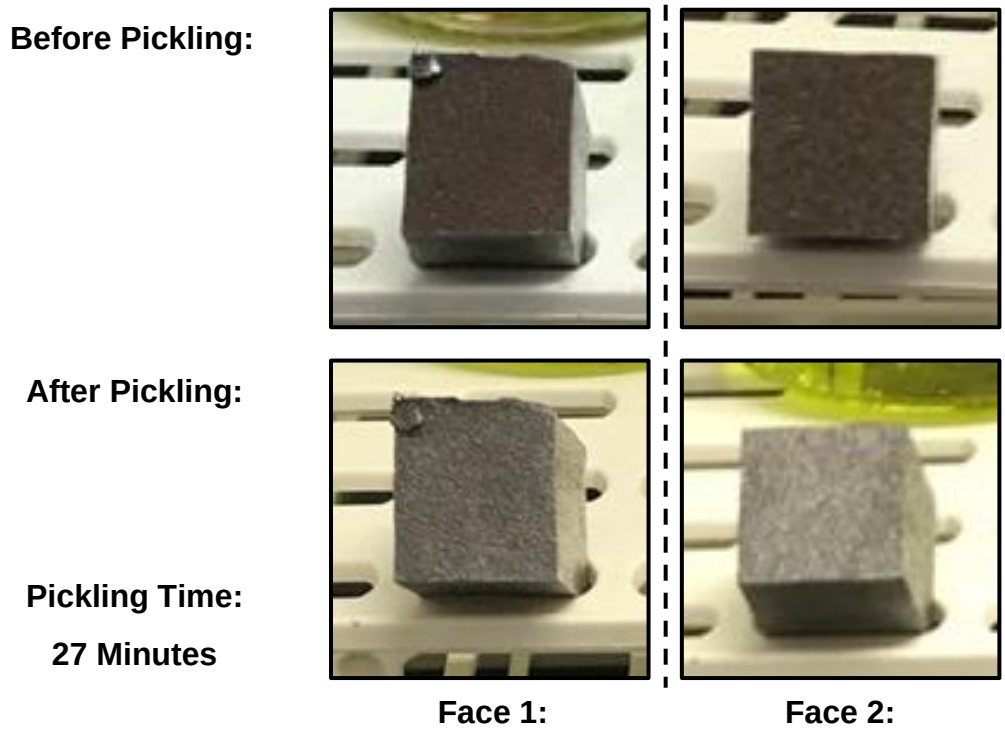


Figure B-1: Solution 3A96F – Coupon 1 Photos

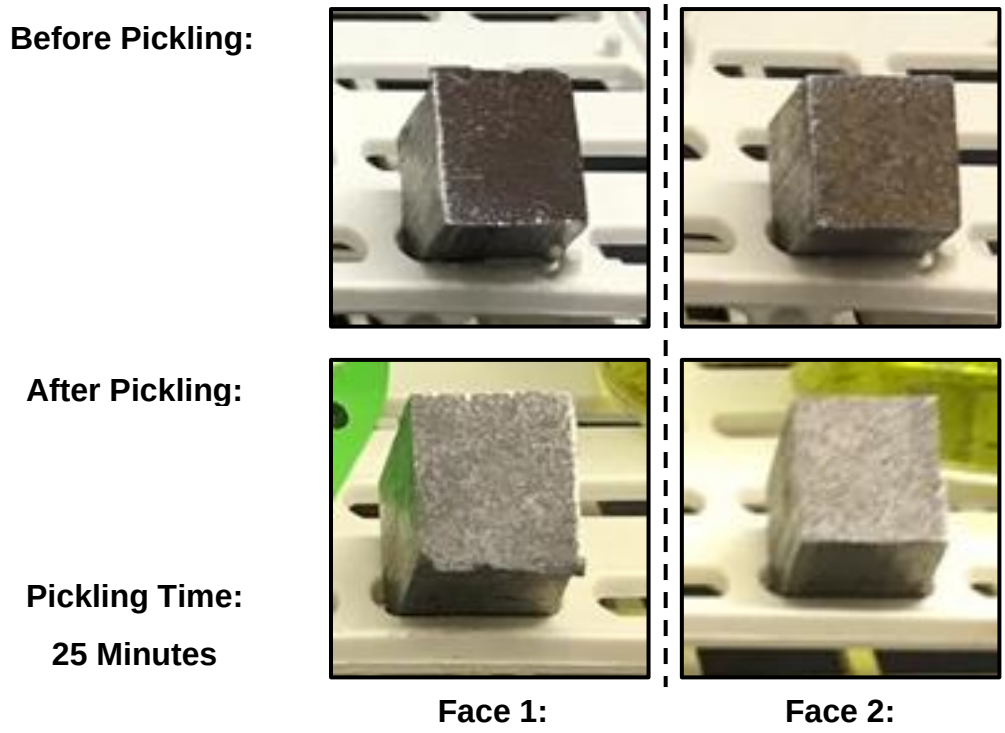


Figure B-2: Solution 3A96F – Coupon 2 photos

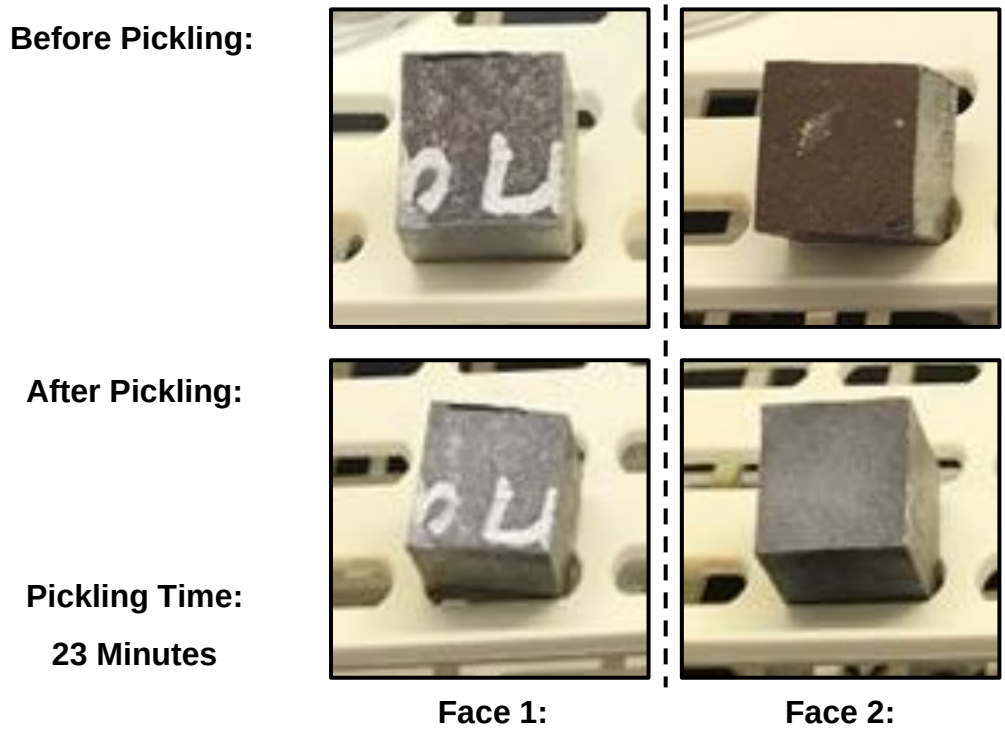


Figure B-3: Solution 4.5A82F – Coupon 1 Photos

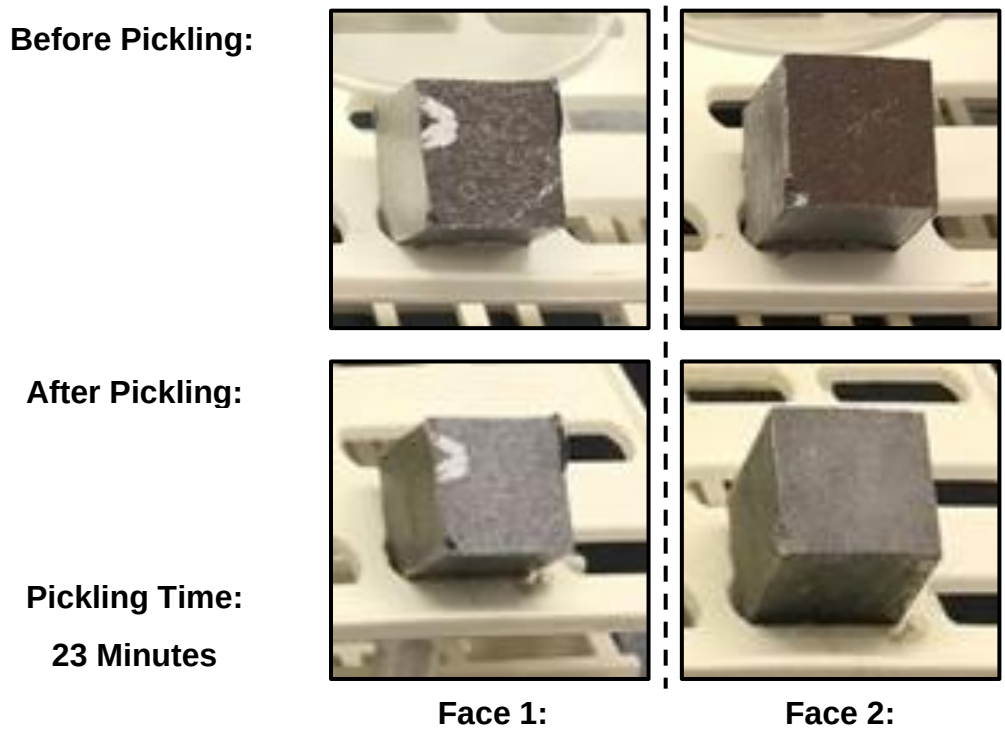


Figure B-4: Solution 4.5A82F – Coupon 2 photos

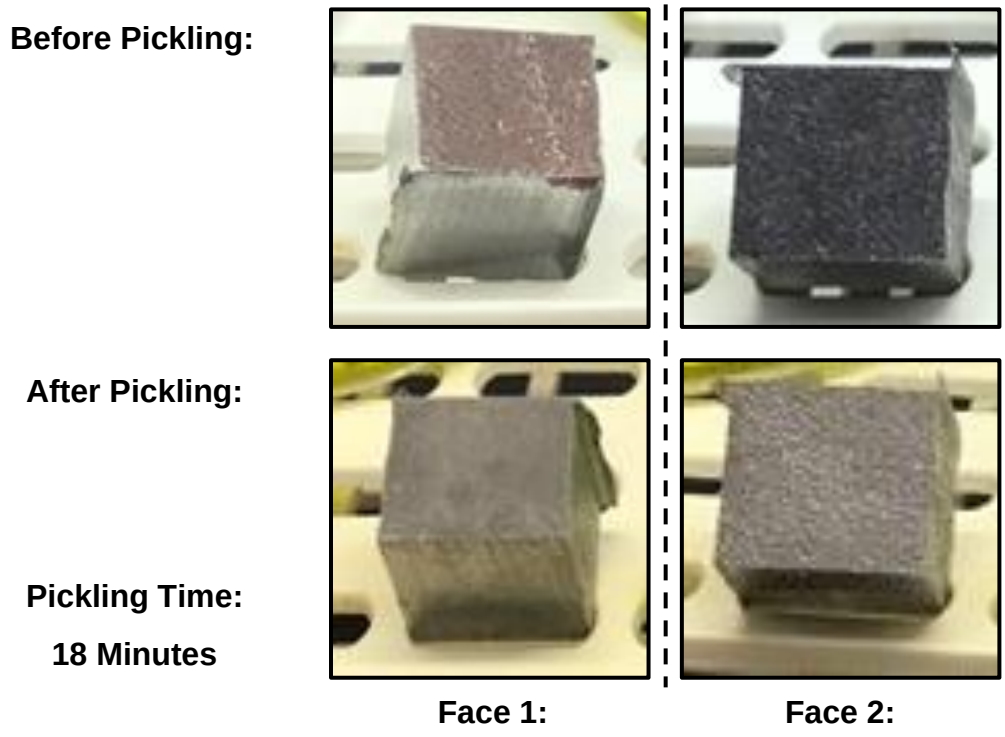


Figure B-5: Solution 6A68F – Coupon 1 Photos

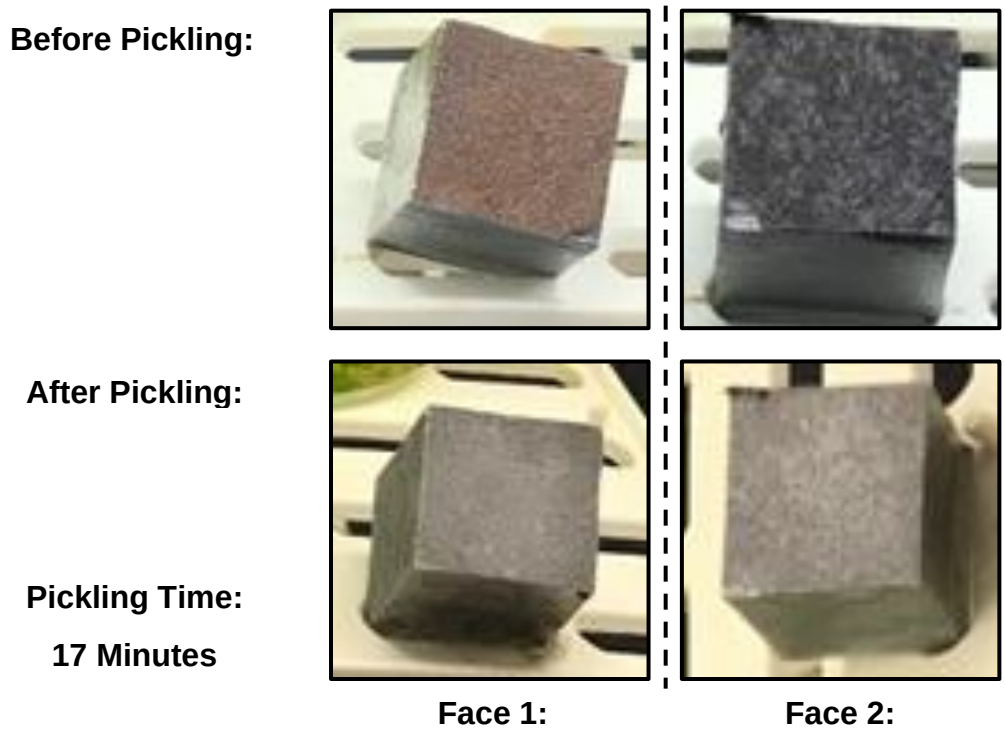


Figure B-6: Solution 6A68F – Coupon 2 photos

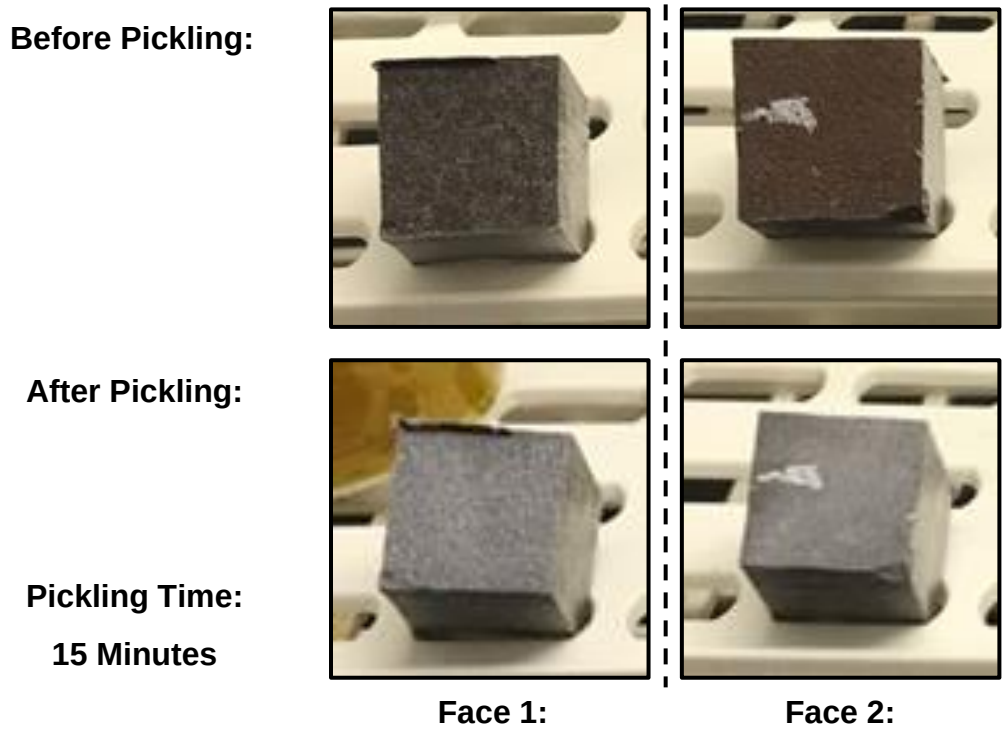


Figure B-7: Solution 8A51F – Coupon 1 Photos

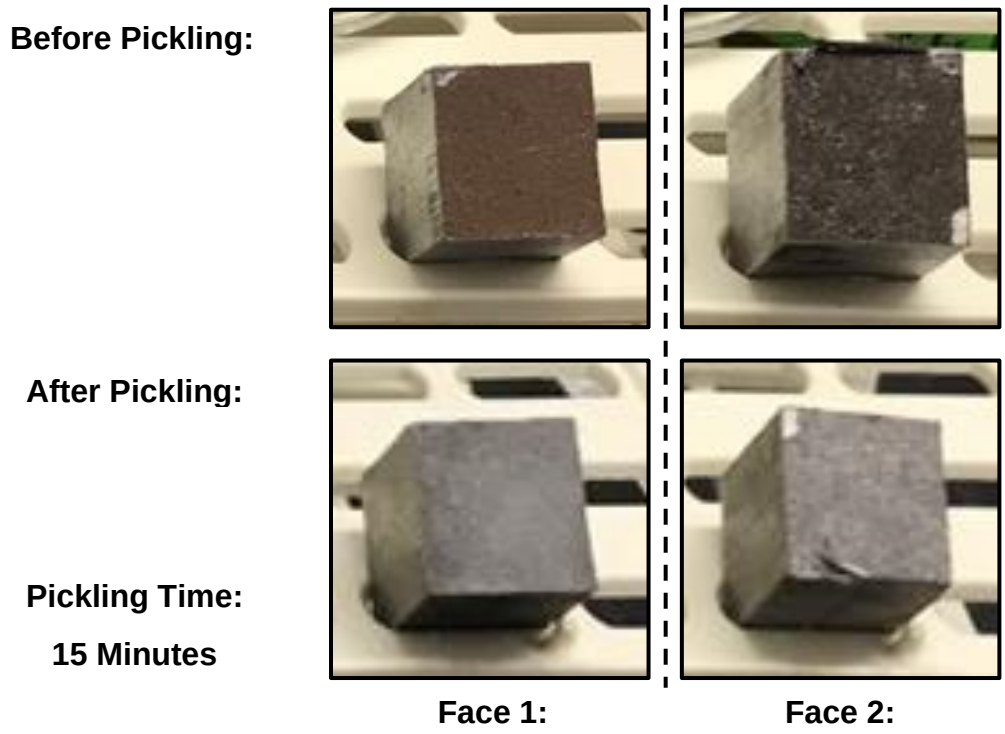


Figure B-8: Solution 8A51F – Coupon 2 photos

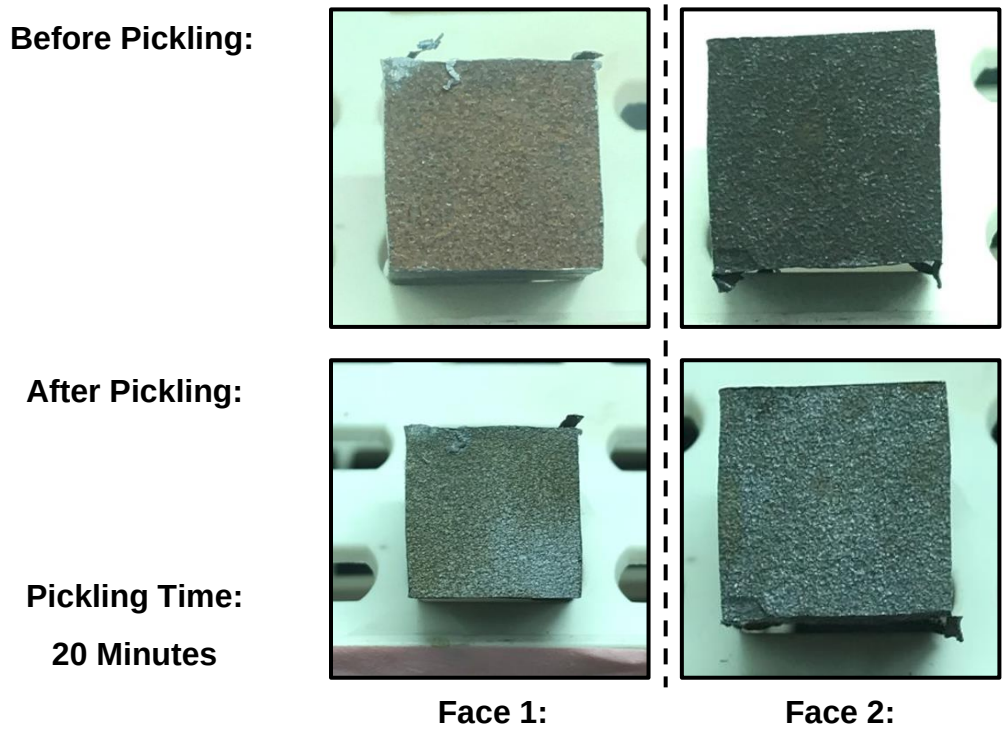


Figure B-9: Solution 16A60F (2A103F Regenerated) – Coupon 1 Photos

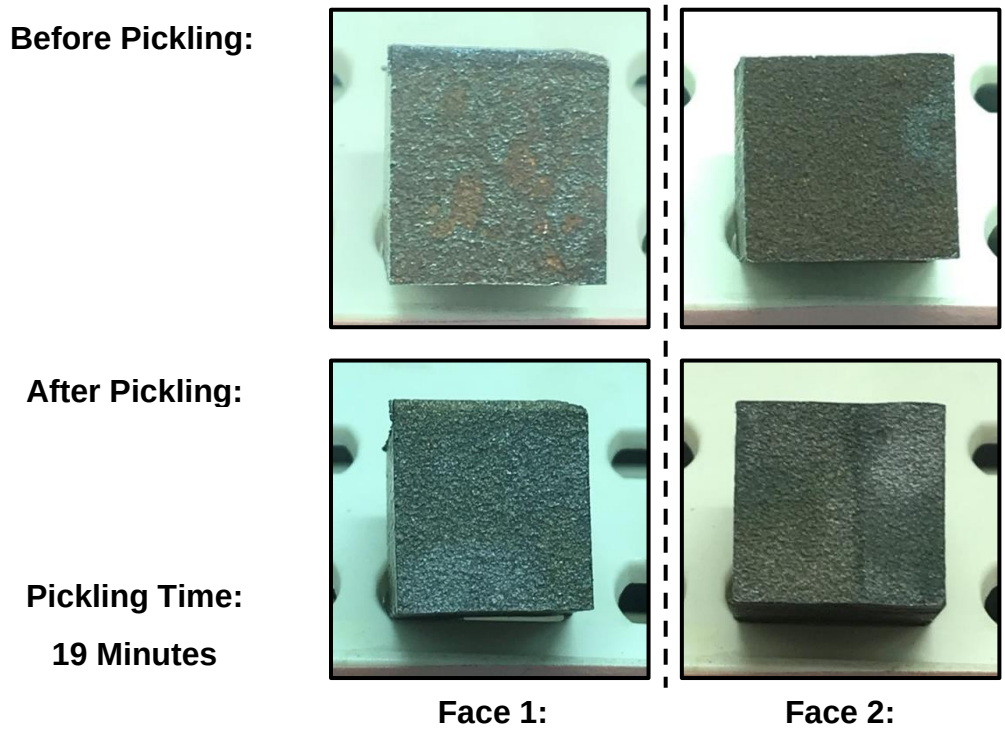


Figure B-10: Solution 16A60F (2A103F Regenerated) – Coupon 2 Photos

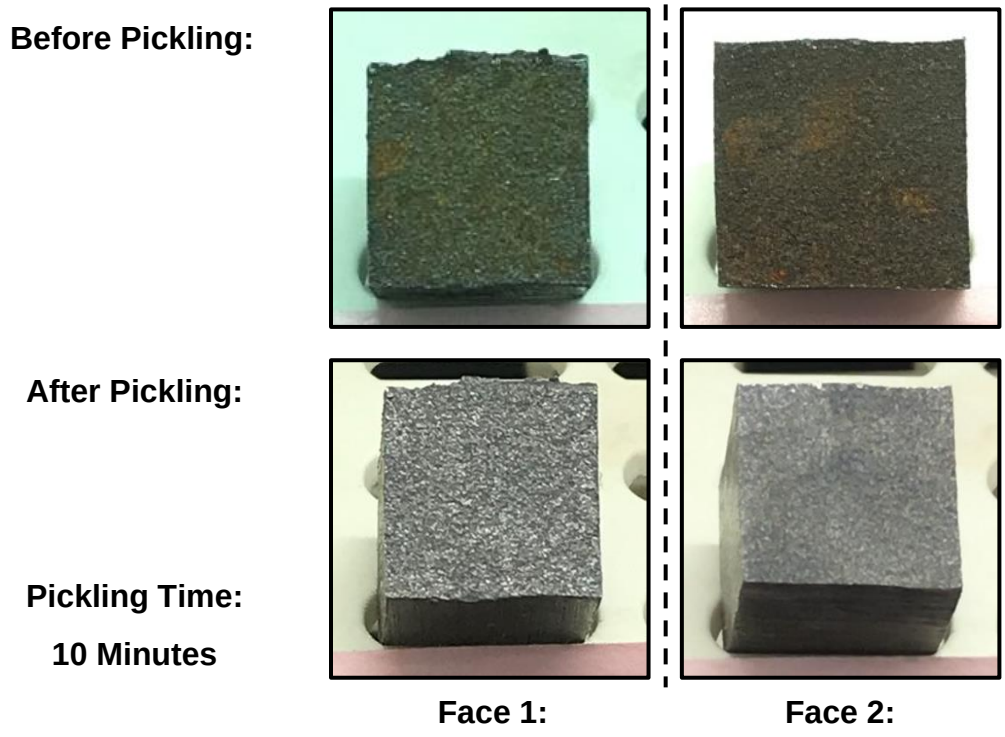


Figure B-11: Solution 19A46F (4.5A82F Regenerated) – Coupon 1 Photos

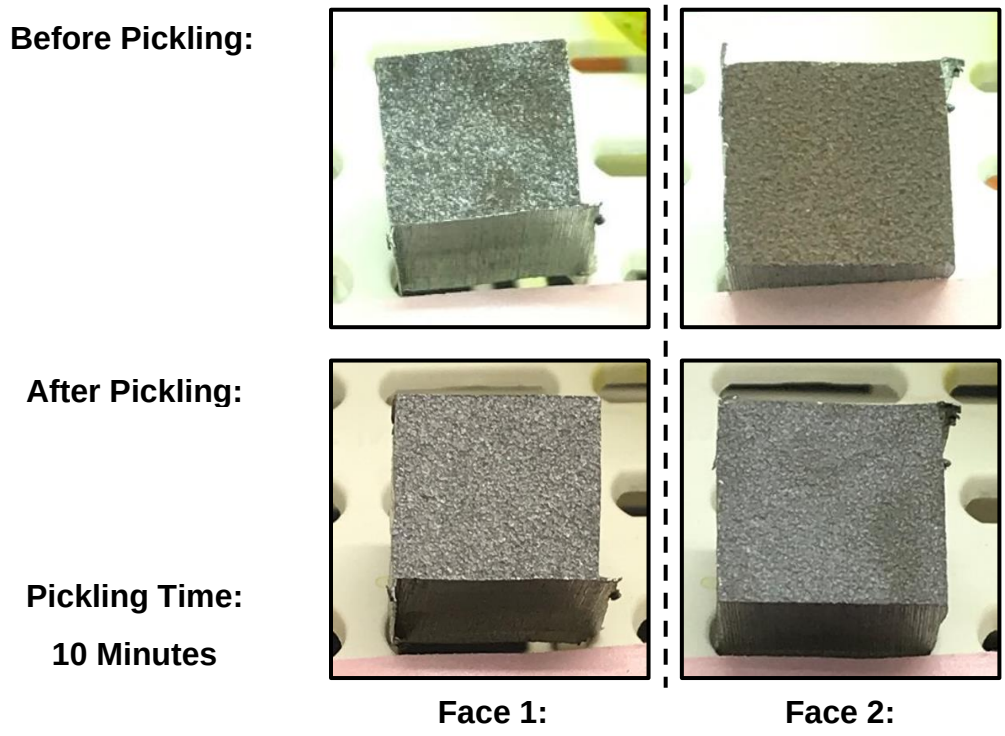


Figure B-12: Solution 19A46F (4.5A82F Regenerated) – Coupon 2 Photos

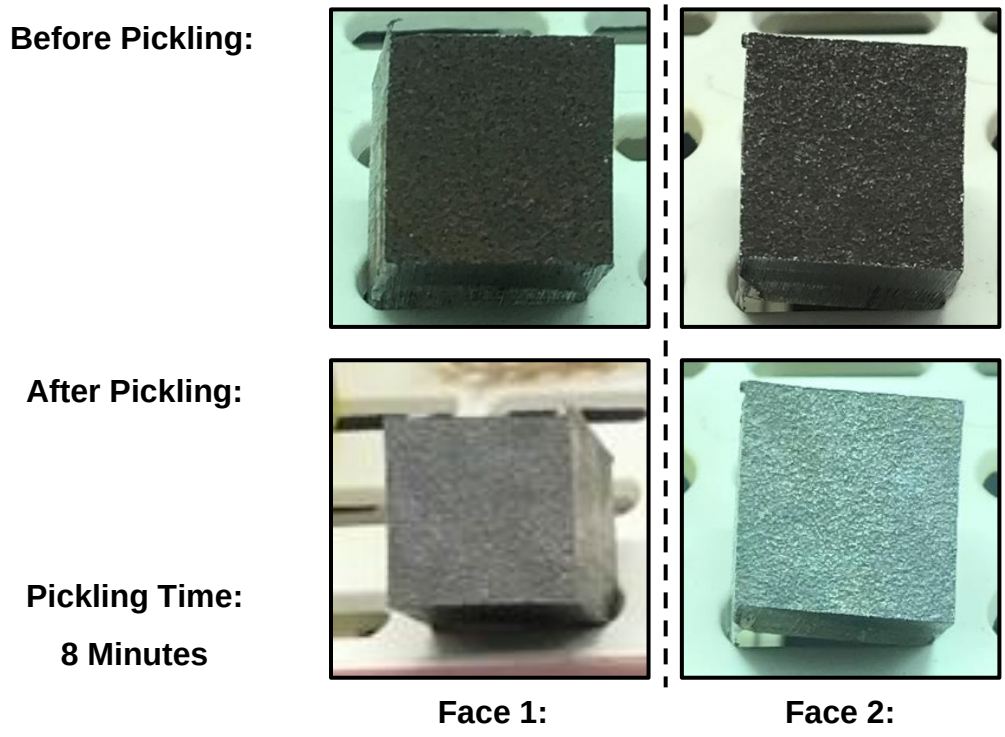


Figure B-13: Solution 22A25F (8A51F Regenerated) – Coupon 1 Photos

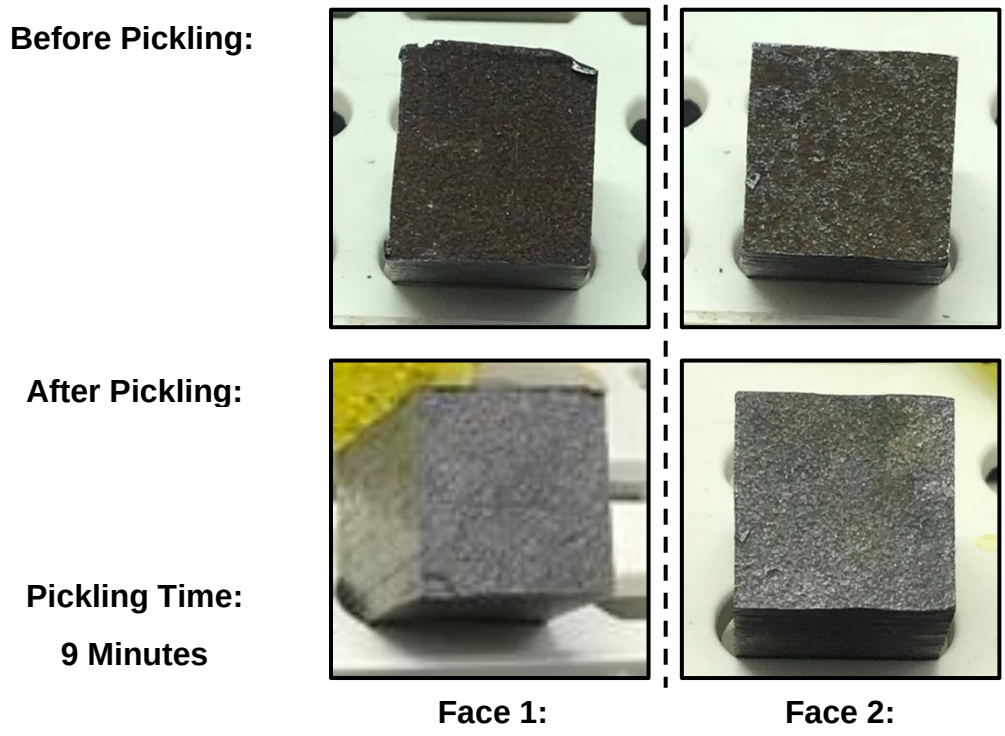


Figure B-14: Solution 22A25F (8A51F Regenerated) – Coupon 2 Photos

Saturation/Solubility Limit Tests

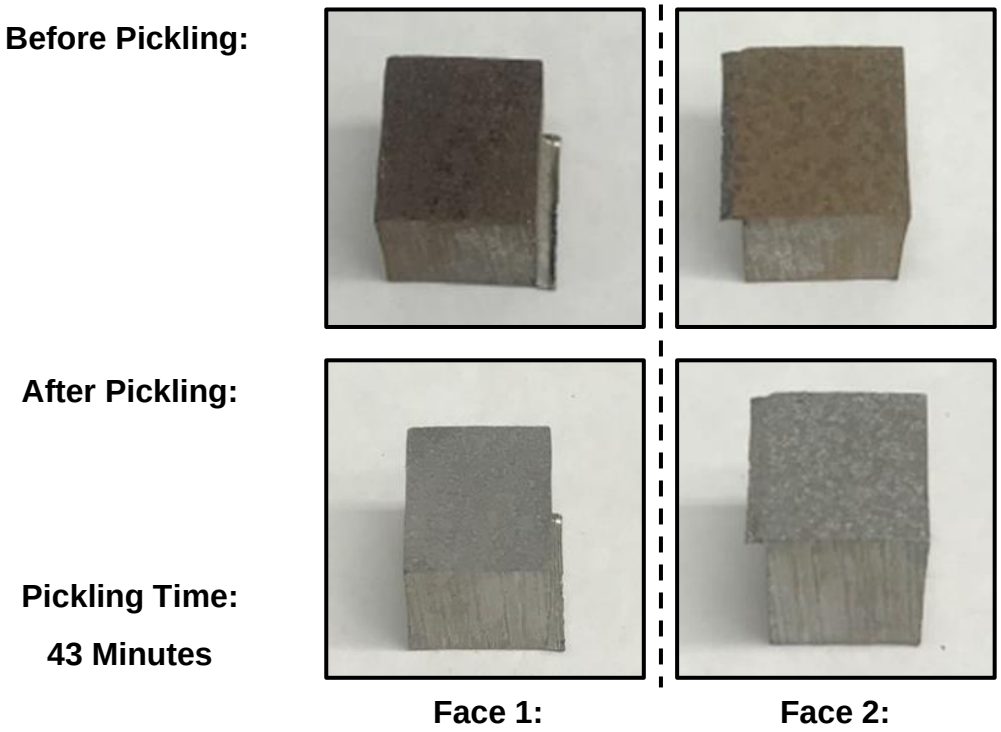


Figure B-15: Solution 3A163F – Coupon 1 Photos

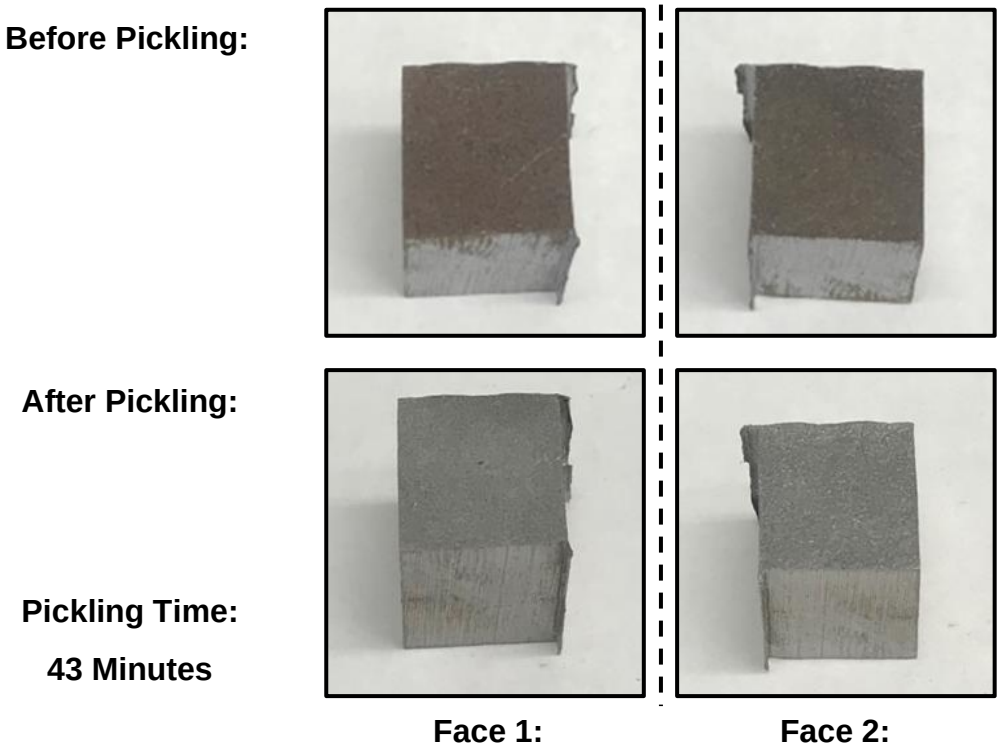


Figure B-16: Solution 3A163F – Coupon 2 Photos

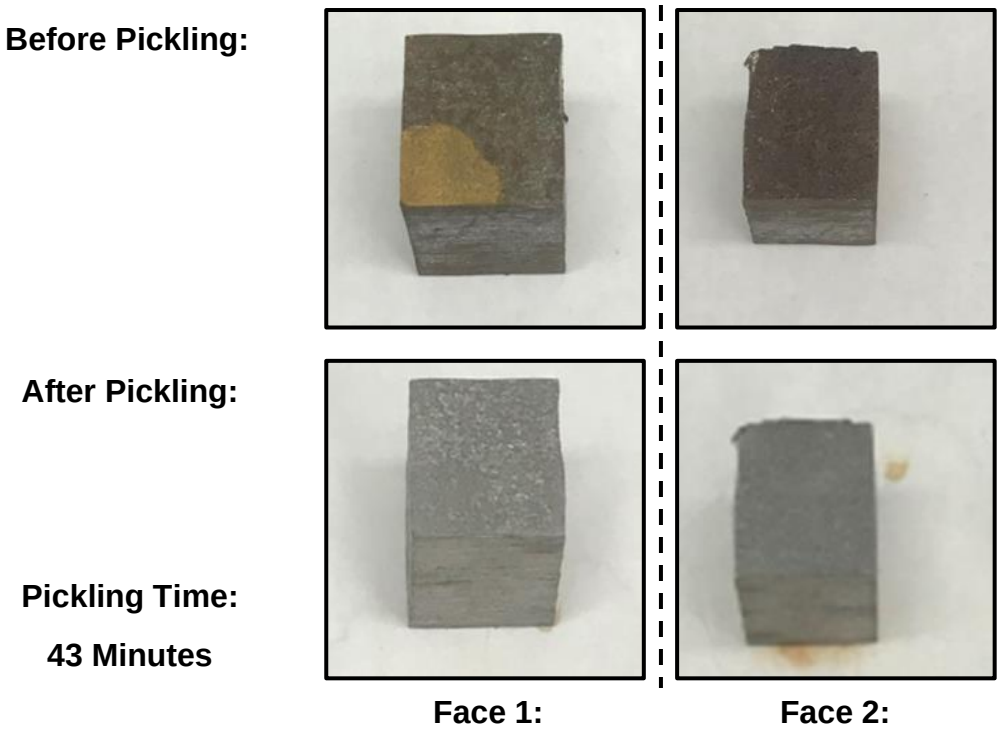


Figure B-17: Solution 4A156F – Coupon 1 Photos

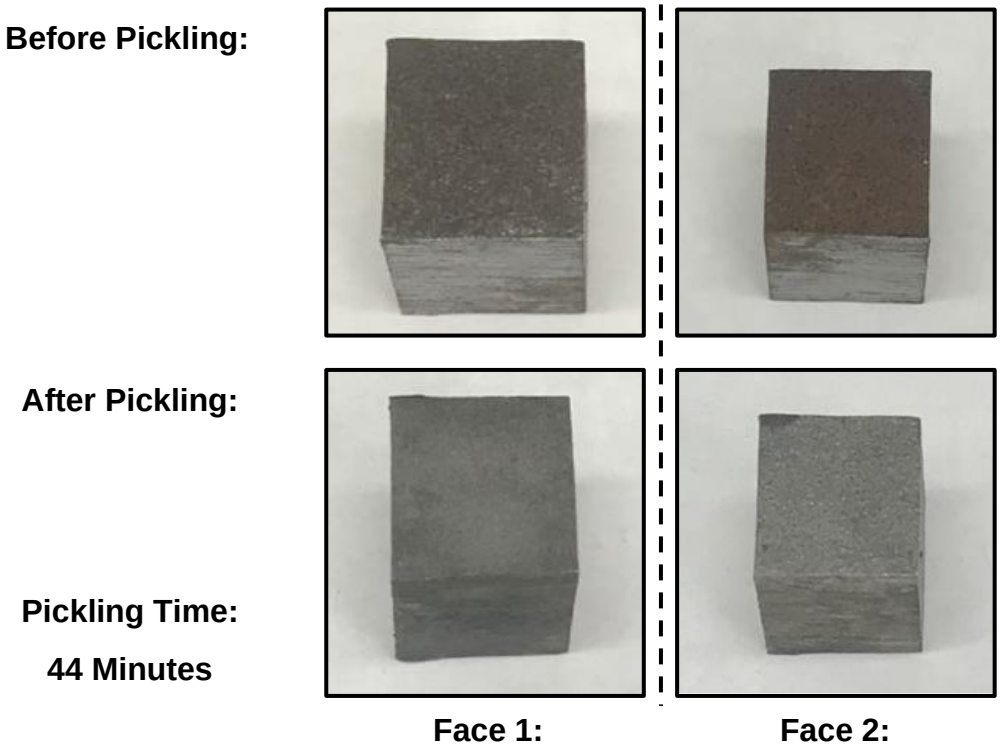


Figure B-18: Solution 4A156F – Coupon 2 Photos

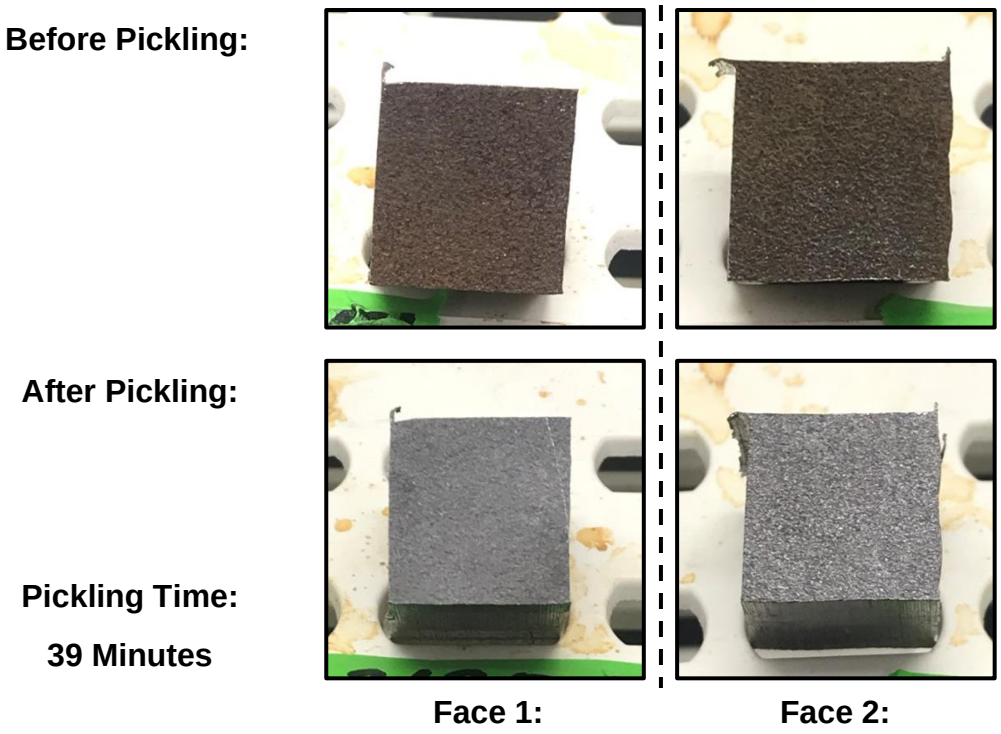


Figure B-19: Solution 5A149F – Coupon 1 Photos

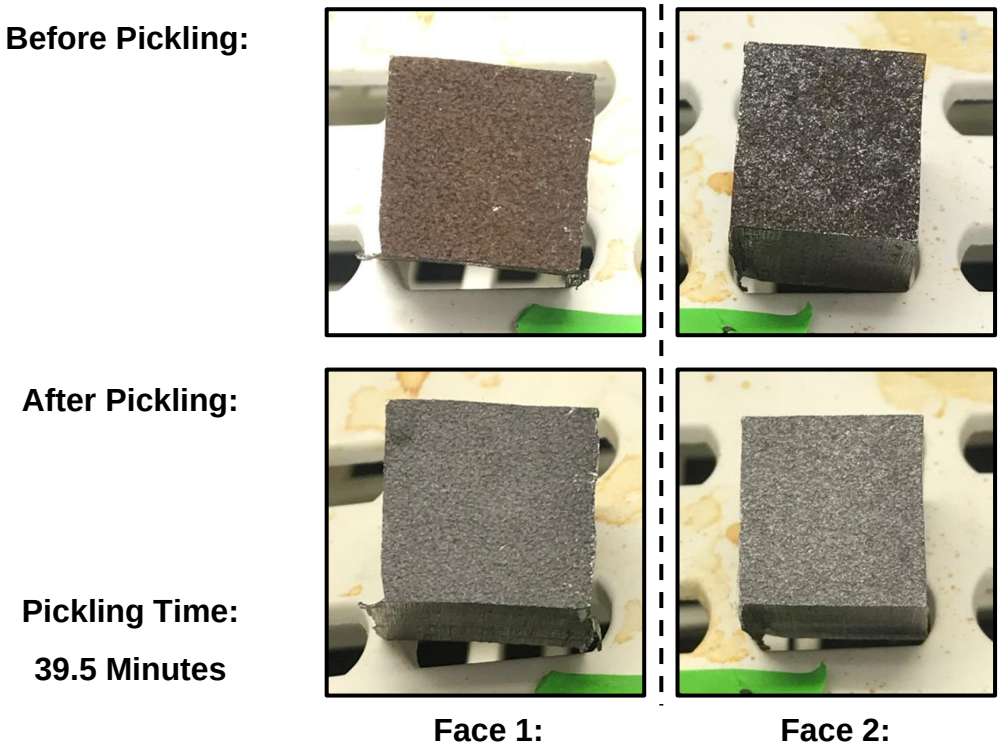
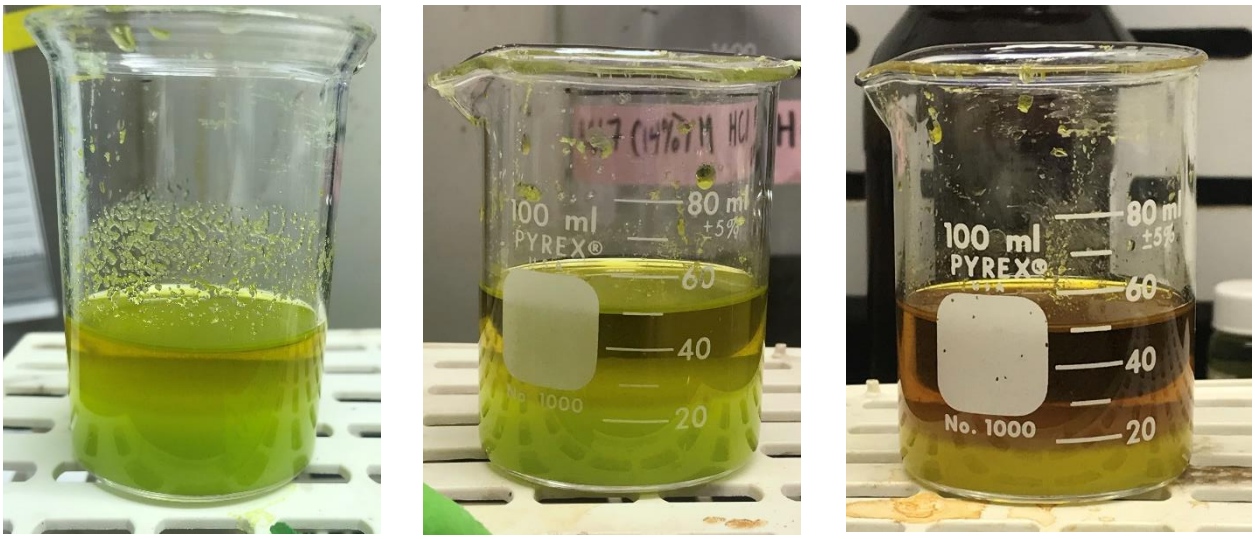


Figure B-20: Solution 5A149F – Coupon 2 Photos



(a) ***(b)*** ***(c)***

Figure B-21: Precipitates from regenerating solution beyond saturation:
a.) 3A163F; b.) 4A154F; c.) 5A149F

APPENDIX C – TASK 2 TEST RESULTS

Table C-1: Solution data for all initial solutions tested for optimum pickling time curve

Initial Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)
2.5A80F	2.5	25.9	79.7
5A63F	5.2	55.9	62.6
8A46F	7.9	85.9	45.5
10.5A29F	10.5	115.9	28.5
13A11F	13.0	145.9	11.4
0.7A125F	0.7	7.6	125.3
2.6A114F	2.6	27.6	113.9
4A103F	4.5	47.6	102.5

Table C-2: Regeneration solution data for lower group of three initial solutions in Table C-1

Solution	Initial Acid Conc. (g/L)	Initial Iron Conc. (g/L)	Regen. Acid Conc. (g/L)	Regen. Iron Conc. (g/L)
0.7A125F - 2.5%R	7.6	125.3	26.3	119.5
0.7A125F - 4%R	7.6	125.3	45.8	113.5
0.7A125F - 7%R	7.6	125.3	73.6	105.2
2.6A114F - 4%R	27.6	113.9	46.9	108.1
2.6A114F - 7%R	27.6	113.9	75.8	100.2
2.6A114F - 9%R	27.6	113.9	97.6	94.1
2.6A114F - 12%R	27.6	113.9	131.8	85.0
4A103F - 7%R	47.6	102.5	75.8	95.0
4A103F - 9%R	47.6	102.5	98.8	89.2
4A103F- 12%R	47.6	102.5	133.0	80.6

Table C-3: Regeneration solution data for upper group of five initial solutions in Table C-1

Solution	Initial Acid Conc. (g/L)	Initial Iron Conc. (g/L)	Regen. Acid Conc. (g/L)	Regen. Iron Conc. (g/L)
2.5A80F - 10%R	25.9	79.7	111.6	62.9
2.5A80F - 15%R	25.9	79.7	169.6	52.4
2.5A80F- 20%R	25.9	79.7	230.9	42.0
2.5A80F - 25%R	25.9	79.7	298.2	31.5
2.5A80F - 30%R	25.9	79.7	368.1	21.0
5A63F - 10%R	55.9	62.6	110.4	62.9
5A63F - 15%R	55.9	62.6	169.6	52.4
5A63F- 20%R	55.9	62.6	230.9	42.0
5A63F - 25%R	55.9	62.6	296.8	31.5
5A63F - 30%R	55.9	62.6	366.6	21.0
8A46F - 10%R	85.9	45.6	108.1	42.7
8A46F - 15%R	85.9	45.6	167.1	35.6
8A46F- 20%R	85.9	45.6	229.6	28.5
8A46F - 25%R	85.9	45.6	295.4	21.4
8A46F - 30%R	85.9	45.6	366.6	14.2
10.5A29F - 15%R	115.9	28.5	168.4	24.1
10.5A29F- 20%R	115.9	28.5	230.9	19.3
10.5A29F - 25%R	115.9	28.5	296.8	14.5
10.5A29F - 30%R	115.9	28.5	366.6	9.6
13A11F - 15%R	145.9	11.4	164.7	10.7
13A11F- 20%R	145.9	11.4	226.9	8.6
13A11F - 25%R	145.9	11.4	294.0	6.4
13A11F - 30%R	145.9	11.4	365.1	4.3

Table C-4: Coupon mass changes from pickling for solution 0.7A125F and its regenerations

0.7A125F Coupon 1		0.7A125F Coupon 2		0.7A125F - 2.5%R Coupon 1		0.7A125F - 2.5%R Coupon 2	
Mass Before (g)	47.68	Mass Before (g)	41.96	Mass Before (g)	45.48	Mass Before (g)	45.16
Mass After (g)	47.42	Mass After (g)	41.66	Mass After (g)	45.31	Mass After (g)	44.97
Loss (g)	0.26	Loss (g)	0.3	Loss (g)	0.17	Loss (g)	0.19
0.7A125F - 4%R Coupon 1		**0.7A125F - 4%R Coupon 2**		**0.7A125F - 7%R Coupon 1**		**0.7A125F - 7%R Coupon 2**	
Mass Before (g)	42.09	Mass Before (g)	47.71	Mass Before (g)	46.9	Mass Before (g)	44.9
Mass After (g)	41.95	Mass After (g)	47.57	Mass After (g)	46.78	Mass After (g)	44.8
Loss (g)	0.14	Loss (g)	0.14	Loss (g)	0.12	Loss (g)	0.1

Table C-5: Coupon mass changes from pickling for solution 2.6A114F and its regenerations

2.6A114F Coupon 1		2.6A114F Coupon 2		2.6A114F - 4%R Coupon 1		2.6A114F - 4%R Coupon 2		2.6A114F - 7%R Coupon 1		2.6A114F - 7%R Coupon 2	
Mass Before (g)	24.86	Mass Before (g)	37.13	Mass Before (g)	46.52	Mass Before (g)	46.03	Mass Before (g)	24.39	Mass Before (g)	30.09
Mass After (g)	24.76	Mass After (g)	37	Mass After (g)	46.39	Mass After (g)	45.92	Mass After (g)	24.29	Mass After (g)	30.03
Loss (g)	0.1	Loss (g)	0.13	Loss (g)	0.13	Loss (g)	0.11	Loss (g)	0.1	Loss (g)	0.06
		2.6A114F- 9%R Coupon 1		**2.6A114F- 9%R Coupon 2**		**2.6A114F - 12%R Coupon 1**		**2.6A114F - 12%R Coupon 2**			
		Mass Before (g)	35.94	Mass Before (g)	35.88	Mass Before (g)	26.14	Mass Before (g)	34.78		
		Mass After (g)	35.88	Mass After (g)	35.82	Mass After (g)	26.09	Mass After (g)	34.73		
		Loss (g)	0.06	Loss (g)	0.06	Loss (g)	0.05	Loss (g)	0.05		

Table C-6: Coupon mass changes from pickling for solution 4A103F and its regenerations

4A103F Coupon 1		**4A103F Coupon 2**		**4A103F - 7%R Coupon 1**		**4A103F - 7%R Coupon 2**	
Mass Before (g)	43.34	Mass Before (g)	36.5	Mass Before (g)	43.65	Mass Before (g)	46
Mass After (g)	43.21	Mass After (g)	36.39	Mass After (g)	43.56	Mass After (g)	45.91
Loss (g)	0.26	Loss (g)	0.11	Loss (g)	0.09	Loss (g)	0.09
4A103F - 9%R Coupon 1		**4A103F - 9%R Coupon 2**		**4A103F- 12%R Coupon 1**		**4A103F- 12%R Coupon 2**	
Mass Before (g)	35.15	Mass Before (g)	30.09	Mass Before (g)	42.41	Mass Before (g)	45.51
Mass After (g)	35.02	Mass After (g)	29.96	Mass After (g)	42.33	Mass After (g)	45.44
Loss (g)	0.14	Loss (g)	0.13	Loss (g)	0.08	Loss (g)	0.07

Table C-7: Coupon mass changes from pickling for solution 2.5A80F and its regenerations

2.5A80F Coupon 1		**2.5A80F Coupon 2**		**2.5A80F - 10%R Coupon 1**		**2.5A80F - 10%R Coupon 2**		**2.5A80F - 15%R Coupon 1**		**2.5A80F - 15%R Coupon 2**	
Mass Before (g)	32.62	Mass Before (g)	29.99	Mass Before (g)	28.26	Mass Before (g)	30.99	Mass Before (g)	29.35	Mass Before (g)	32.68
Mass After (g)	32.5	Mass After (g)	29.87	Mass After (g)	28.16	Mass After (g)	30.87	Mass After (g)	29.29	Mass After (g)	32.61
Loss (g)	0.12	Loss (g)	0.12	Loss (g)	0.1	Loss (g)	0.12	Loss (g)	0.06	Loss (g)	0.07
2.5A80F-20%R Coupon 1		**2.5A80F-20%R Coupon 2**		**2.5A80F - 25%R Coupon 1**		**2.5A80F - 25%R Coupon 2**		**2.5A80F - 30%R Coupon 1**		**2.5A80F - 30%R Coupon 2**	
Mass Before (g)	35.87	Mass Before (g)	34.56	Mass Before (g)	35.51	Mass Before (g)	36.99	Mass Before (g)	27.75	Mass Before (g)	30.69
Mass After (g)	35.82	Mass After (g)	34.5	Mass After (g)	35.44	Mass After (g)	36.93	Mass After (g)	27.68	Mass After (g)	30.63
Loss (g)	0.05	Loss (g)	0.06	Loss (g)	0.07	Loss (g)	0.06	Loss (g)	0.07	Loss (g)	0.06

Table C-8: Coupon mass changes from pickling for solution 5A63F and its regenerations

5A63F Coupon 1		**5A63F Coupon 2**		**5A63F - 10%R Coupon 1**		**5A63F - 10%R Coupon 2**		**5A63F - 15%R Coupon 1**		**5A63F - 15%R Coupon 2**	
Mass Before (g)	40.68	Mass Before (g)	42.53	Mass Before (g)	42.24	Mass Before (g)	39.08	Mass Before (g)	36.77	Mass Before (g)	42.23
Mass After (g)	40.56	Mass After (g)	42.4	Mass After (g)	42.15	Mass After (g)	38.98	Mass After (g)	36.65	Mass After (g)	42.18
Loss (g)	0.12	Loss (g)	0.13	Loss (g)	0.09	Loss (g)	0.1	Loss (g)	0.12	Loss (g)	0.05
5A63F-20%R Coupon 1		**5A63F-20%R Coupon 2**		**5A63F - 25%R Coupon 1**		**5A63F - 25%R Coupon 2**		**5A63F - 30%R Coupon 1**		**5A63F - 30%R Coupon 2**	
Mass Before (g)	43.88	Mass Before (g)	42.3	Mass Before (g)	38.97	Mass Before (g)	41.29	Mass Before (g)	39.36	Mass Before (g)	34.51
Mass After (g)	43.78	Mass After (g)	42.2	Mass After (g)	38.86	Mass After (g)	41.19	Mass After (g)	39.23	Mass After (g)	34.39
Loss (g)	0.1	Loss (g)	0.1	Loss (g)	0.11	Loss (g)	0.1	Loss (g)	0.13	Loss (g)	0.12

Table C-9: Coupon mass changes from pickling for solution 8A46F and its regenerations

8A46F Coupon 1		8A46F Coupon 2		8A46F - 10%R Coupon 1		8A46F - 10%R Coupon 2		8A46F - 15%R Coupon 1		8A46F - 15%R Coupon 2	
Mass Before (g)	39.14	Mass Before (g)	32.49	Mass Before (g)	35.51	Mass Before (g)	32.44	Mass Before (g)	39.9	Mass Before (g)	28.92
Mass After (g)	39.04	Mass After (g)	32.42	Mass After (g)	35.42	Mass After (g)	32.32	Mass After (g)	39.82	Mass After (g)	28.77
Loss (g)	0.1	Loss (g)	0.07	Loss (g)	0.09	Loss (g)	0.12	Loss (g)	0.08	Loss (g)	0.15
8A46F-20%R Coupon 1		**8A46F-20%R Coupon 2**		**8A46F - 25%R Coupon 1**		**8A46F - 25%R Coupon 2**		**8A46F - 30%R Coupon 1**		**8A46F - 30%R Coupon 2**	
Mass Before (g)	34.1	Mass Before (g)	40.58	Mass Before (g)	32.13	Mass Before (g)	40.31	Mass Before (g)	32.86	Mass Before (g)	31.22
Mass After (g)	34.02	Mass After (g)	40.43	Mass After (g)	32.06	Mass After (g)	40.2	Mass After (g)	32.8	Mass After (g)	31.15
Loss (g)	0.08	Loss (g)	0.15	Loss (g)	0.07	Loss (g)	0.11	Loss (g)	0.06	Loss (g)	0.07

Table C-10: Coupon mass changes from pickling for solution 10.5A29F and its regenerations

10.5A29F Coupon 1		10.5A29F Coupon 2		10.5A29F - 15%R Coupon 1		10.5A29F - 15%R Coupon 2		10.5A29F - 20%R Coupon 1		10.5A29F - 20%R Coupon 2	
Mass Before (g)	41.31	Mass Before (g)	30.12	Mass Before (g)	34.43	Mass Before (g)	29.98	Mass Before (g)	33.64	Mass Before (g)	32.96
Mass After (g)	41.21	Mass After (g)	30.04	Mass After (g)	34.36	Mass After (g)	29.91	Mass After (g)	33.58	Mass After (g)	32.91
Loss (g)	0.1	Loss (g)	0.08	Loss (g)	0.07	Loss (g)	0.07	Loss (g)	0.06	Loss (g)	0.05

10.5A29F - 25%R Coupon 1		10.5A29F - 25%R Coupon 2		10.5A29F - 30%R Coupon 1		10.5A29F - 30%R Coupon 2	
Mass Before (g)	35.82	Mass Before (g)	36.01	Mass Before (g)	35.28	Mass Before (g)	34.38
Mass After (g)	35.75	Mass After (g)	35.92	Mass After (g)	35.22	Mass After (g)	34.32
Loss (g)	0.07	Loss (g)	0.09	Loss (g)	0.06	Loss (g)	0.06

Table C-11: Coupon mass changes from pickling for solution 13A11F and its regenerations

13A11F Coupon 1		13A11F Coupon 2		13A11F - 15%R Coupon 1		13A11F - 15%R Coupon 2		13A11F - 20%R Coupon 1		13A11F - 20%R Coupon 2	
Mass Before (g)	36.02	Mass Before (g)	36.33	Mass Before (g)	33.54	Mass Before (g)	31.8	Mass Before (g)	30.49	Mass Before (g)	33.8
Mass After (g)	35.94	Mass After (g)	36.24	Mass After (g)	33.47	Mass After (g)	31.73	Mass After (g)	30.43	Mass After (g)	33.72
Loss (g)	0.08	Loss (g)	0.09	Loss (g)	0.07	Loss (g)	0.07	Loss (g)	0.06	Loss (g)	0.08

13A11F - 25%R Coupon 1		13A11F - 25%R Coupon 2		13A11F - 30%R Coupon 1		13A11F - 30%R Coupon 2	
Mass Before (g)	32.4	Mass Before (g)	40.88	Mass Before (g)	30.54	Mass Before (g)	34.77
Mass After (g)	32.33	Mass After (g)	40.78	Mass After (g)	30.49	Mass After (g)	34.7
Loss (g)	0.07	Loss (g)	0.1	Loss (g)	0.05	Loss (g)	0.07

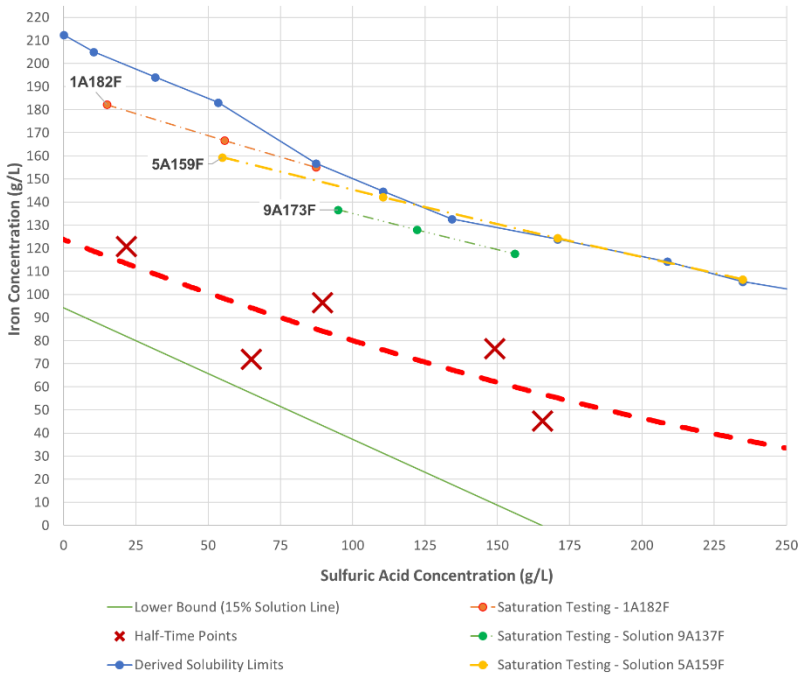


Figure C-1: Solution information shown and plotted for saturation test initial solutions

Table C-12: Solution data for all initial solutions tested for saturation curve

Initial Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)
1A182F	1.4	14.9	182.2
5A159F	5.1	54.9	159.4
9A137F	8.7	94.9	136.6

Table C-13: Regeneration solution data for initial solutions in Table C-12

Solution	Initial Acid Conc. (g/L)	Initial Iron Conc. (g/L)	Regen. Acid Conc. (g/L)	Regen. Iron Conc. (g/L)
1A182F - 5%R	14.9	182.2	55.7	166.7
1A182F - 8%R	14.9	182.2	87.2	155.1
5A159F - 10%R	54.9	159.4	110.5	142.1
5A159F - 15%R	54.9	159.4	170.9	124.3
5A159F - 20%R	54.9	159.4	234.8	106.6
9A137F - 11%R	94.9	136.6	122.2	128.0
9A137F - 14%R	94.9	136.6	156.1	117.6

APPENDIX D – TASK 2 TEST PHOTOS

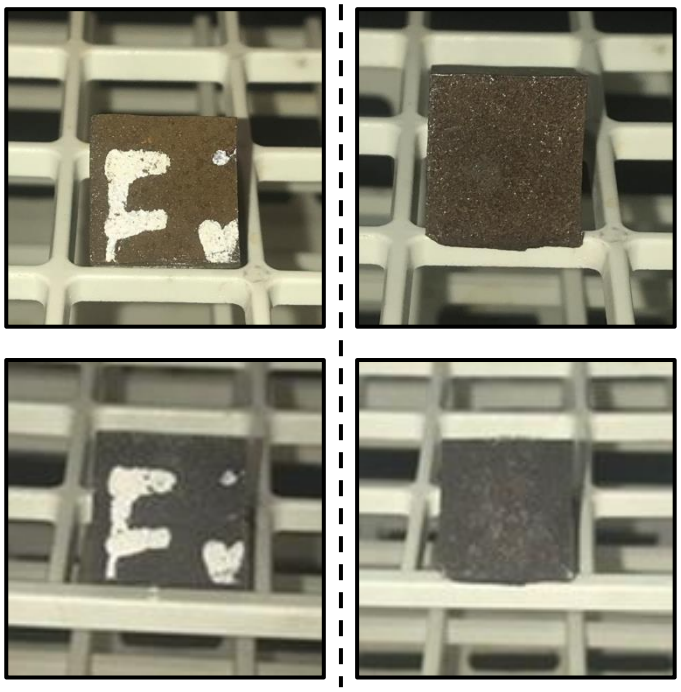
Optimum Pickling Time Curve Tests

Before Pickling:

After Pickling:

Pickling Time:

26.75 Minutes



Face 1: **Face 2:**

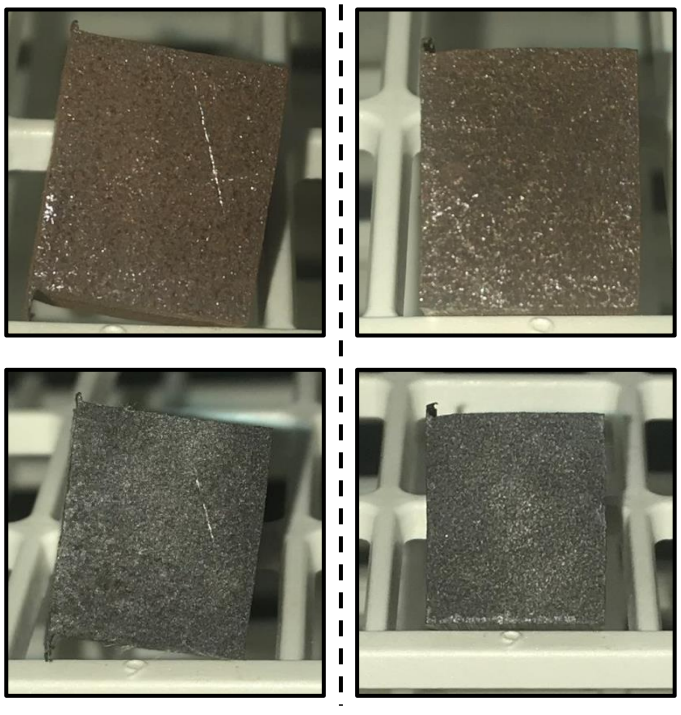
Figure D-1: Solution 2.5A80F – Coupon 1 Photos

Before Pickling:

After Pickling:

Pickling Time:

27.75 Minutes



Face 1: **Face 2:**

Figure D-2: Solution 2.5A80F – Coupon 2 Photos

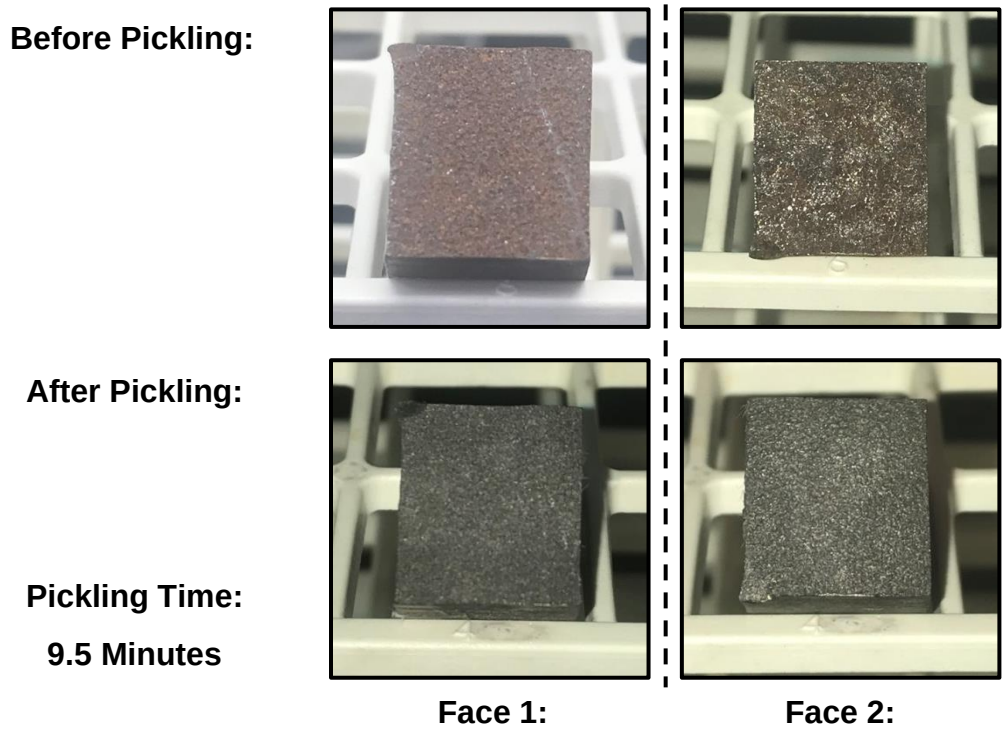


Figure D-3: Solution 2.5A80F regenerated to 10% acid – Coupon 1 Photos

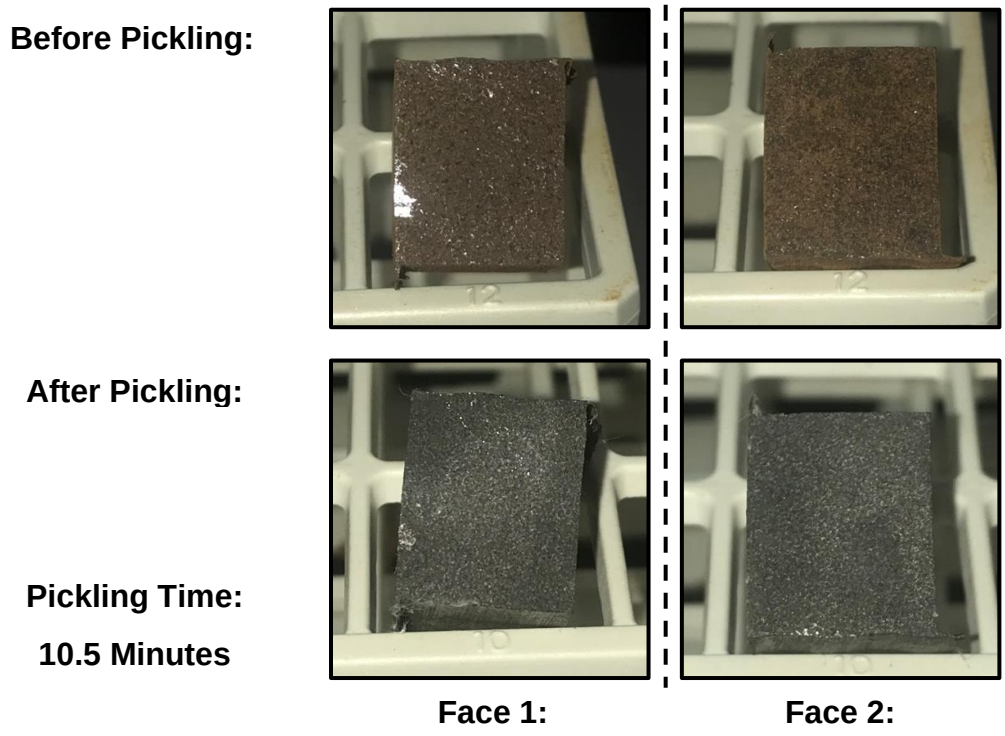


Figure D-4: Solution 2.5A80F regenerated to 10% acid – Coupon 2 Photos

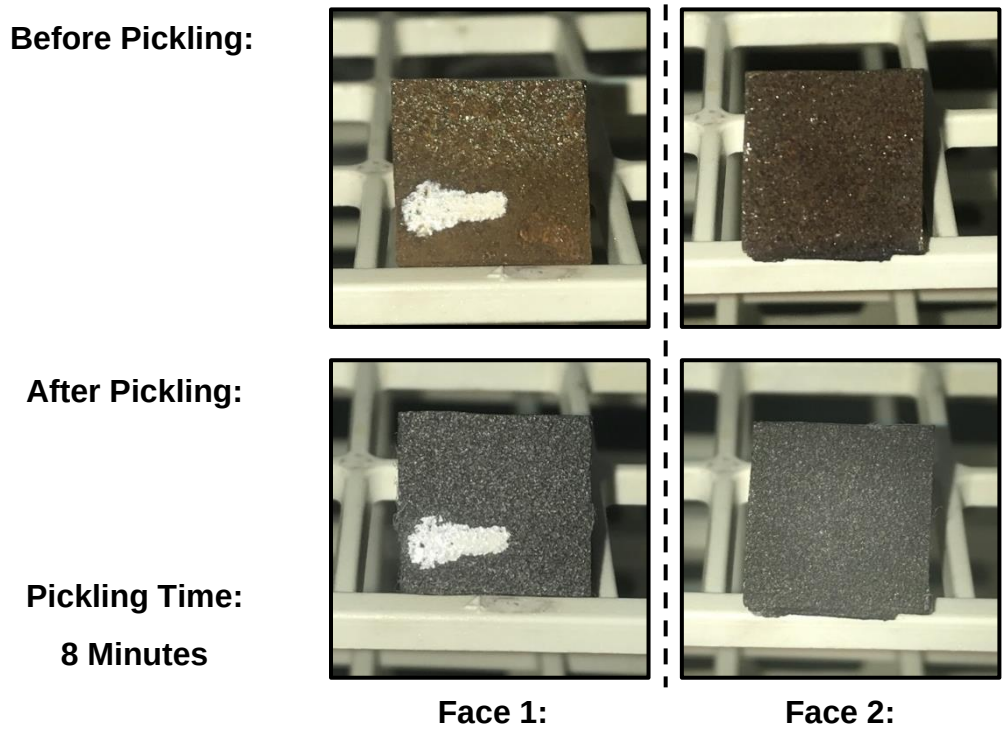


Figure D-5: Solution 2.5A80F regenerated to 15% acid – Coupon 1 Photos

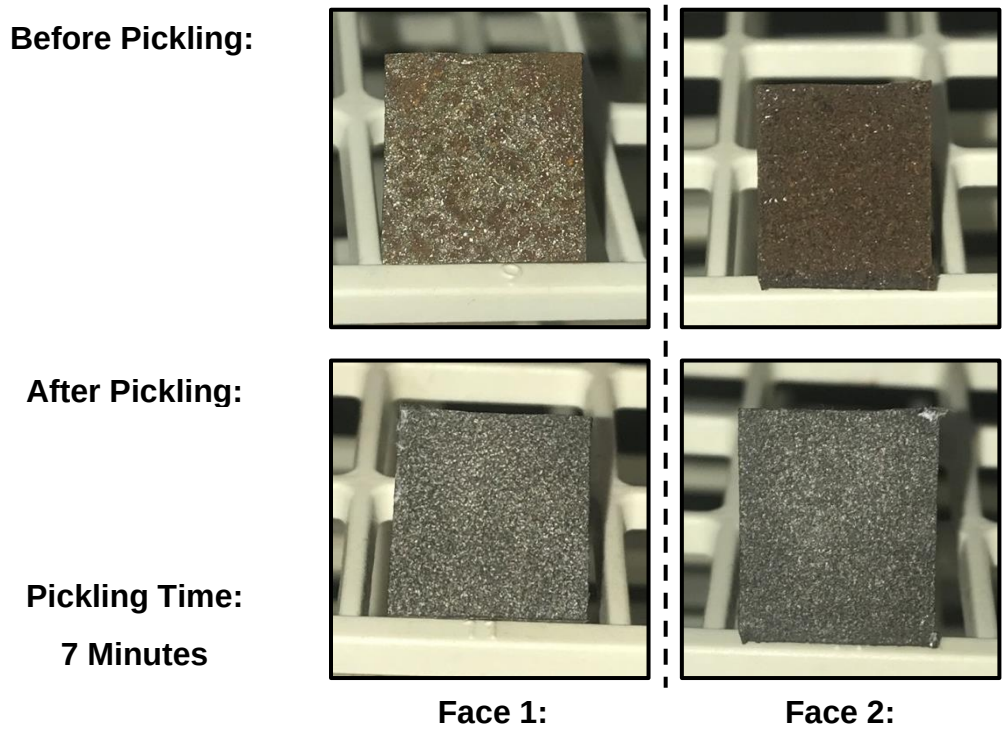


Figure D-6: Solution 2.5A80F regenerated to 15% acid – Coupon 2 Photos

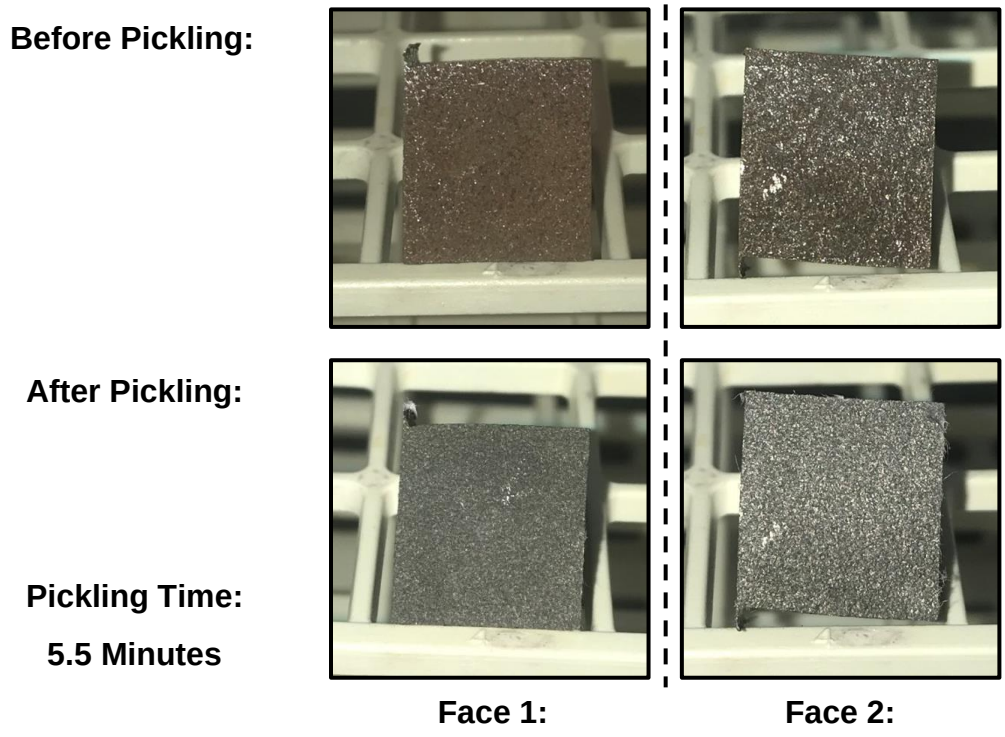


Figure D-7: Solution 2.5A80F regenerated to 20% acid – Coupon 1 Photos

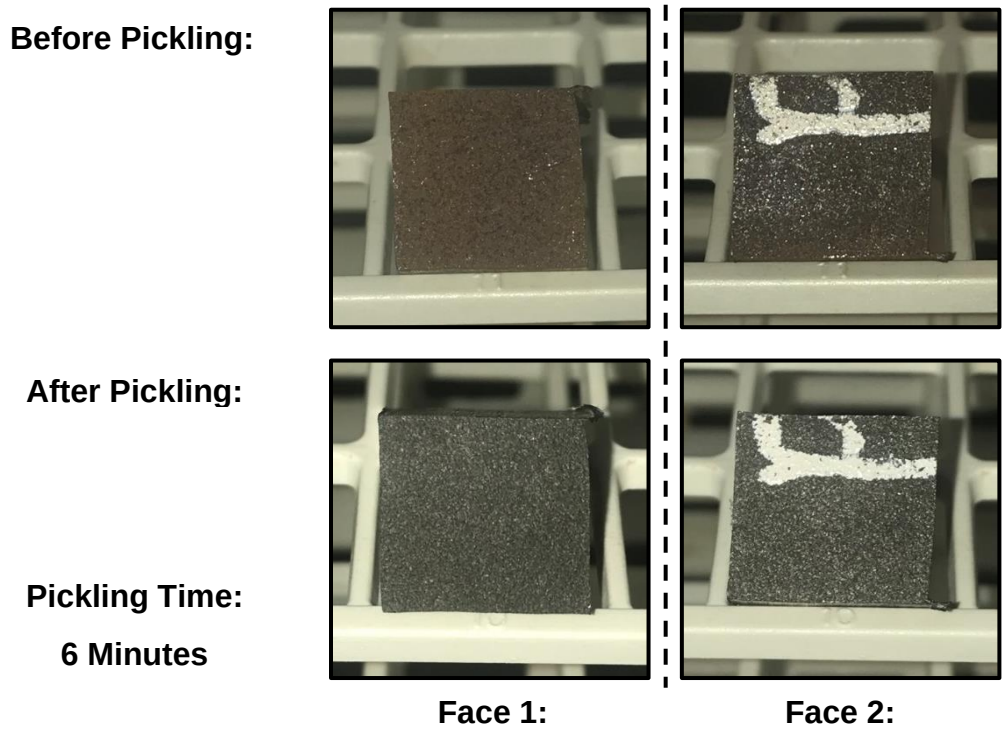


Figure D-8: Solution 2.5A80F regenerated to 20% acid – Coupon 2 Photos

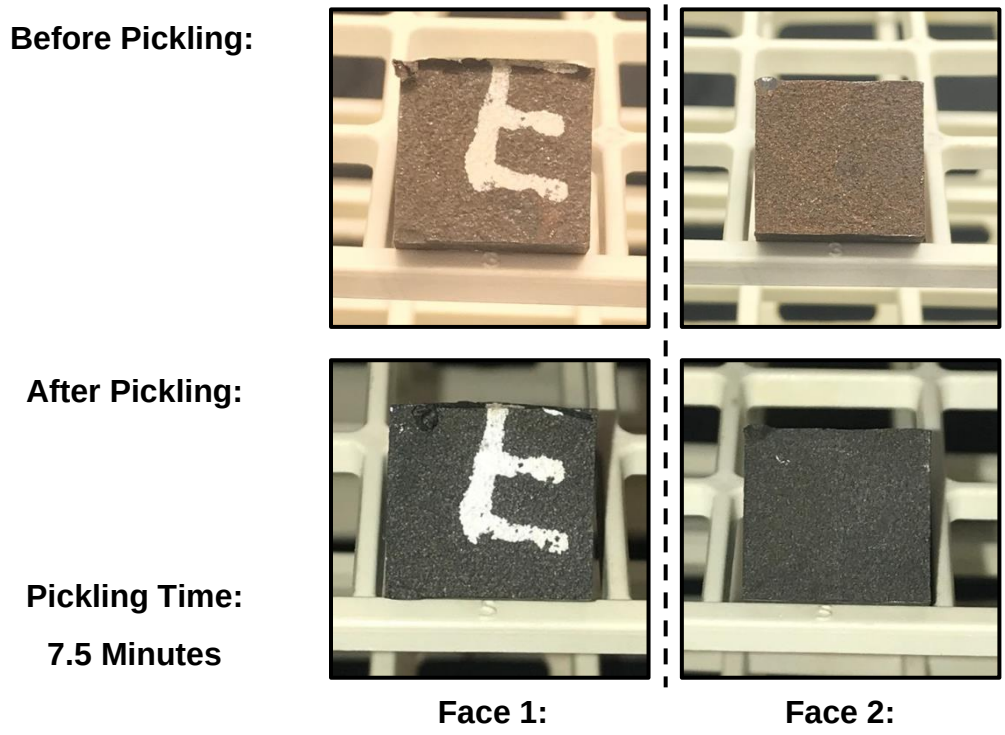


Figure D-9: Solution 2.5A80F regenerated to 25% acid – Coupon 1 Photos

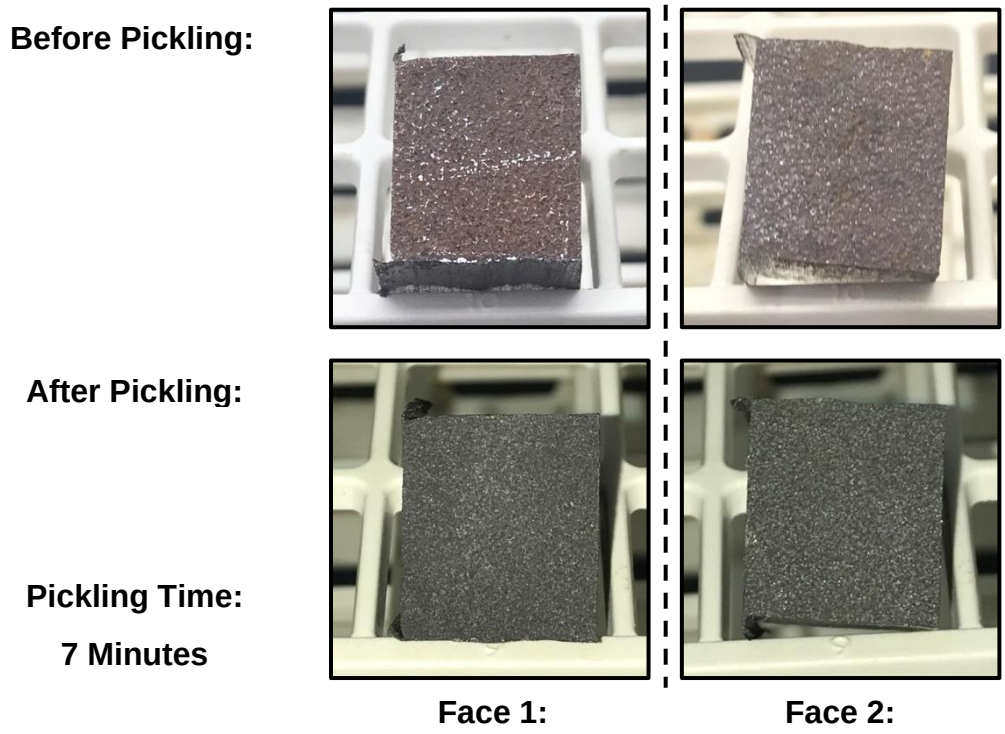


Figure D-10: Solution 2.5A80F regenerated to 25% acid – Coupon 2 Photos

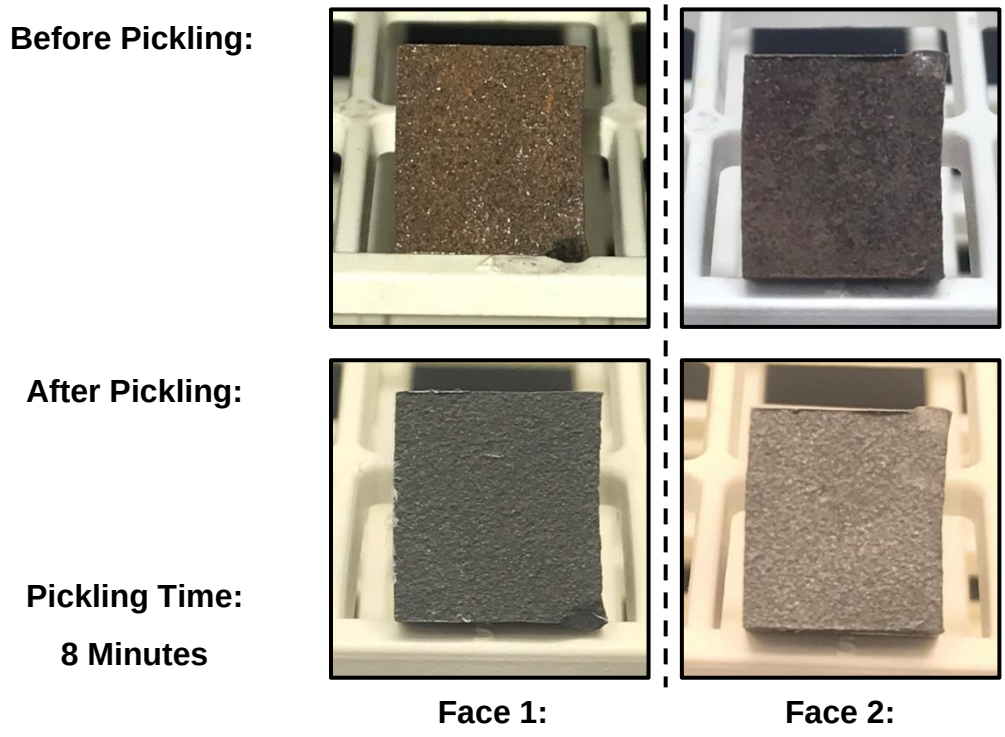


Figure D-11: Solution 2.5A80F regenerated to 30% acid – Coupon 1 Photos

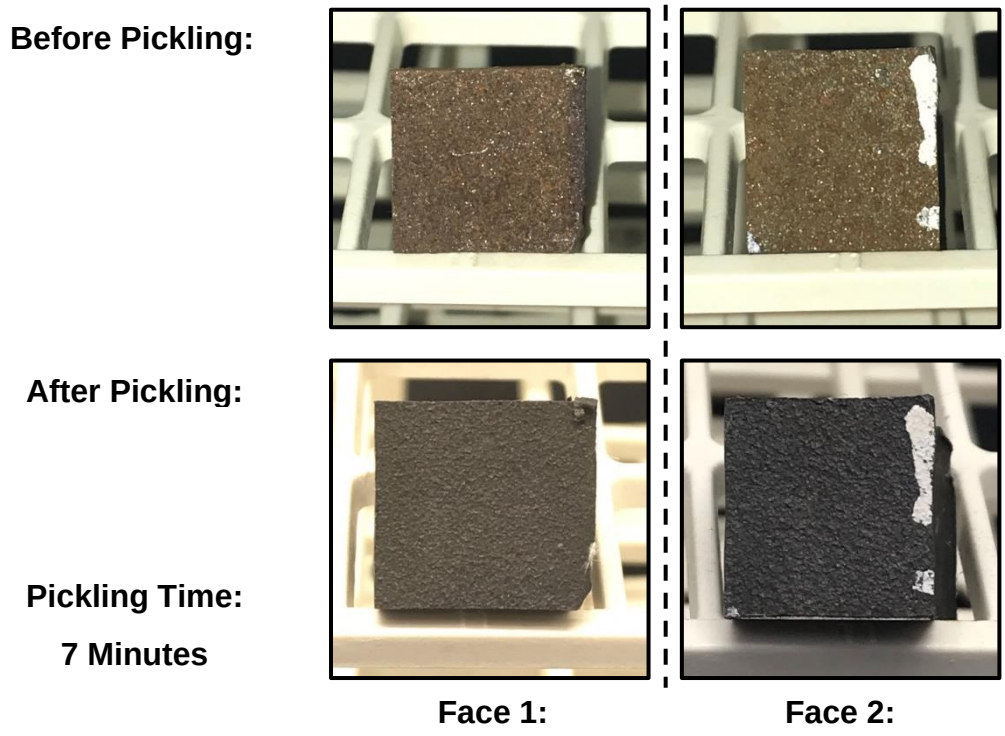


Figure D-12: Solution 2.5A80F regenerated to 30% acid – Coupon 2 Photos

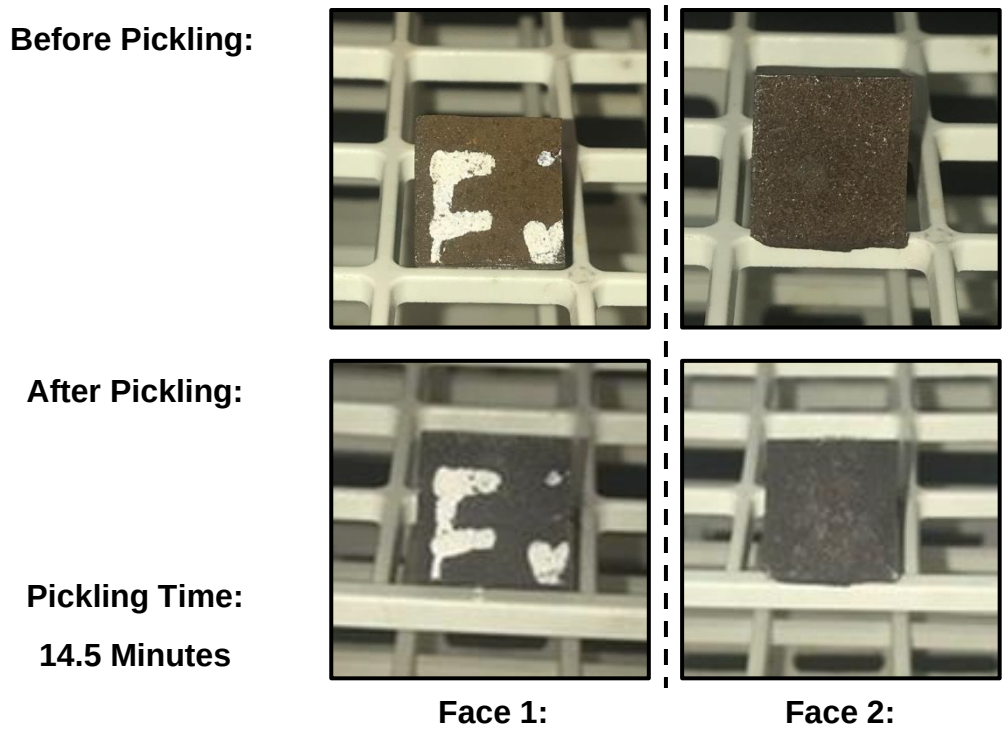


Figure D-13: Solution 5A63F – Coupon 1 Photos

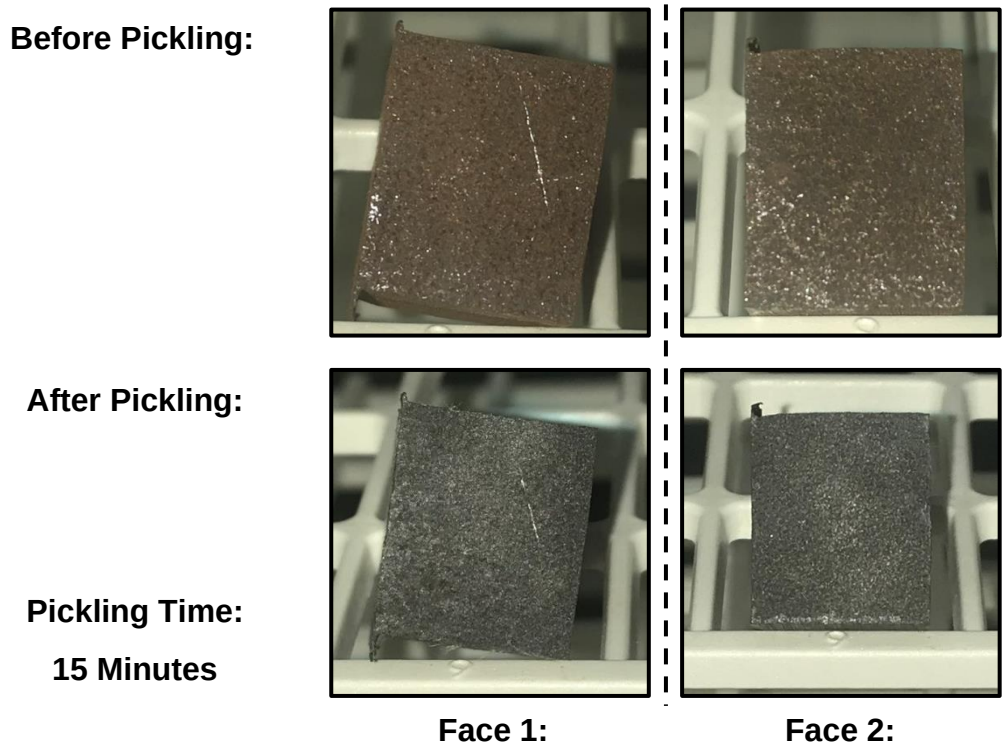


Figure D-14: Solution 5A63F – Coupon 2 Photos

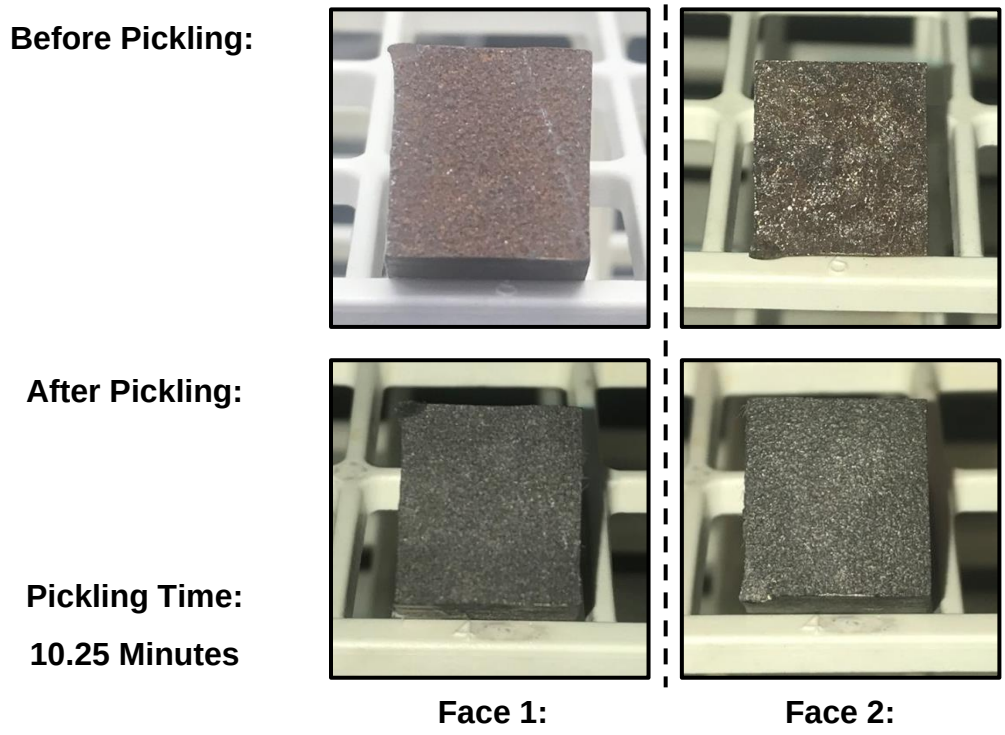


Figure D-15: Solution 5A63F regenerated to 10% acid – Coupon 1 Photos

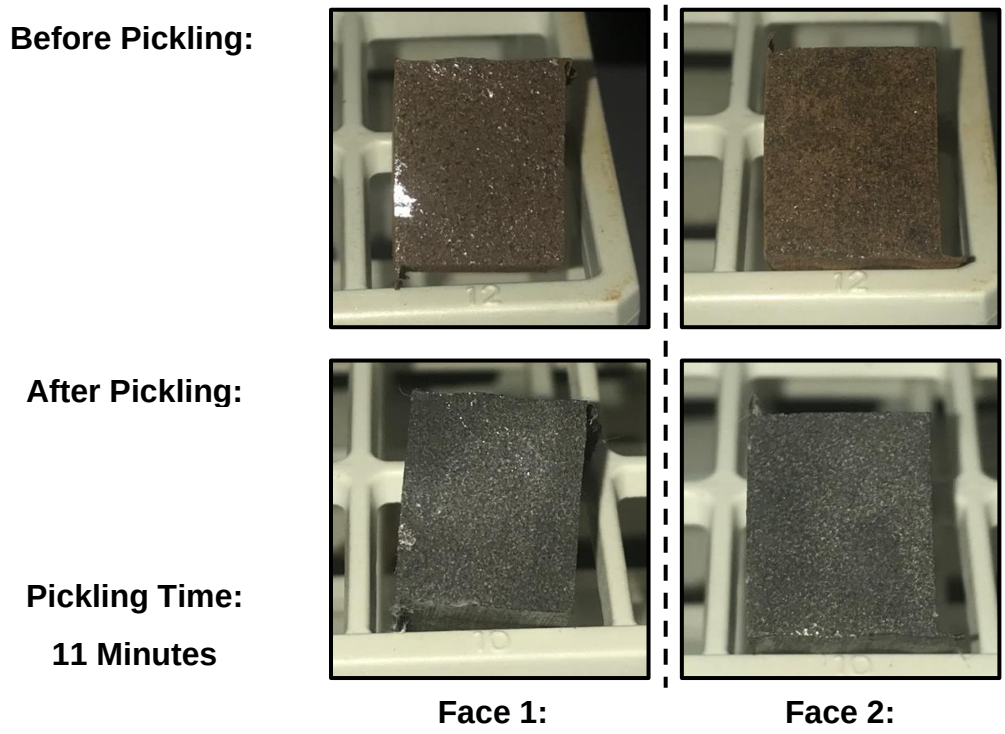


Figure D-16: Solution 5A63F regenerated to 10% acid – Coupon 2 Photos

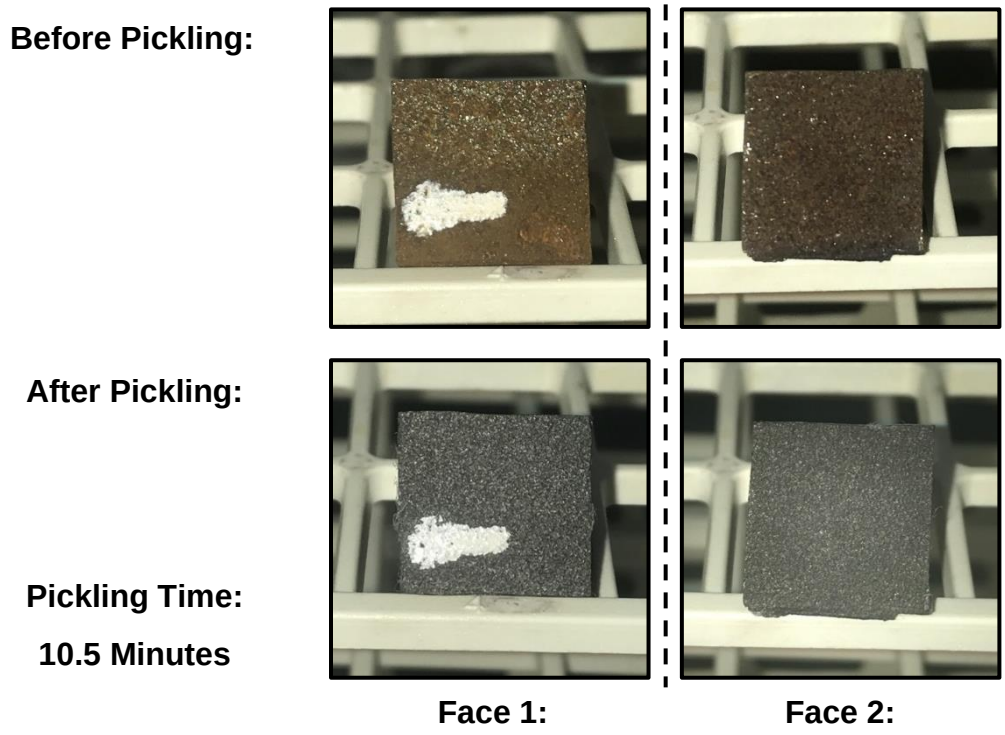


Figure D-17: Solution 5A63F regenerated to 15% acid – Coupon 1 Photos

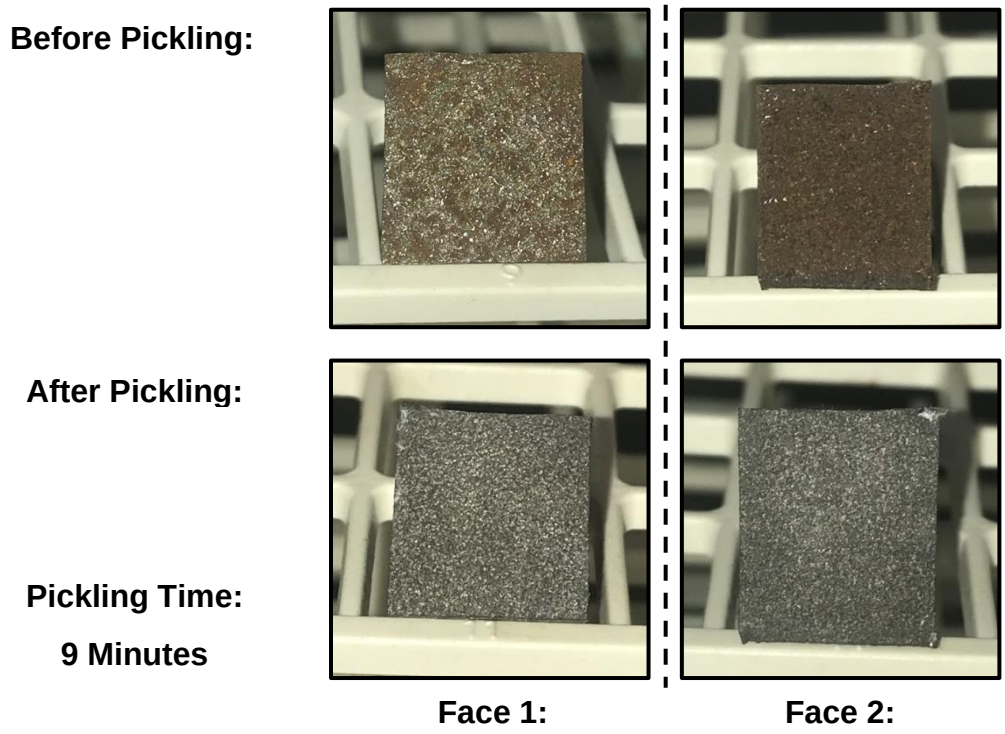


Figure D-18: Solution 5A63F regenerated to 15% acid – Coupon 2 Photos

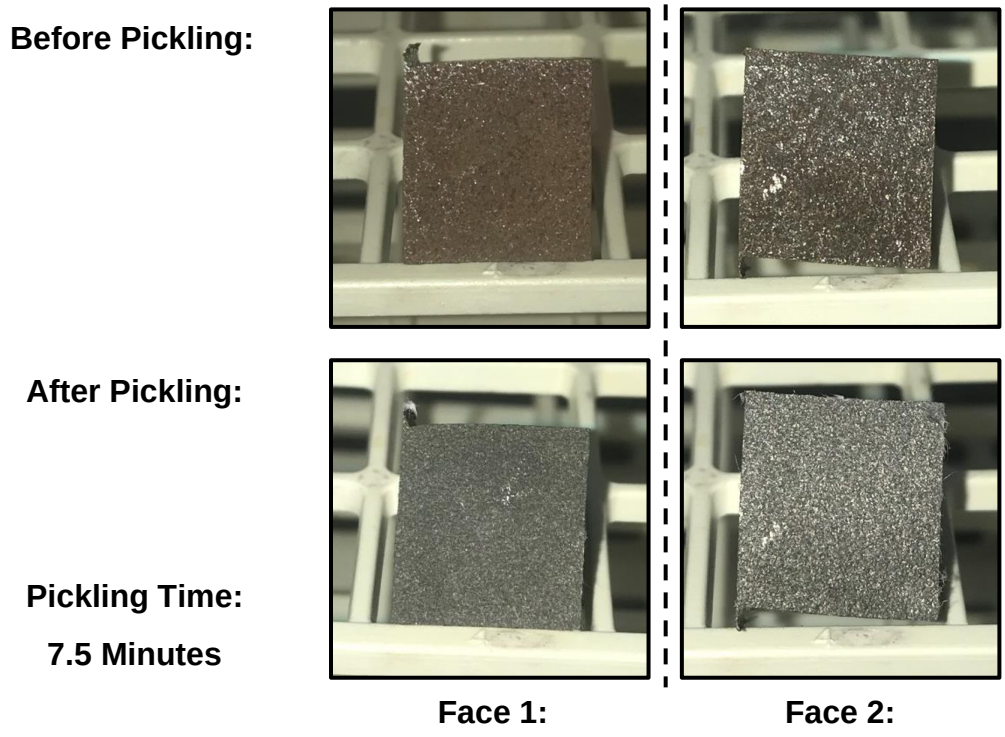


Figure D-19: Solution 5A63F regenerated to 20% acid – Coupon 1 Photos

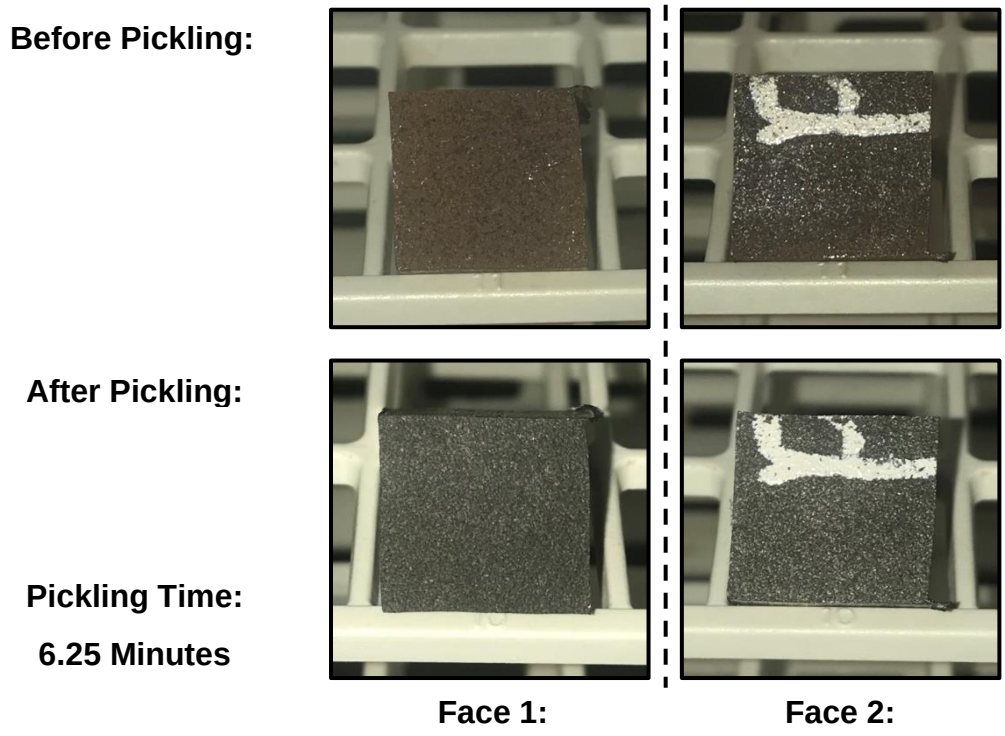


Figure D-20: Solution 5A63F regenerated to 20% acid – Coupon 2 Photos

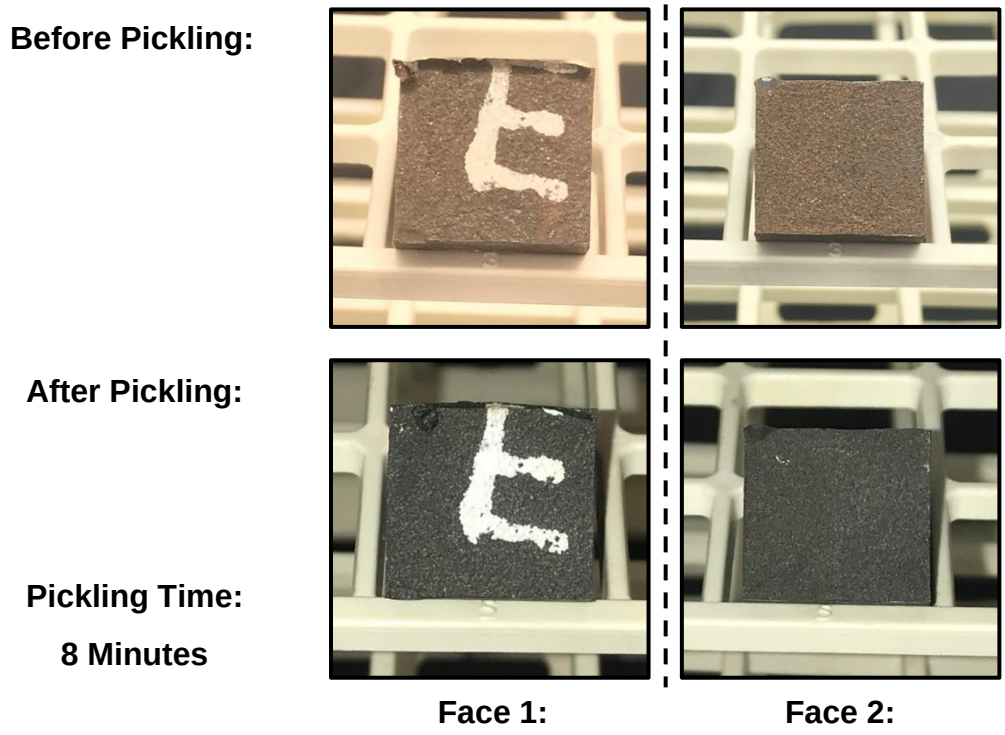


Figure D-21: Solution 5A63F regenerated to 25% acid – Coupon 1 Photos

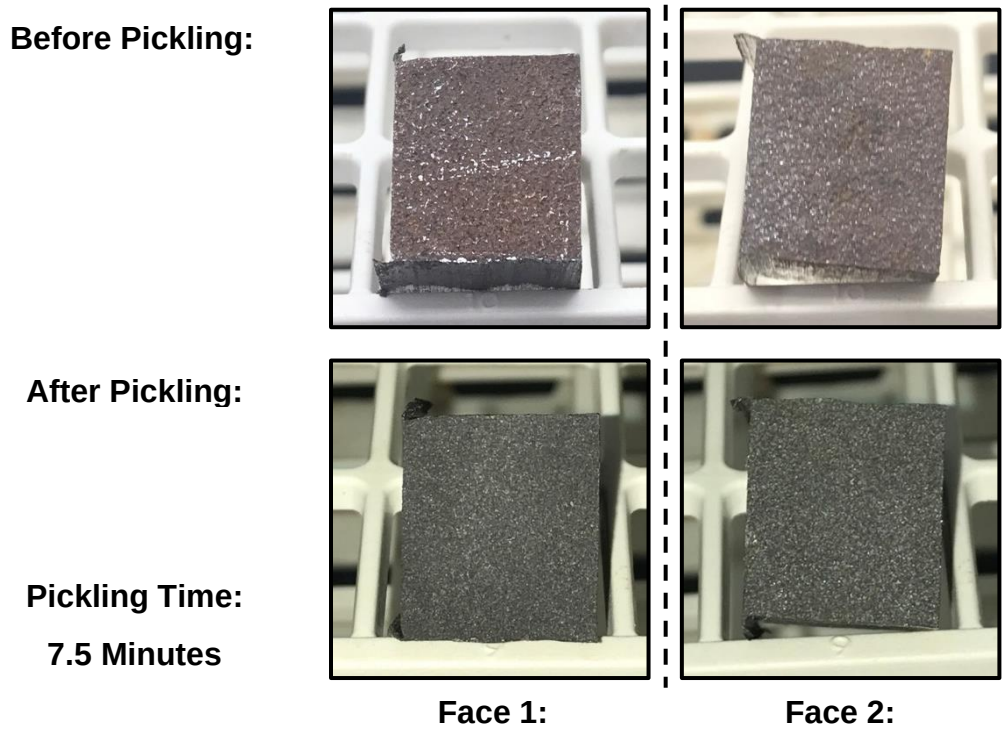


Figure D-22: Solution 5A63F regenerated to 25% acid – Coupon 2 Photos

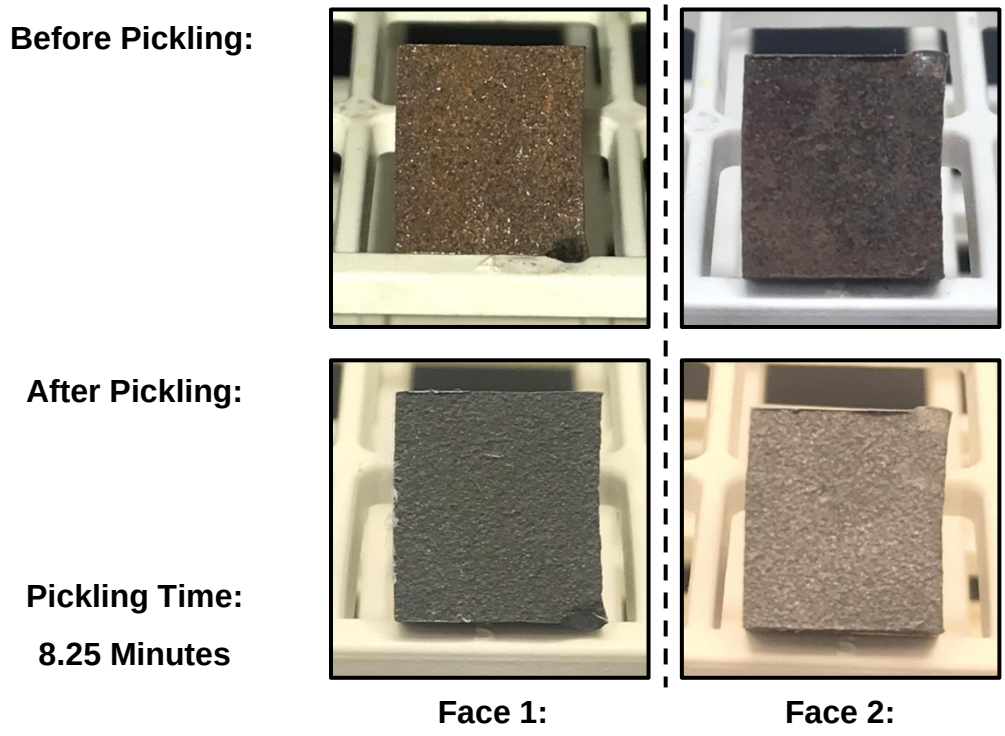


Figure D-23: Solution 5A63F regenerated to 30% acid – Coupon 1 Photos

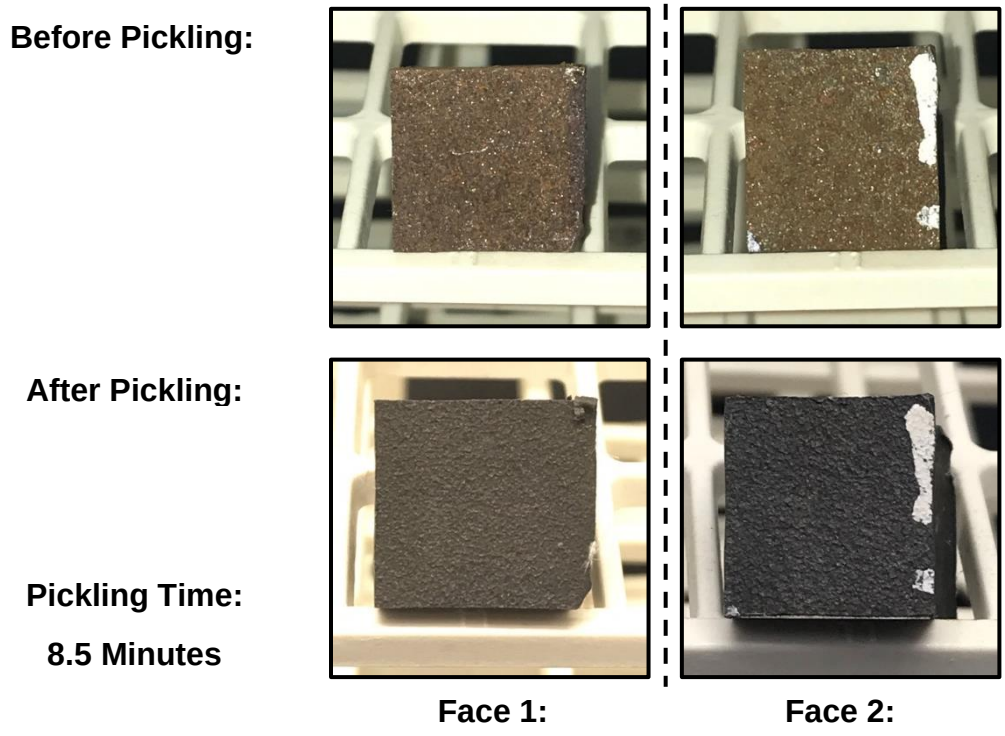


Figure D-24: Solution 5A63F regenerated to 30% acid – Coupon 2 Photos

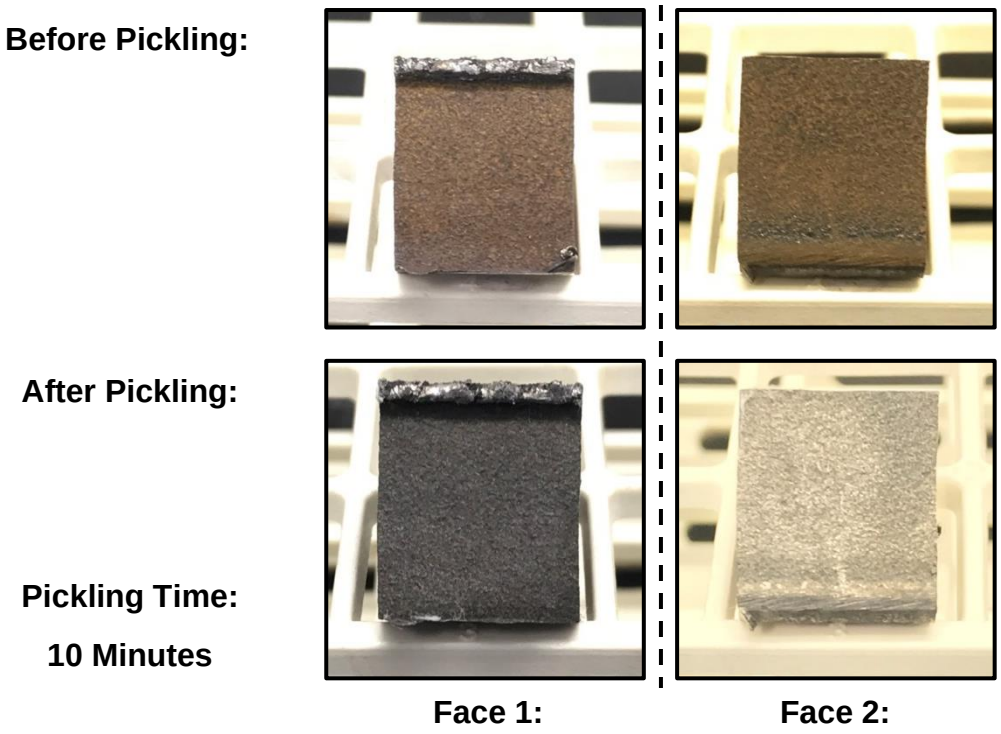


Figure D-25: Solution 8A46F – Coupon 1 Photos

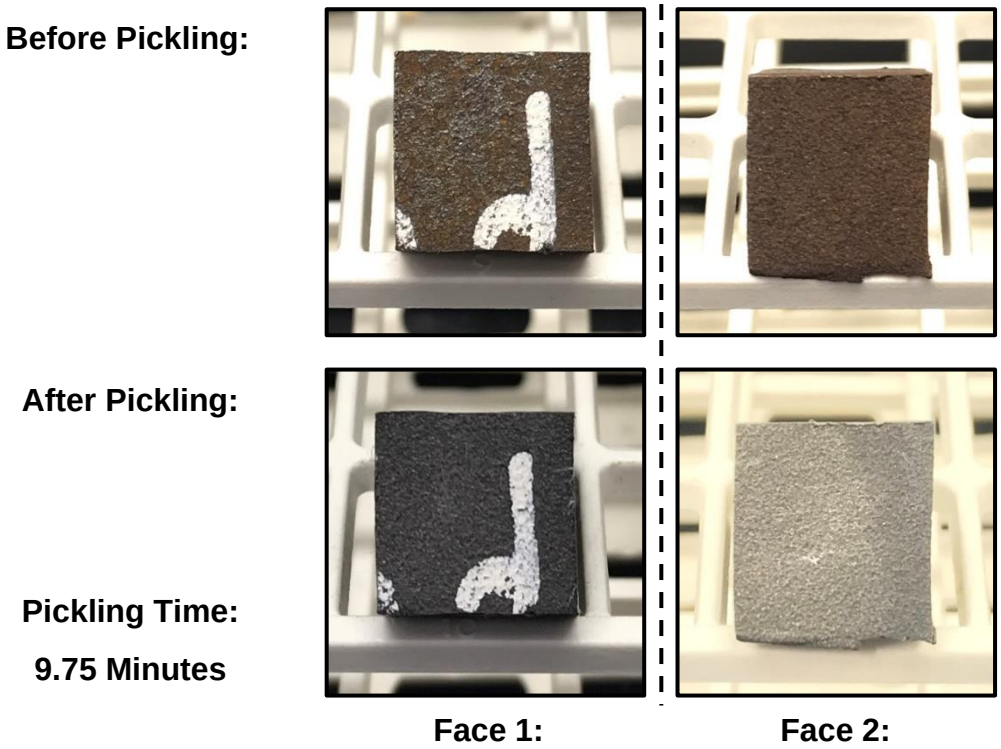


Figure D-26: Solution 8A46F – Coupon 2 Photos

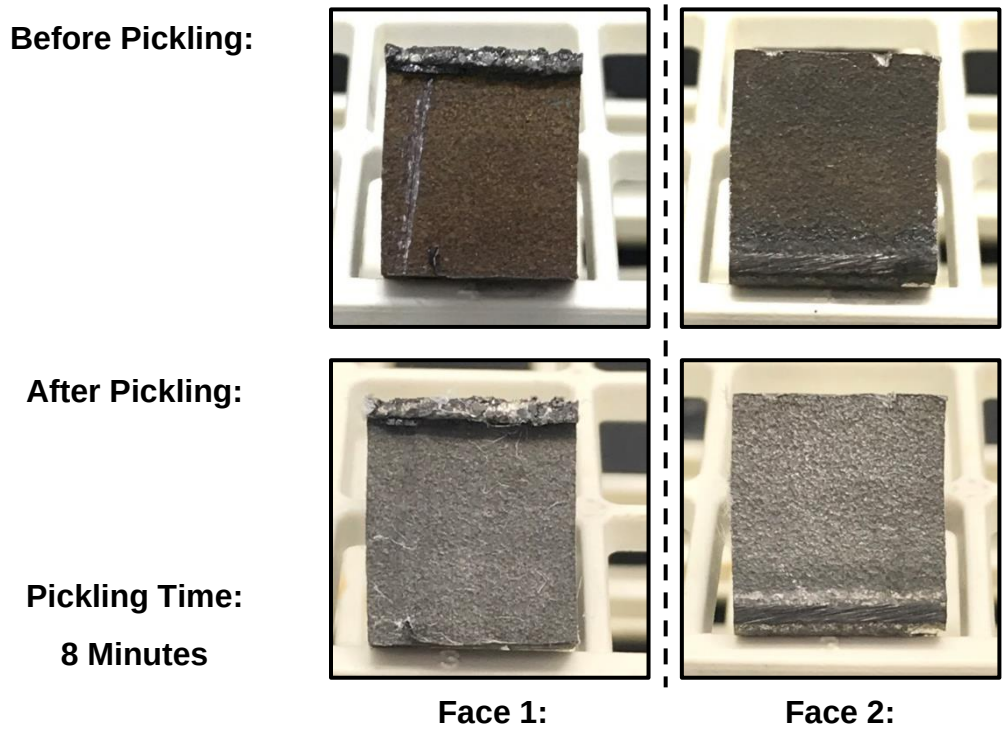


Figure D-27: Solution 8A46F regenerated to 10% acid – Coupon 1 Photos

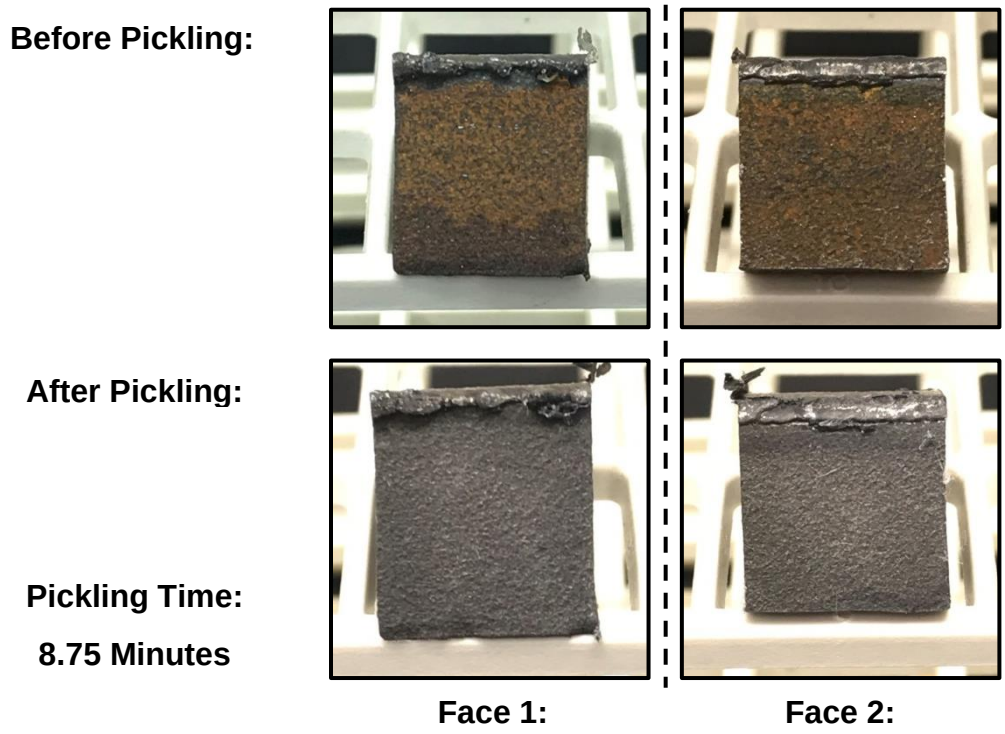


Figure D-28: Solution 8A46F regenerated to 10% acid – Coupon 2 Photos

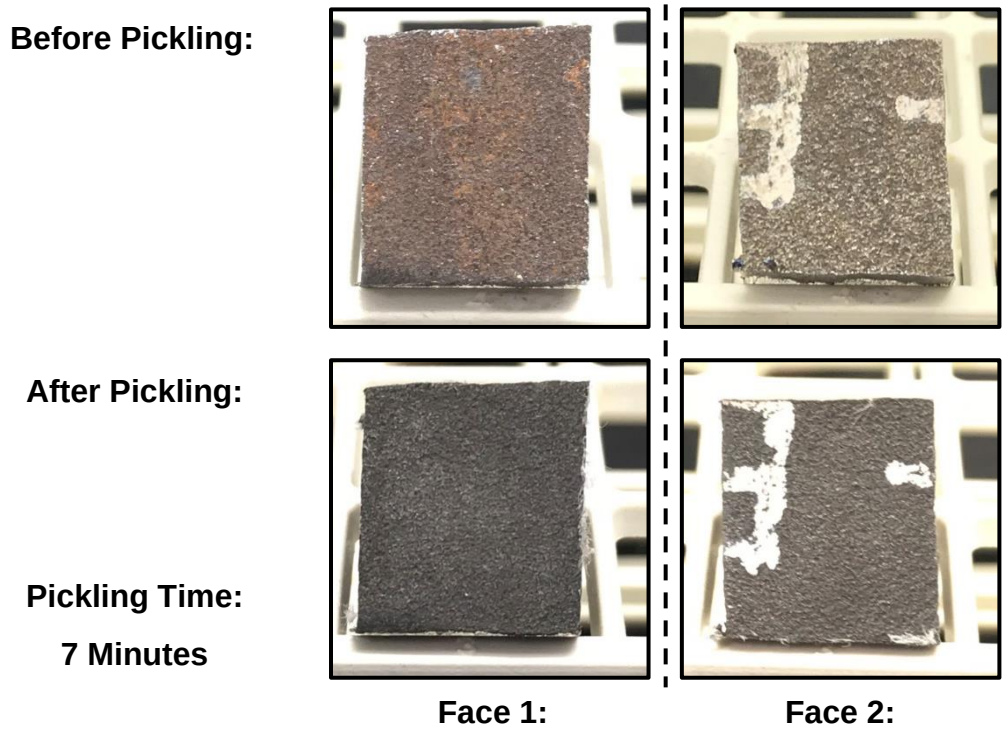


Figure D-29: Solution 8A46F regenerated to 15% acid – Coupon 1 Photos

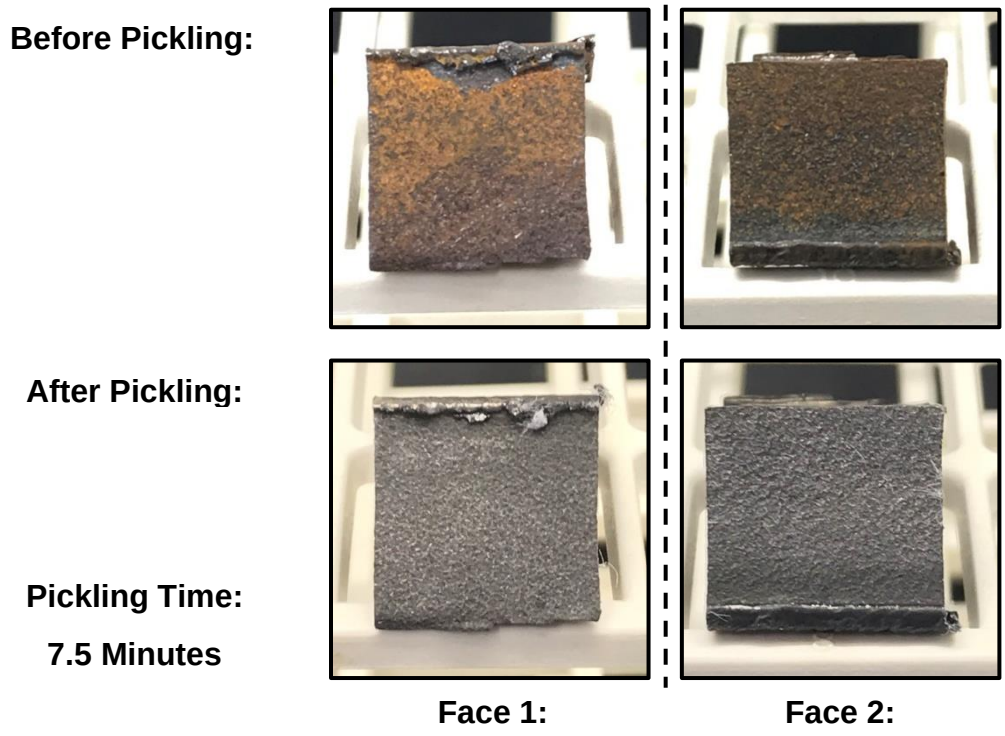


Figure D-30: Solution 8A46F regenerated to 15% acid – Coupon 2 Photos

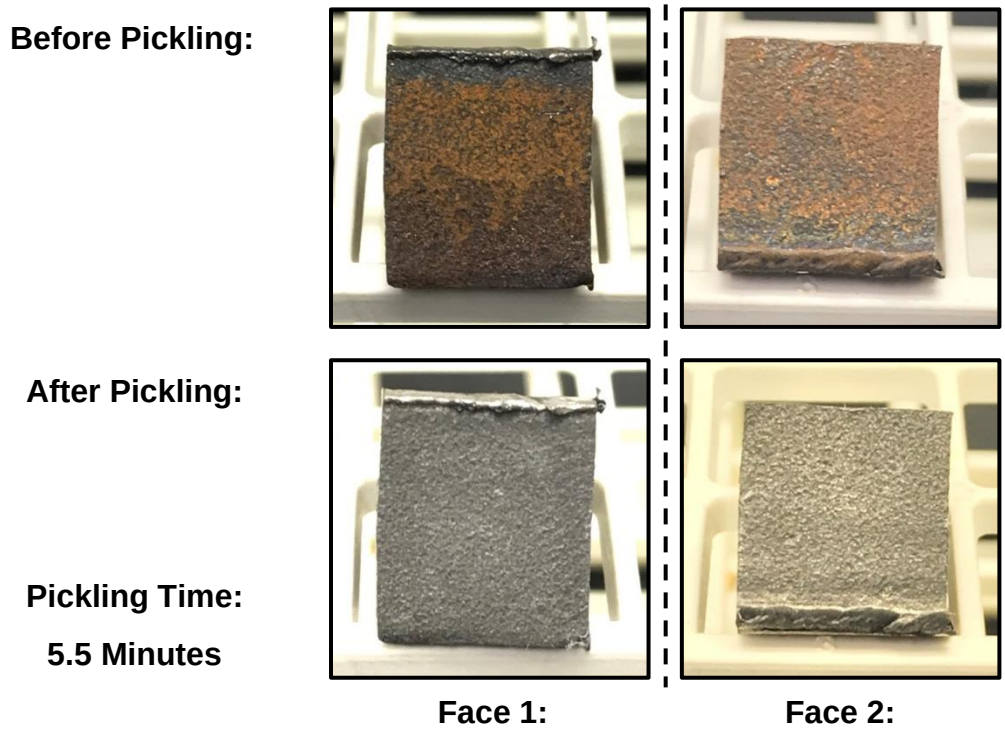


Figure D-31: Solution 8A46F regenerated to 20% acid – Coupon 1 Photos

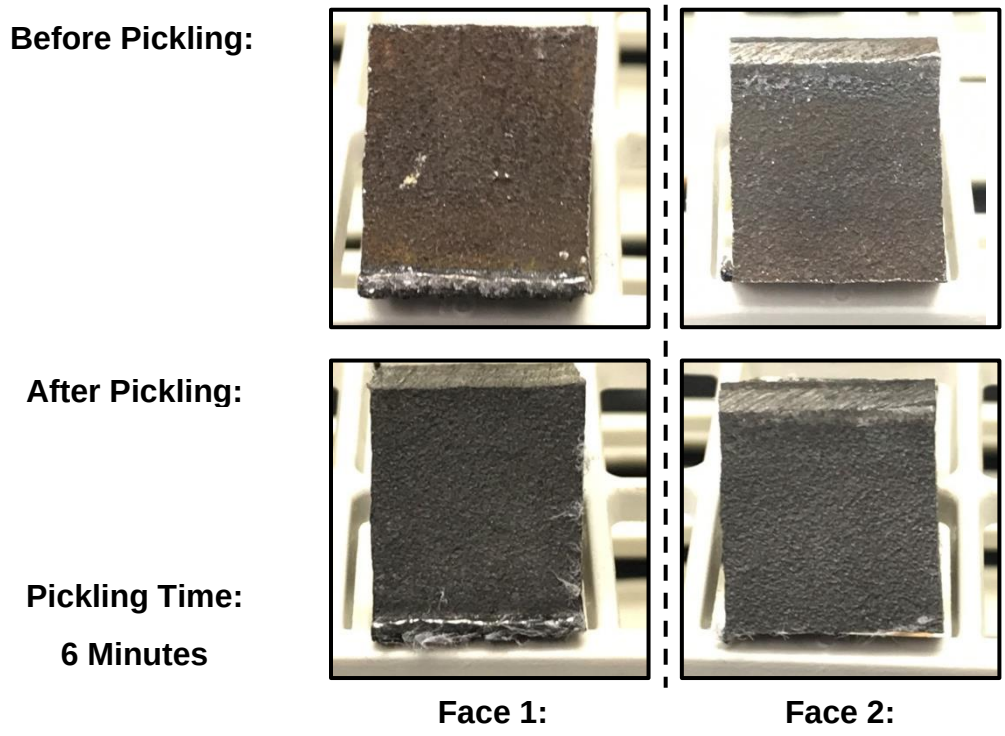


Figure D-32: Solution 8A46F regenerated to 20% acid – Coupon 2 Photos

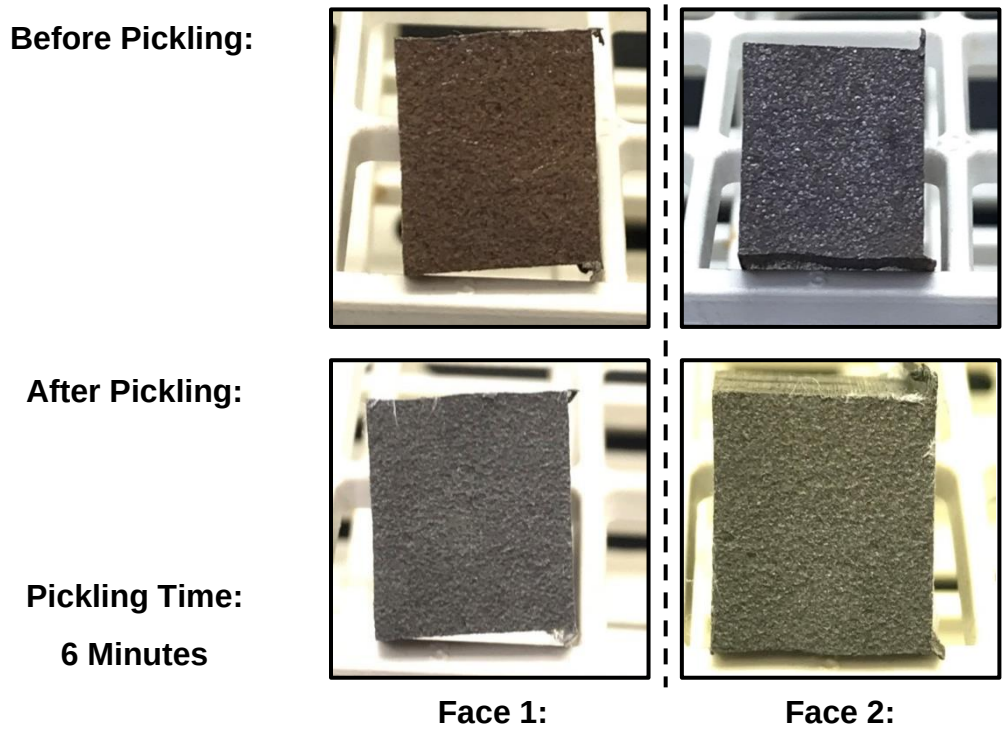


Figure D-33: Solution 8A46F regenerated to 25% acid – Coupon 1 Photos

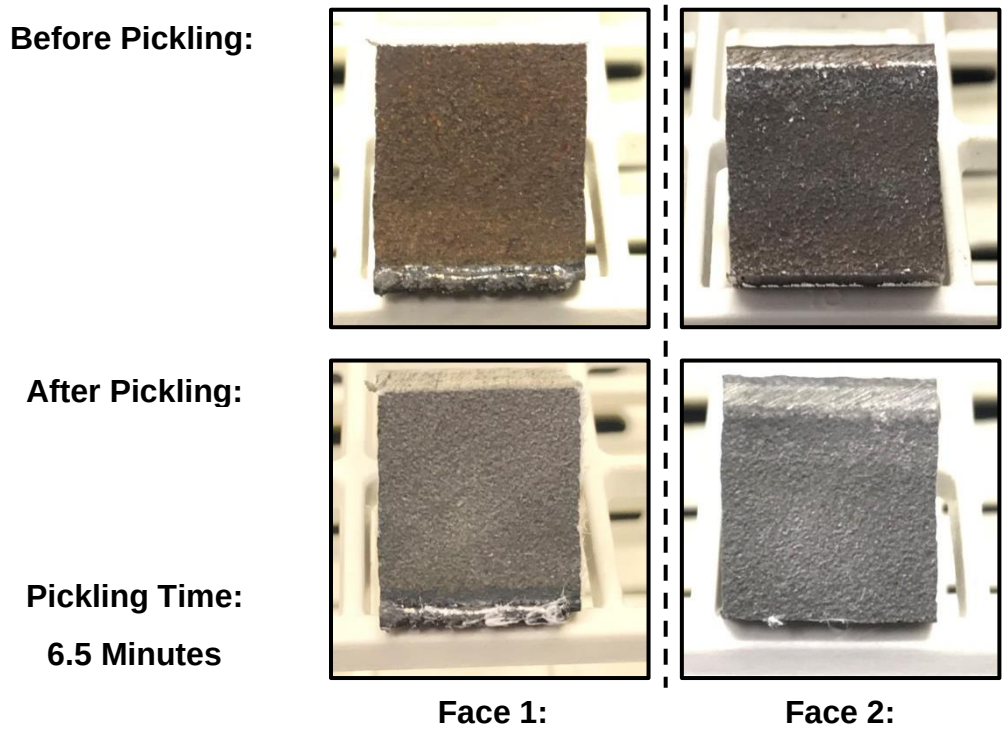


Figure D-34: Solution 8A46F regenerated to 25% acid – Coupon 2 Photos

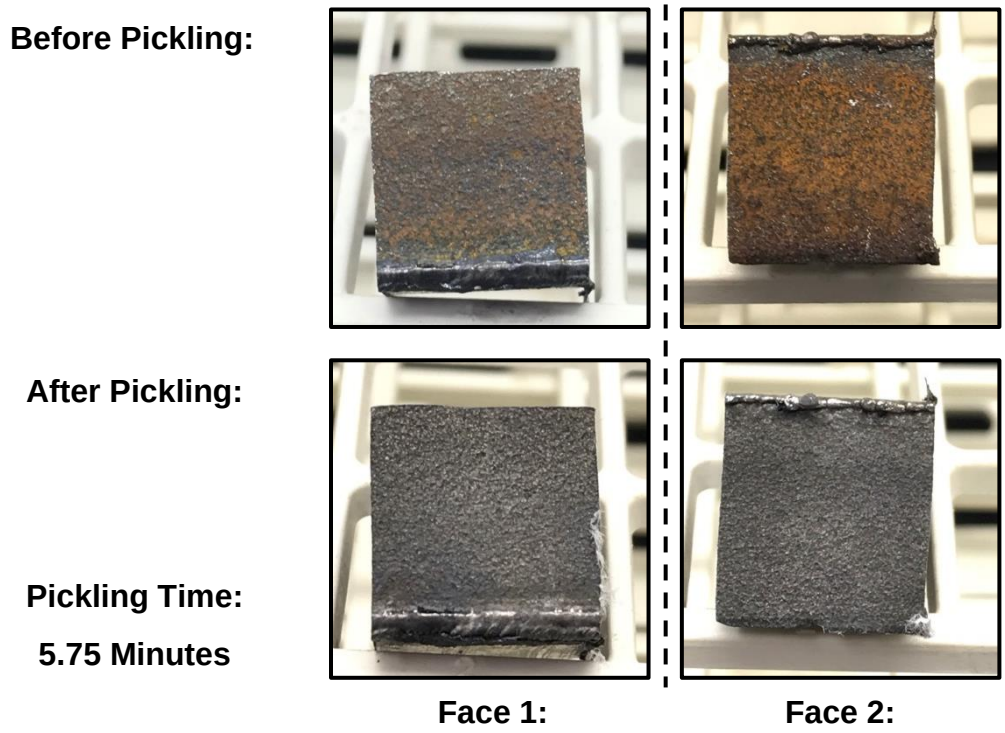


Figure D-35: Solution 8A46F regenerated to 30% acid – Coupon 1 Photos

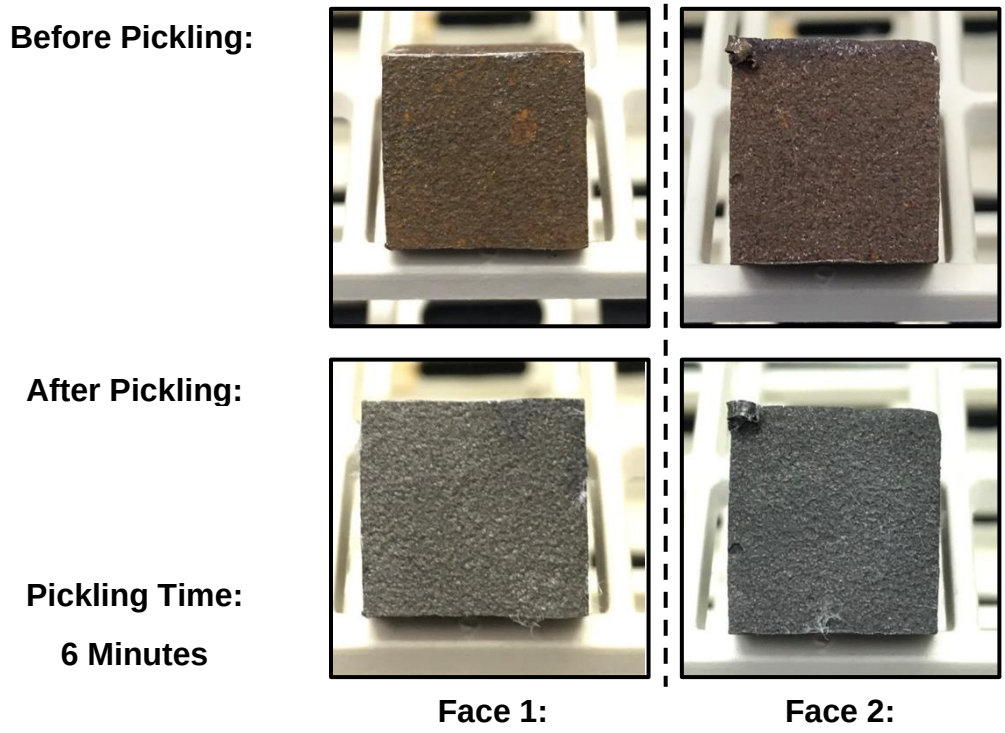


Figure D-36: Solution 8A46F regenerated to 30% acid – Coupon 2 Photos

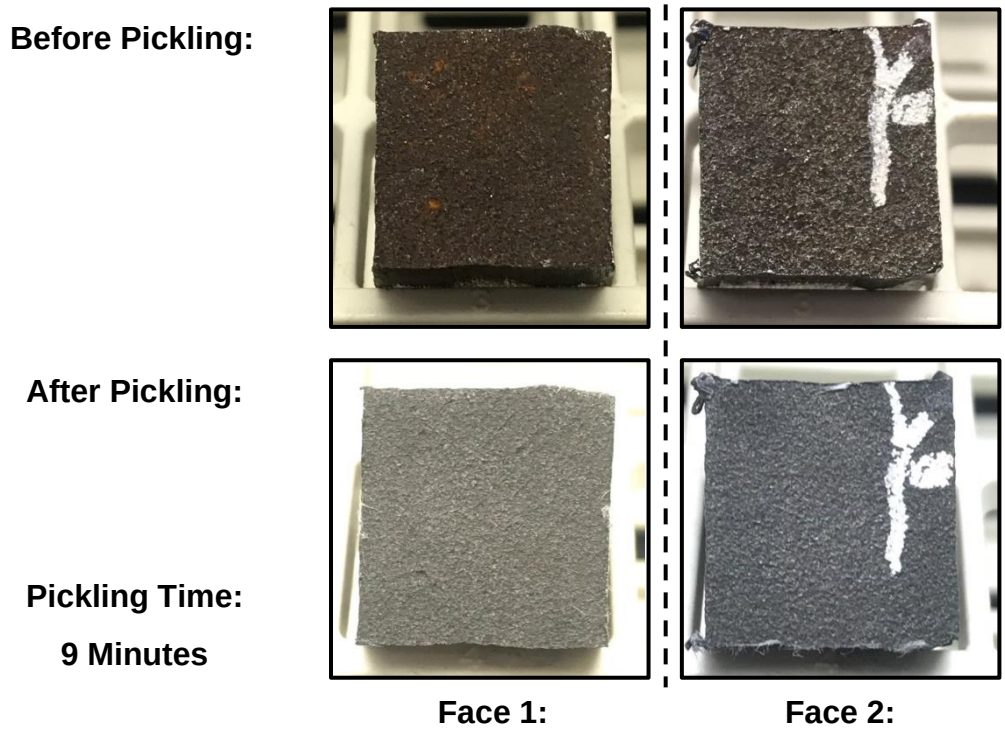


Figure D-37: Solution 10.5A29F – Coupon 1 Photos

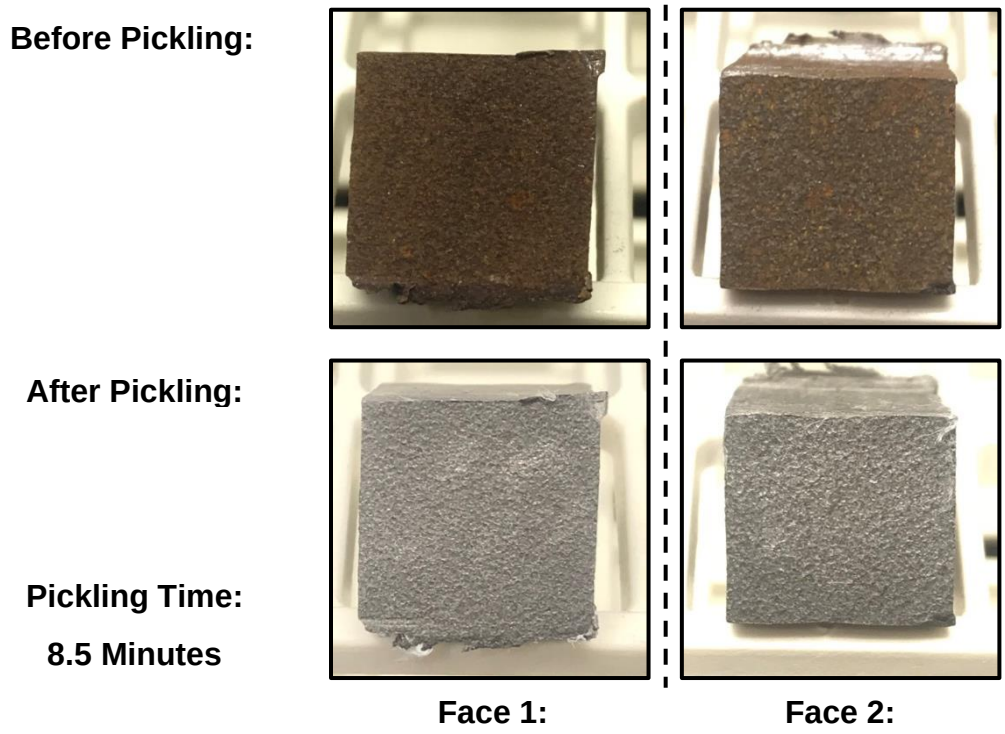


Figure D-38: Solution 10.5A29F – Coupon 2 Photos

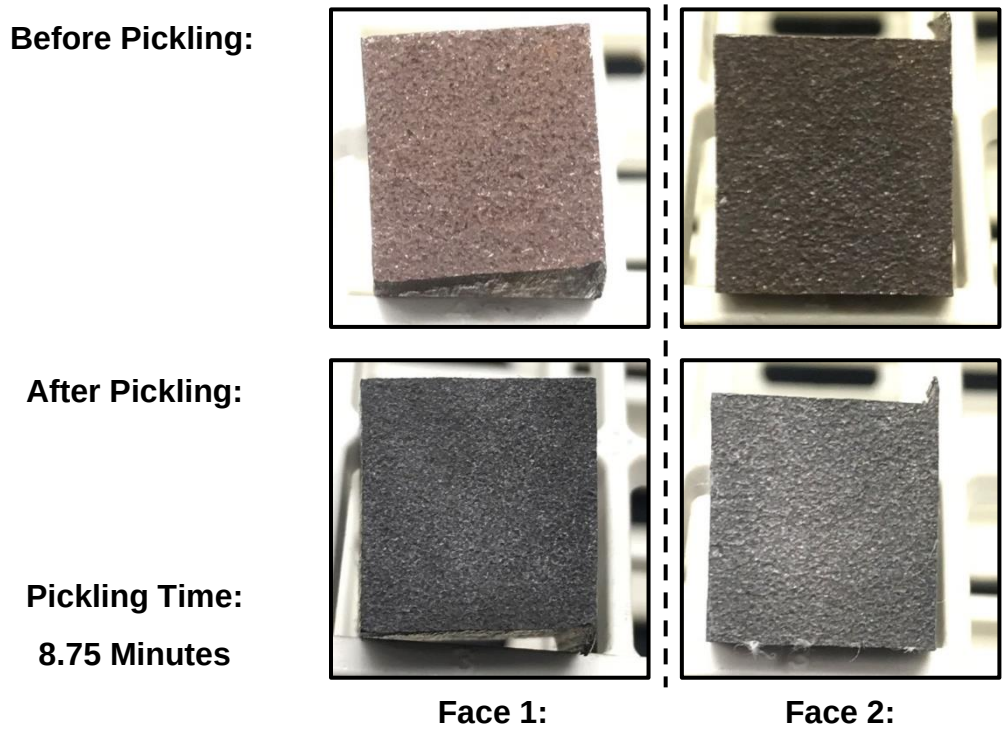


Figure D-39: Solution 10.5A29F regenerated to 15% acid – Coupon 1 Photos

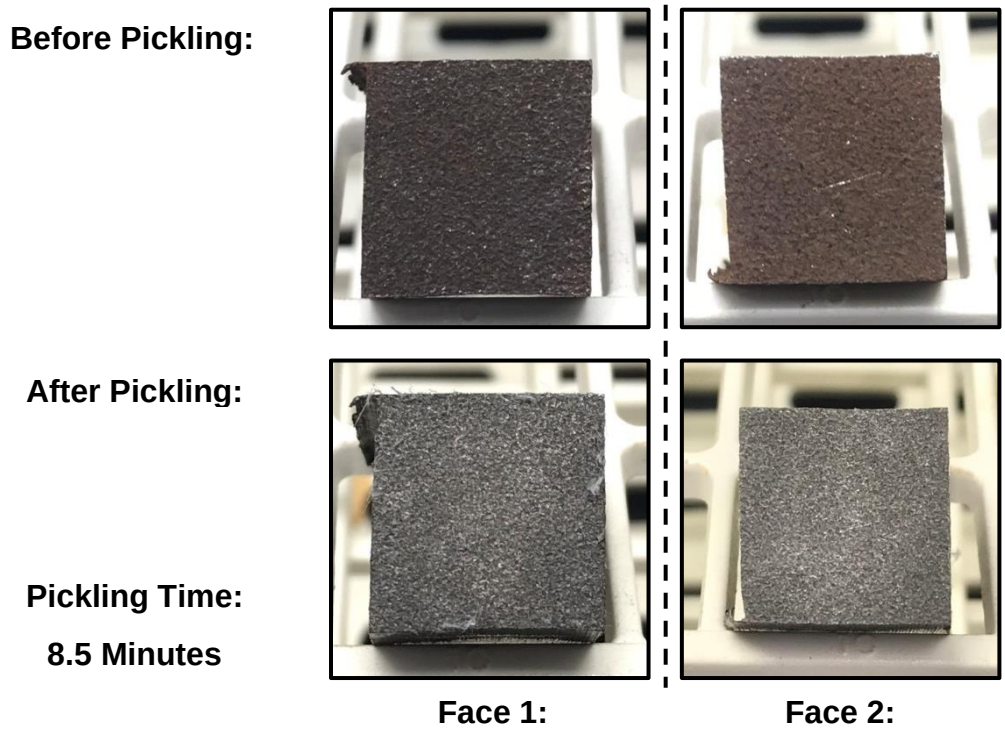


Figure D-40: Solution 10.5A29F regenerated to 15% acid – Coupon 2 Photos

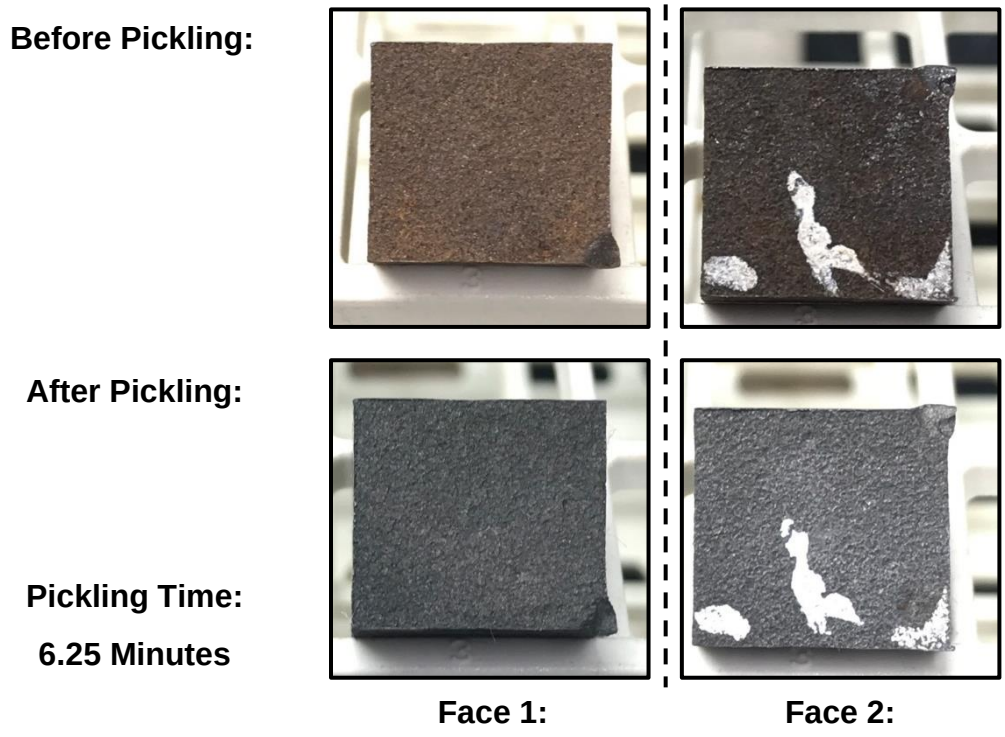


Figure D-41: Solution 10.5A29F regenerated to 20% acid – Coupon 1 Photos

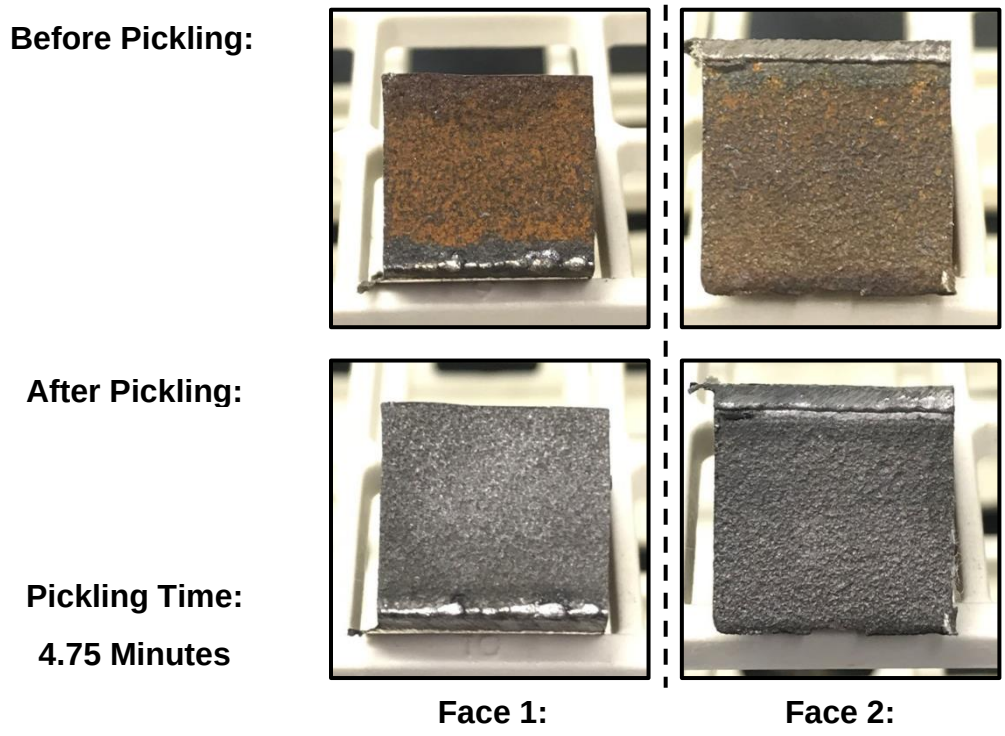


Figure D-42: Solution 10.5A29F regenerated to 20% acid – Coupon 2 Photos

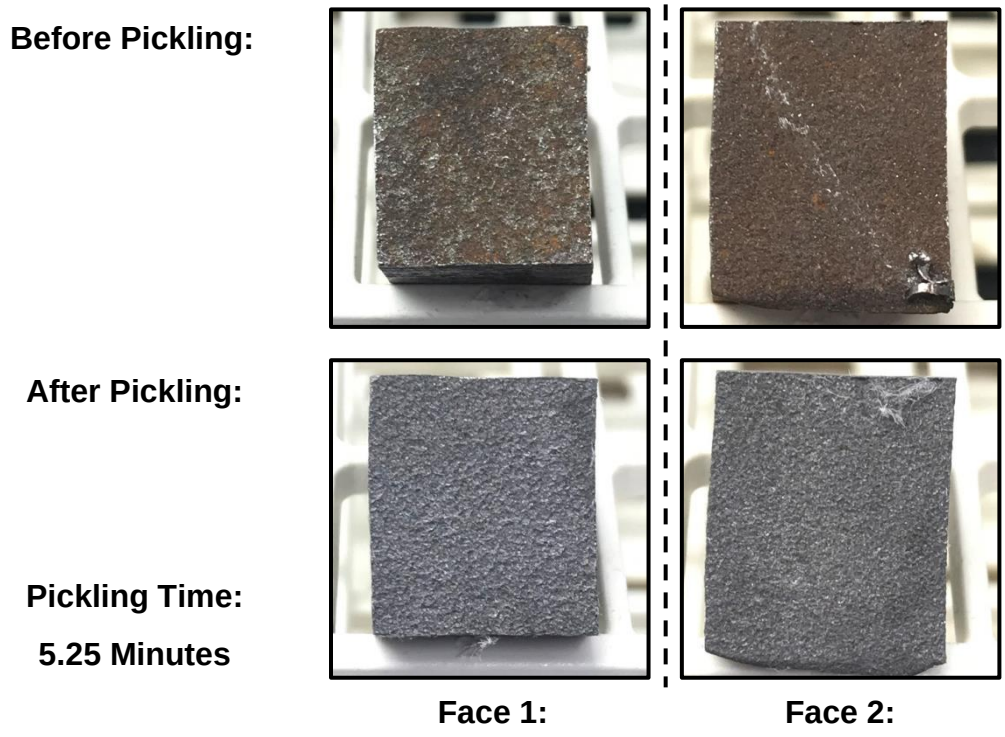


Figure D-43: Solution 10.5A29F regenerated to 25% acid – Coupon 1 Photos

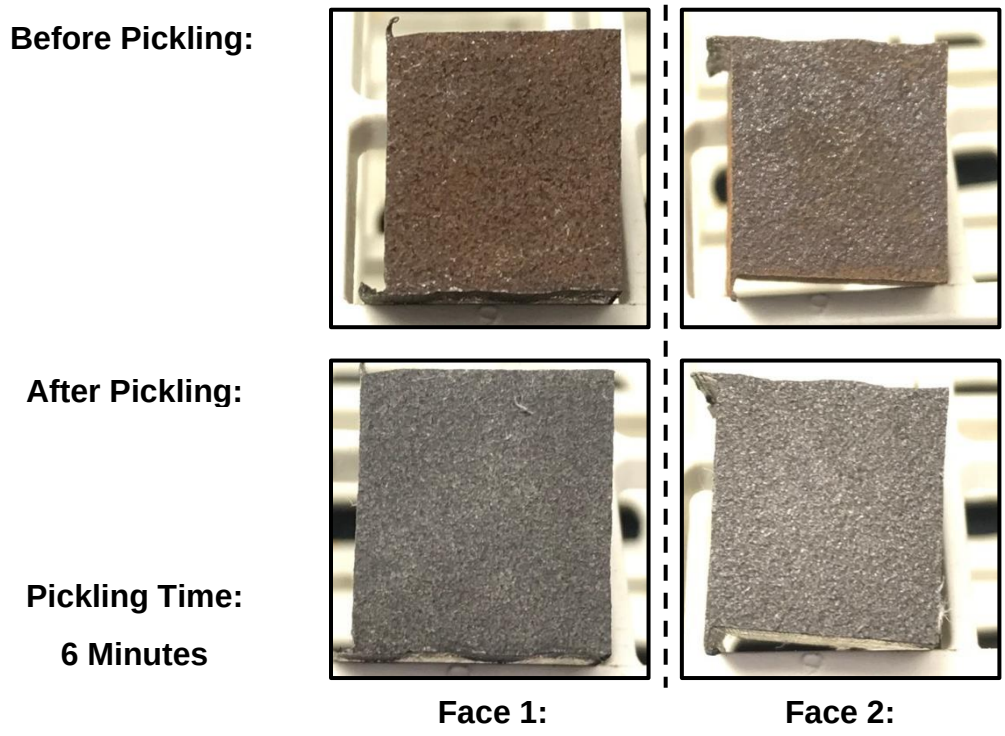


Figure D-44: Solution 10.5A29F regenerated to 25% acid – Coupon 2 Photos

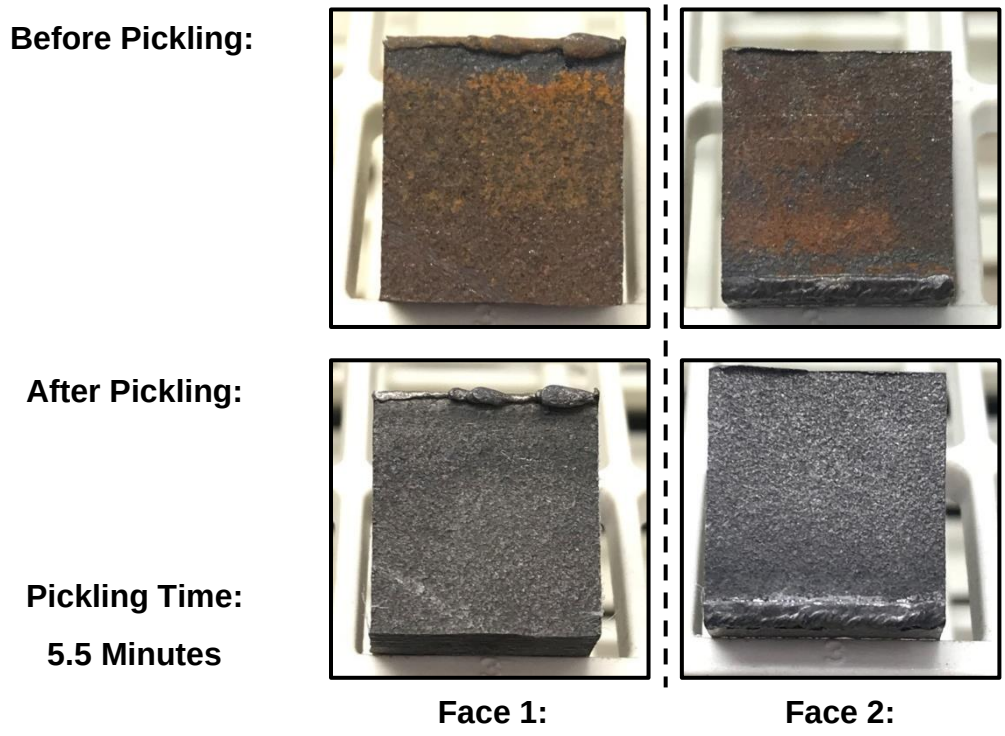


Figure D-45: Solution 10.5A29F regenerated to 30% acid – Coupon 1 Photos

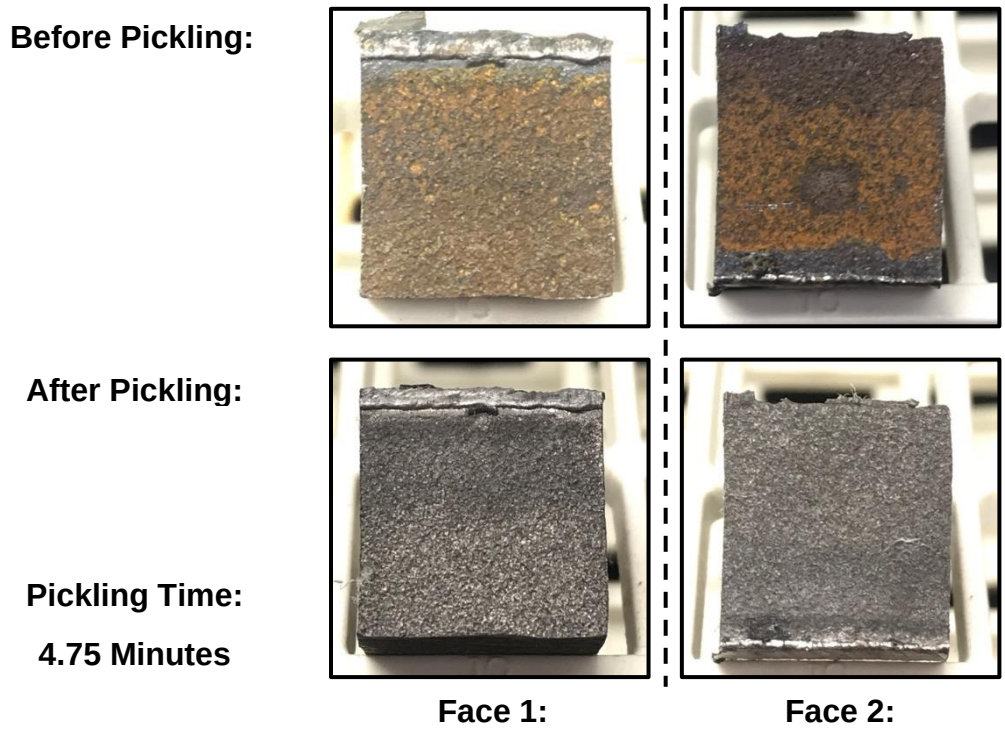


Figure D-46: Solution 10.5A29F regenerated to 30% acid – Coupon 2 Photos

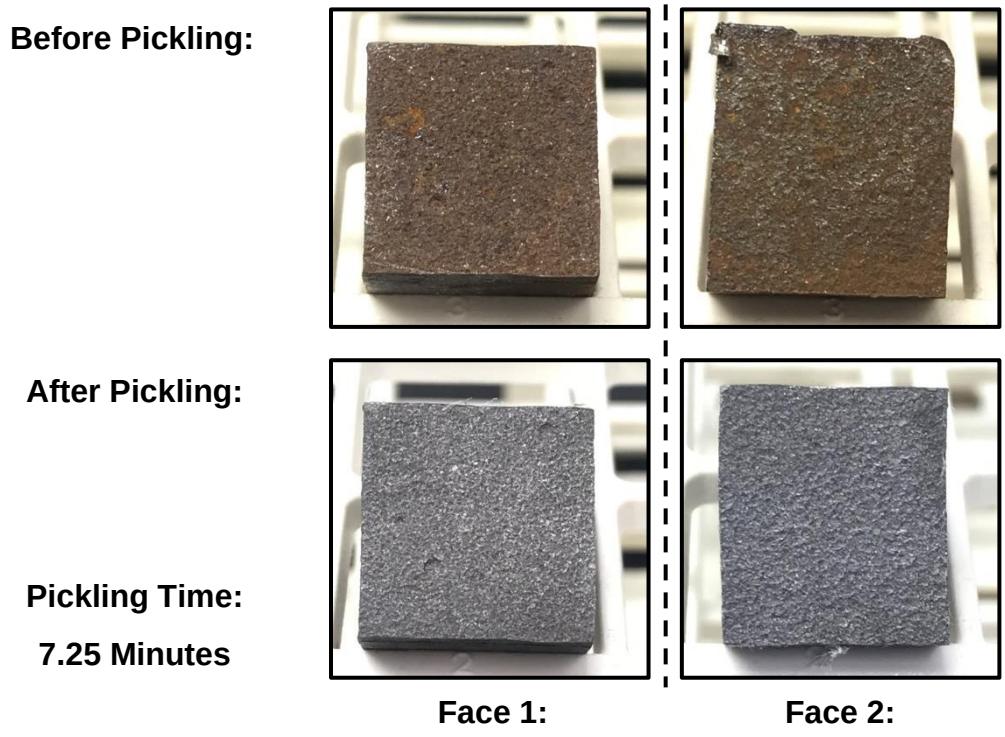


Figure D-47: Solution 13A11F – Coupon 1 Photos

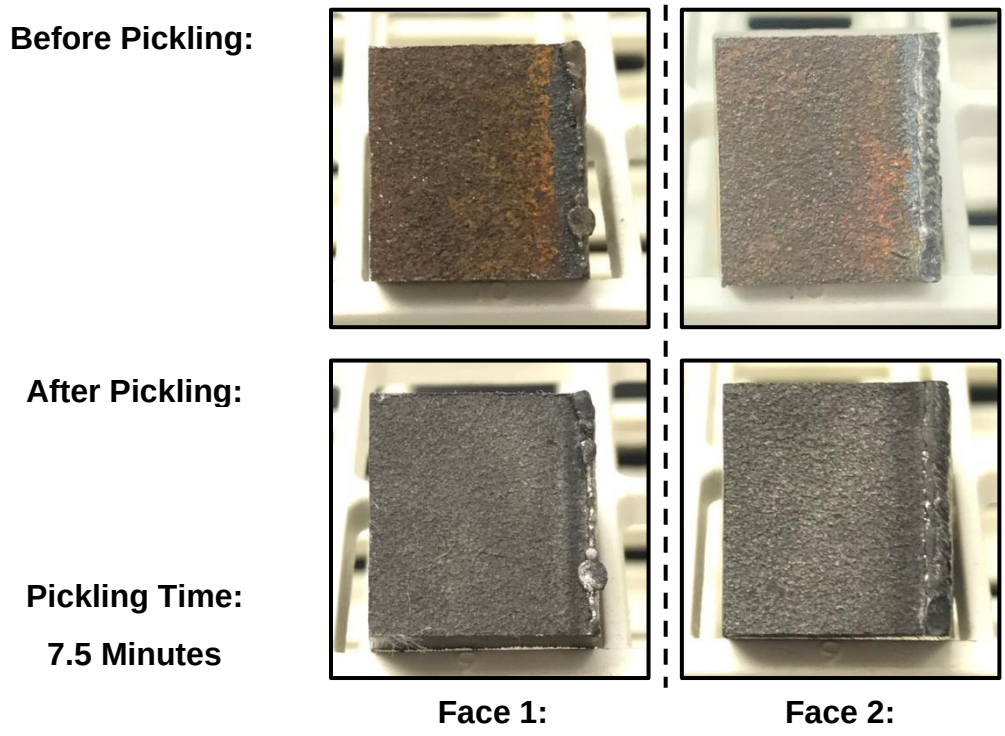


Figure D-48: Solution 13A11F – Coupon 2 Photos

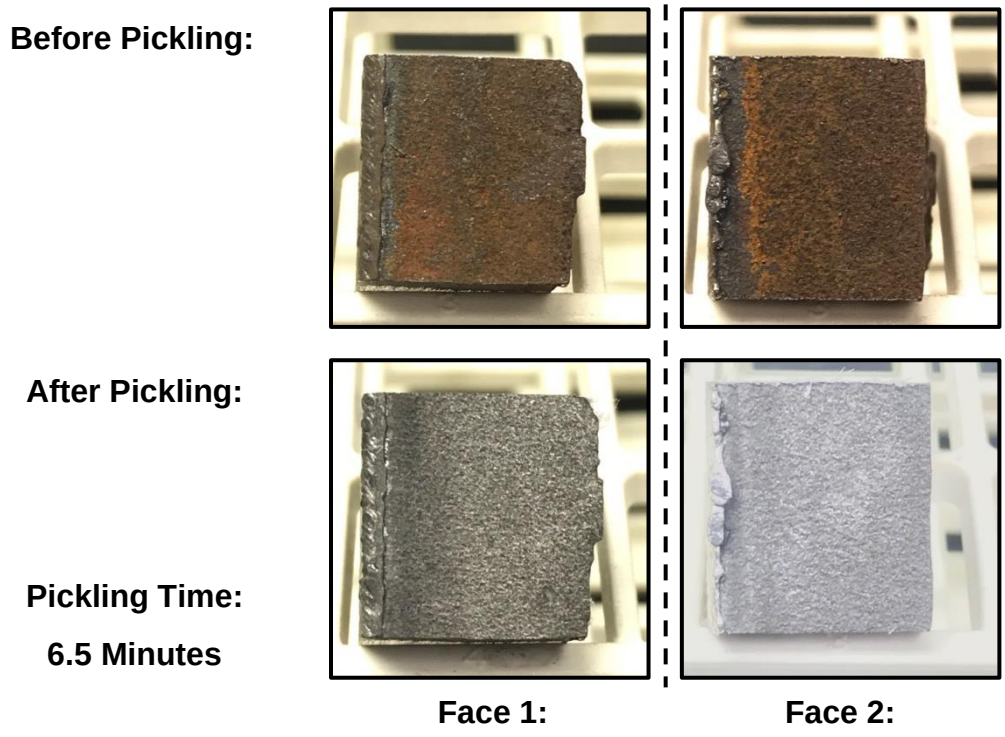


Figure D-49: Solution 13A11F regenerated to 15% acid – Coupon 1 Photos

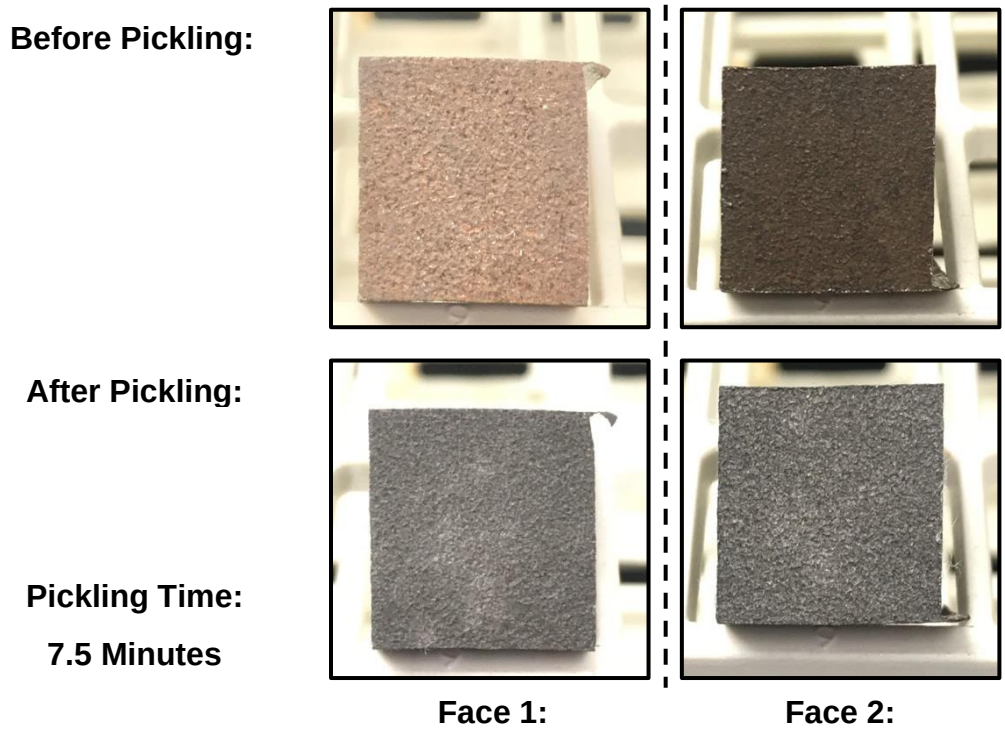


Figure D-50: Solution 13A11F regenerated to 15% acid – Coupon 2 Photos

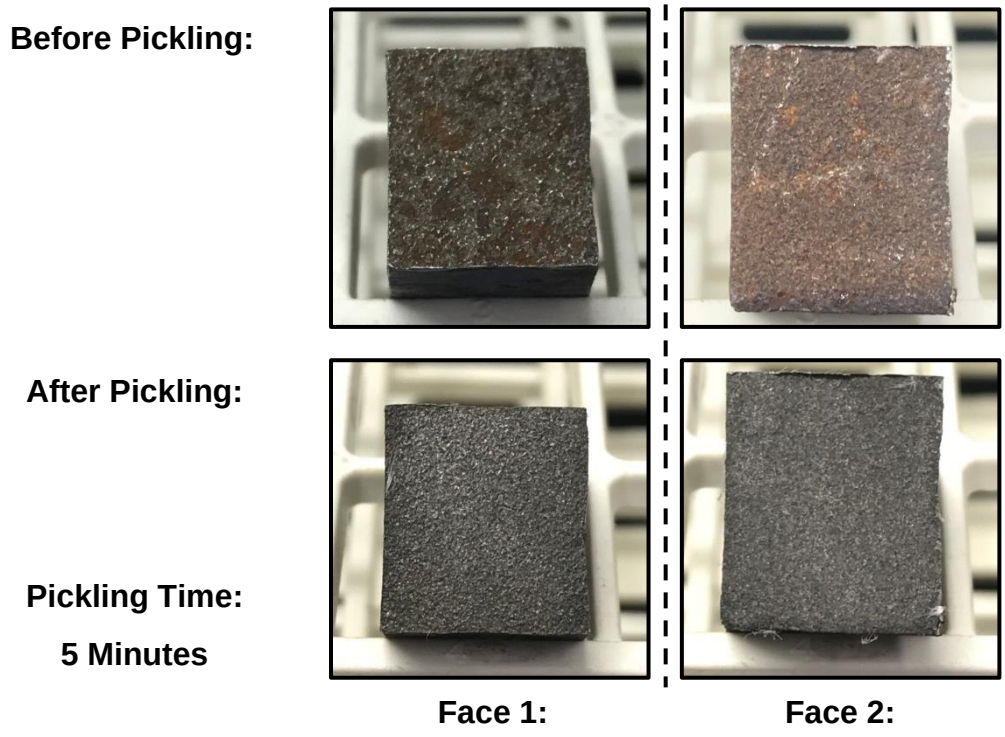


Figure D-51: Solution 13A11F regenerated to 20% acid – Coupon 1 Photos

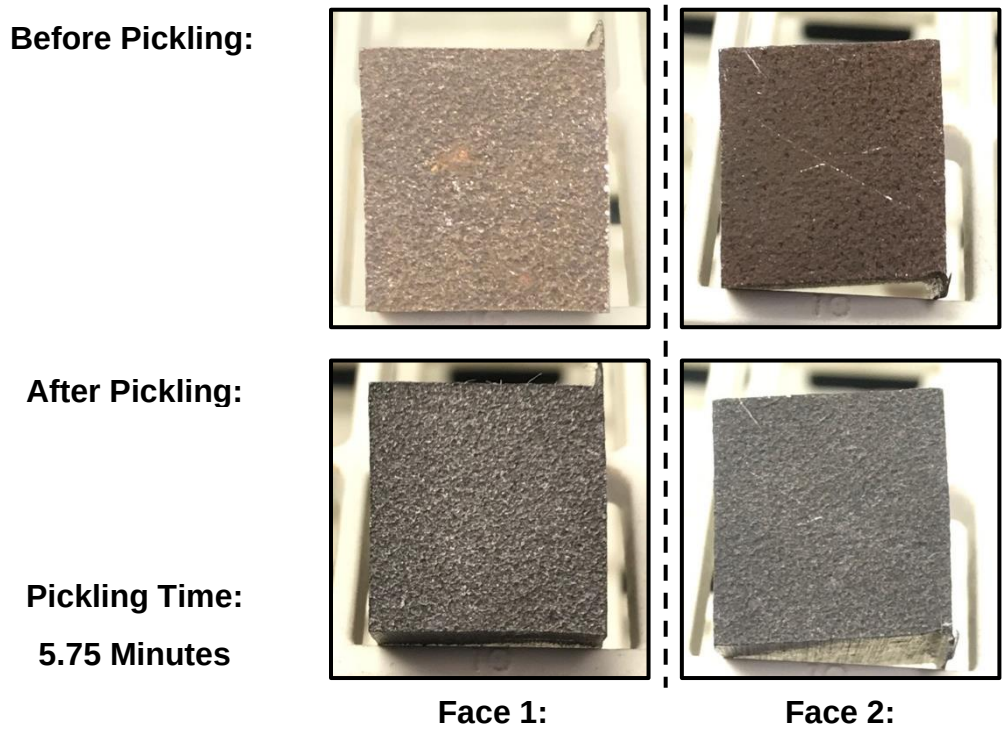


Figure D-52: Solution 13A11F regenerated to 20% acid – Coupon 2 Photos

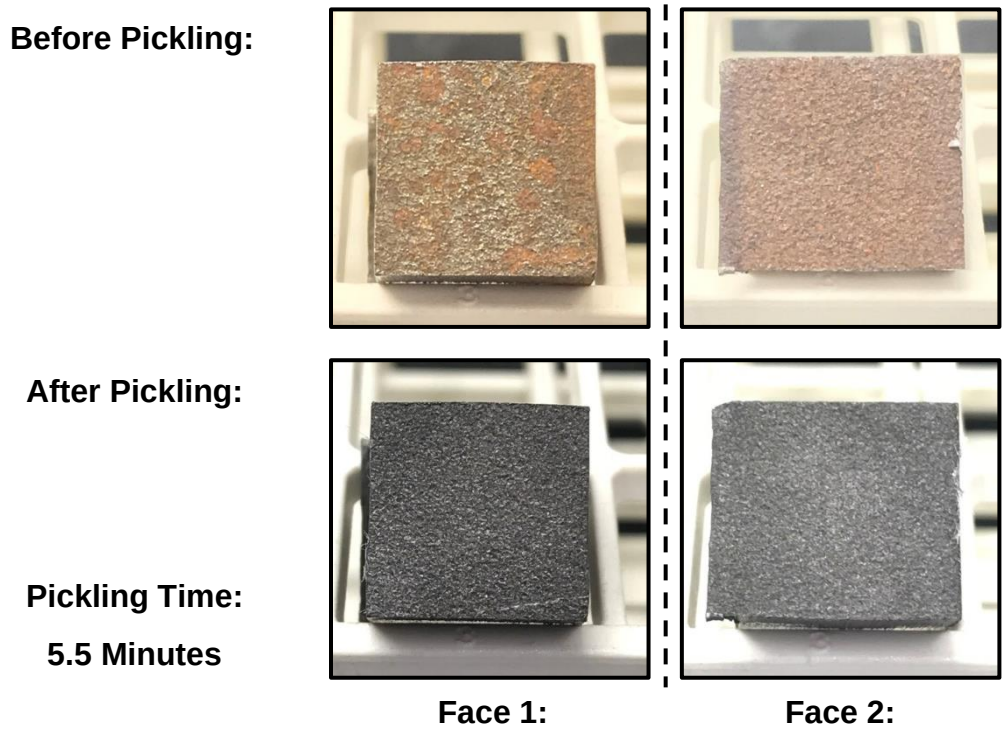


Figure D-53: Solution 13A11F regenerated to 25% acid – Coupon 1 Photos

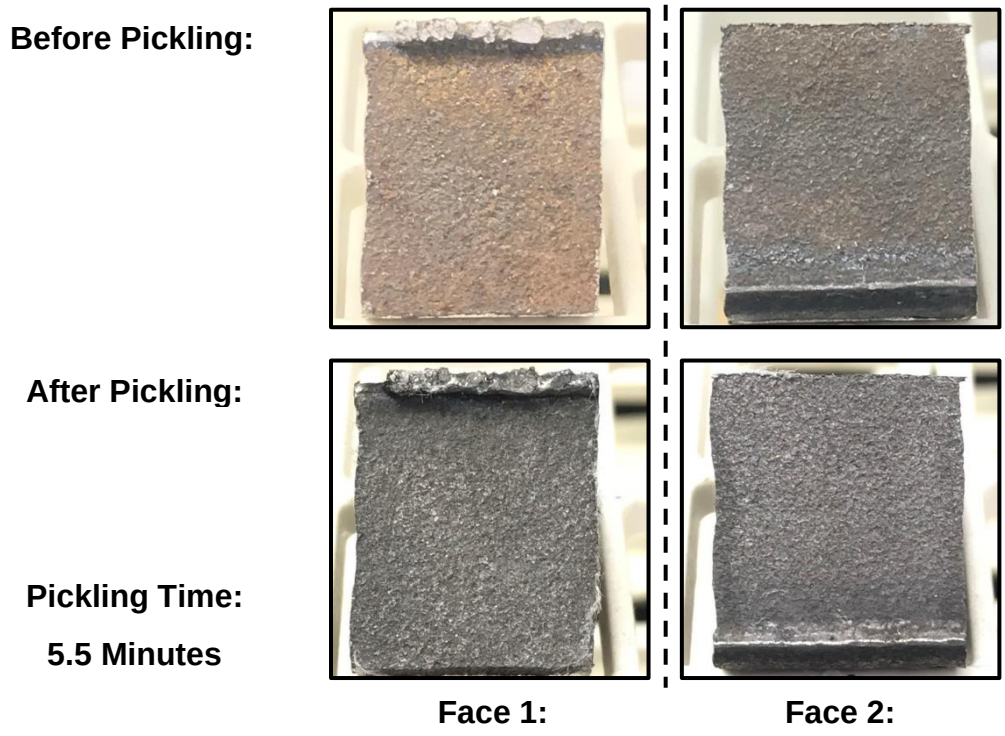


Figure D-54: Solution 13A11F regenerated to 25% acid – Coupon 2 Photos

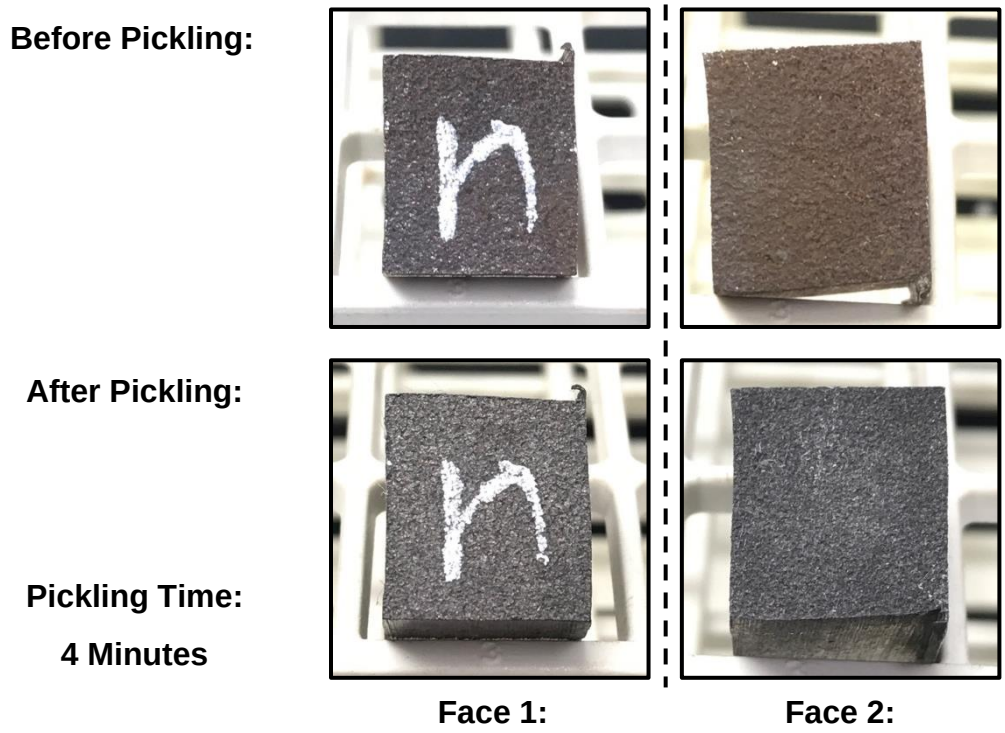


Figure D-55: Solution 13A11F regenerated to 30% acid – Coupon 1 Photos

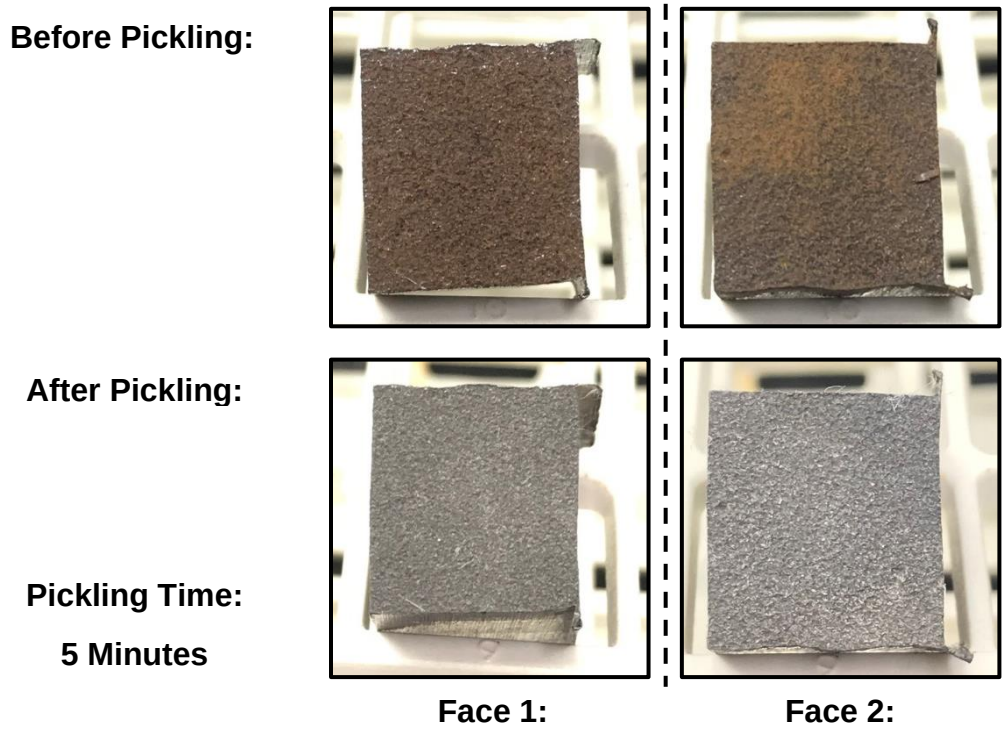


Figure D-56: Solution 13A11F regenerated to 30% acid – Coupon 2 Photos

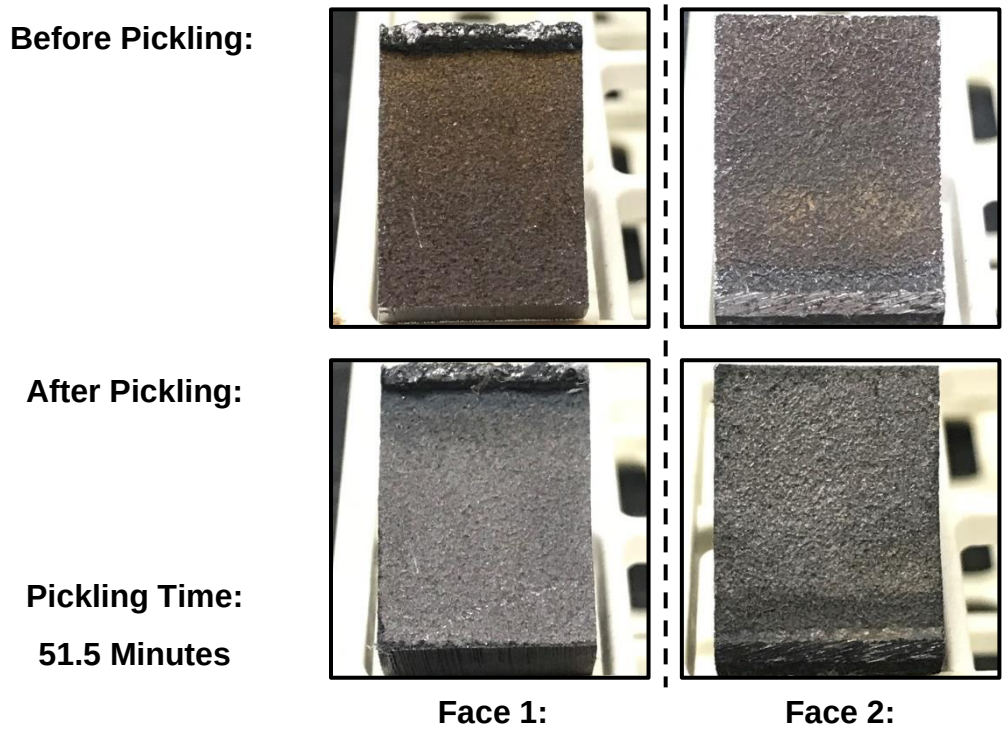


Figure D-57: Solution 0.7A125F – Coupon 1 Photos

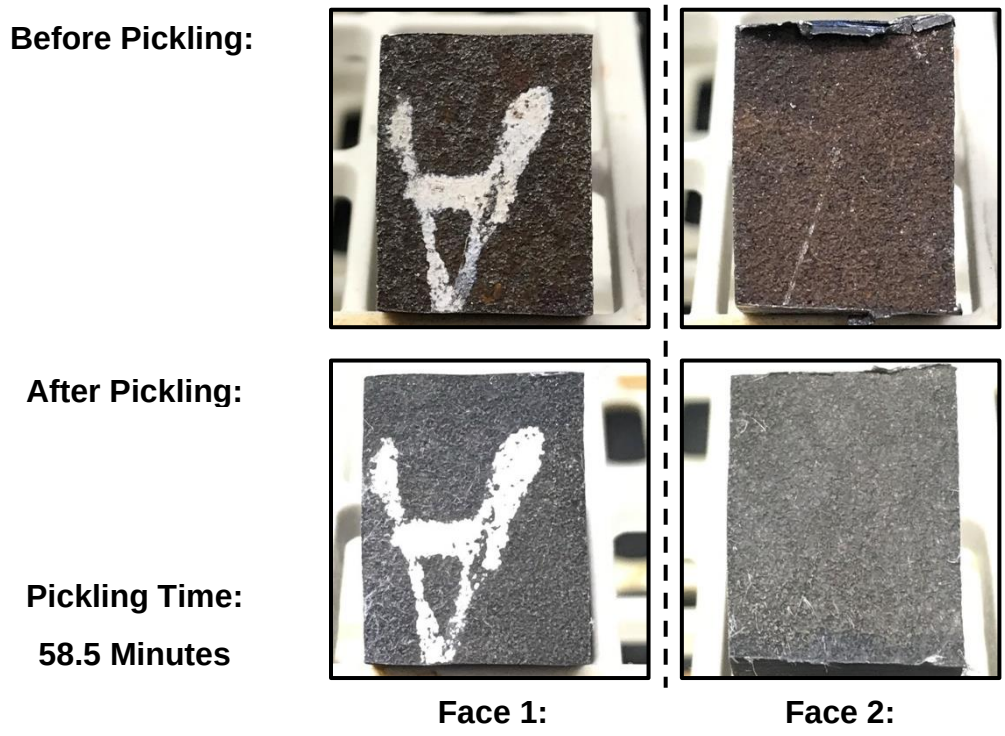


Figure D-58: Solution 0.7A125F – Coupon 2 Photos

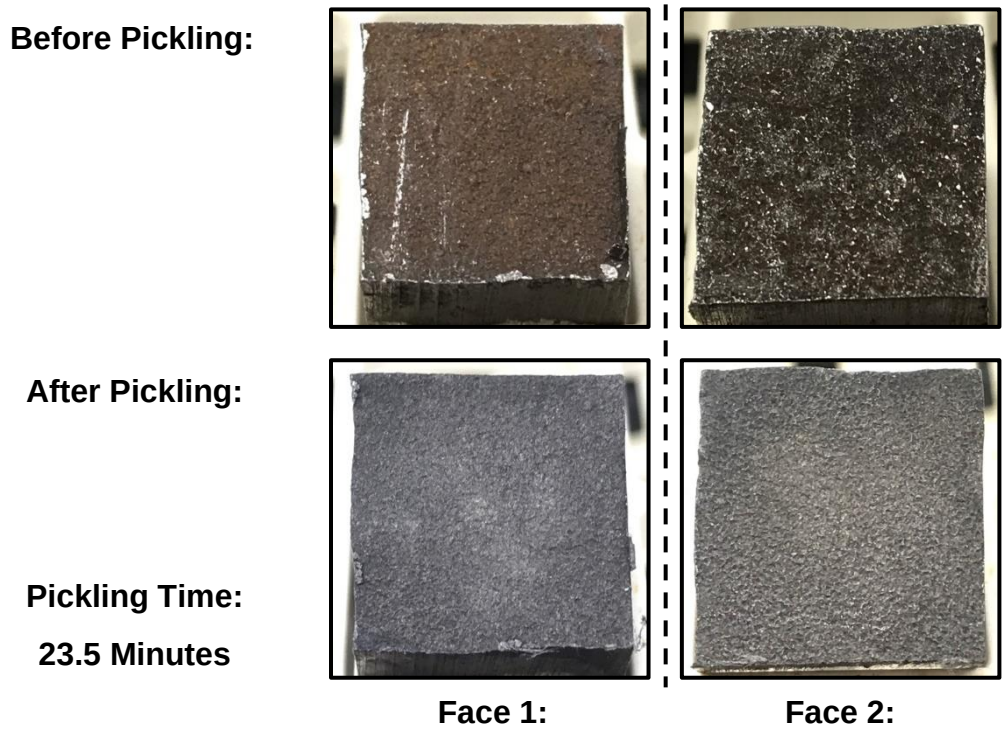


Figure D-59: Solution 0.7A125F regenerated to 2.5% acid – Coupon 1 Photos

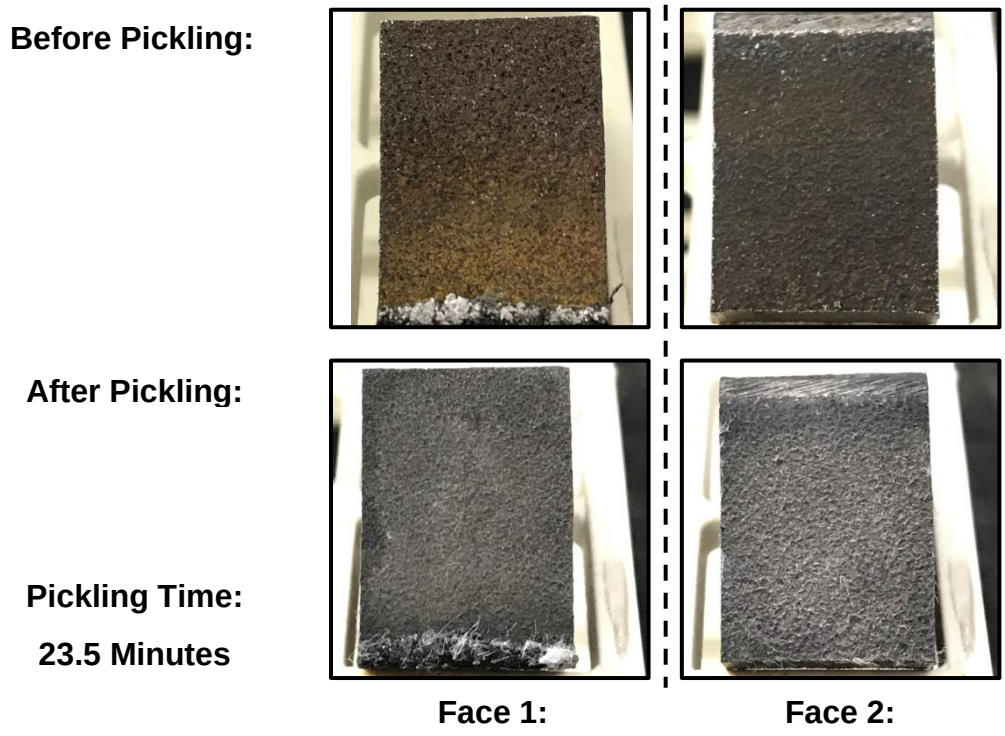


Figure D-60: Solution 0.7A125F regenerated to 2.5% acid – Coupon 2 Photos

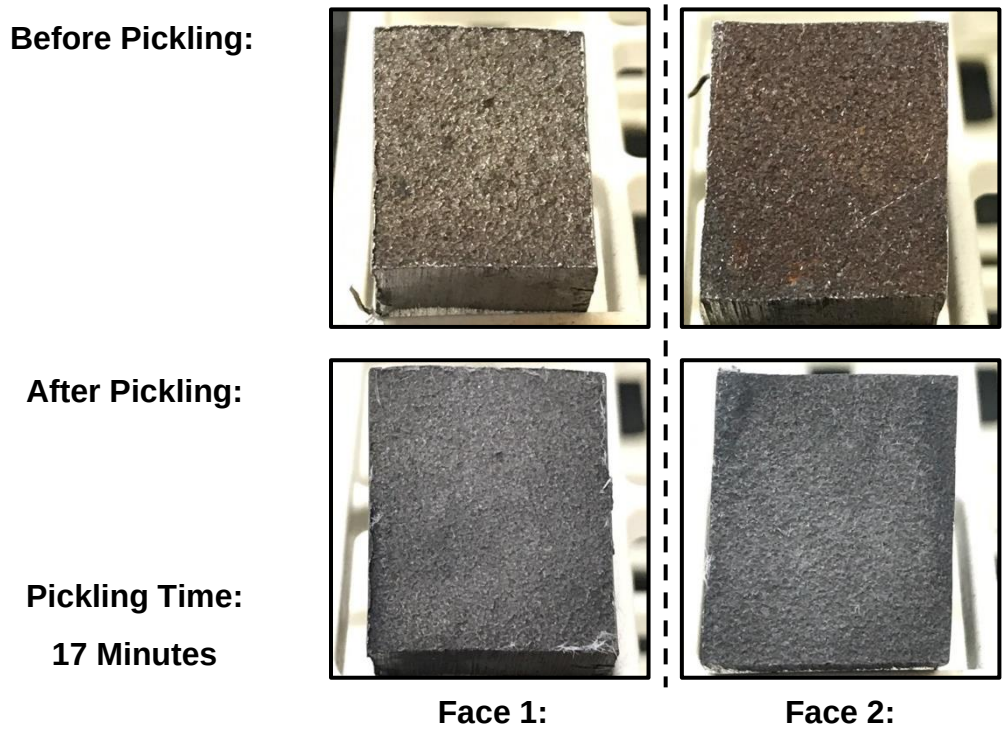


Figure D-61: Solution 0.7A125F regenerated to 4% acid – Coupon 1 Photos

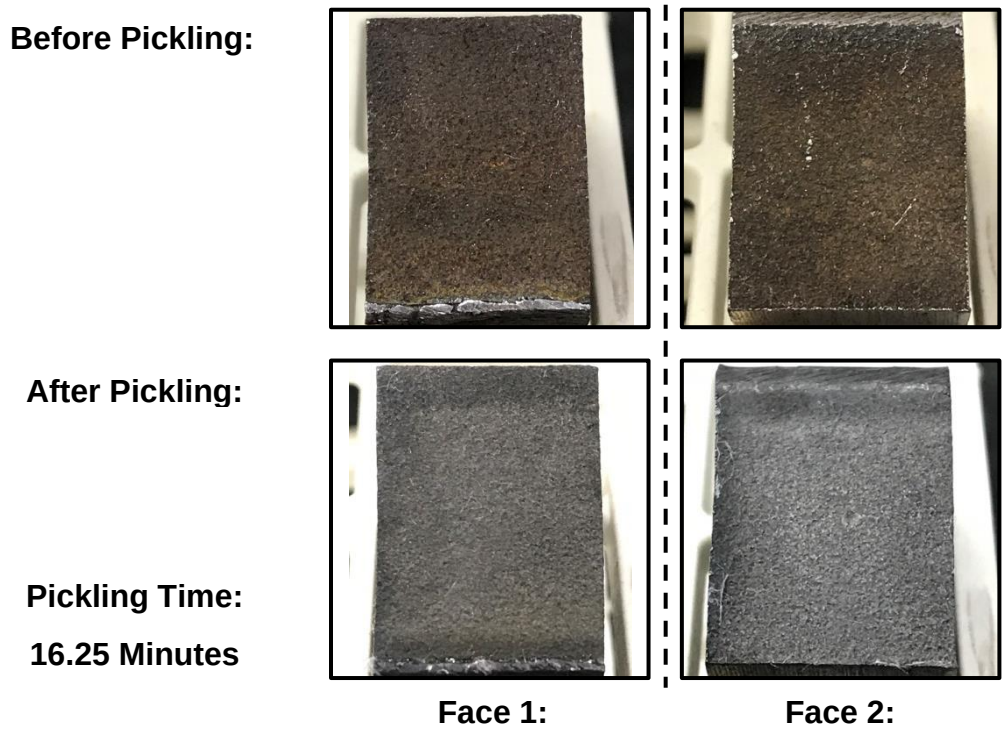


Figure D-62: Solution 0.7A125F regenerated to 4% acid – Coupon 2 Photos

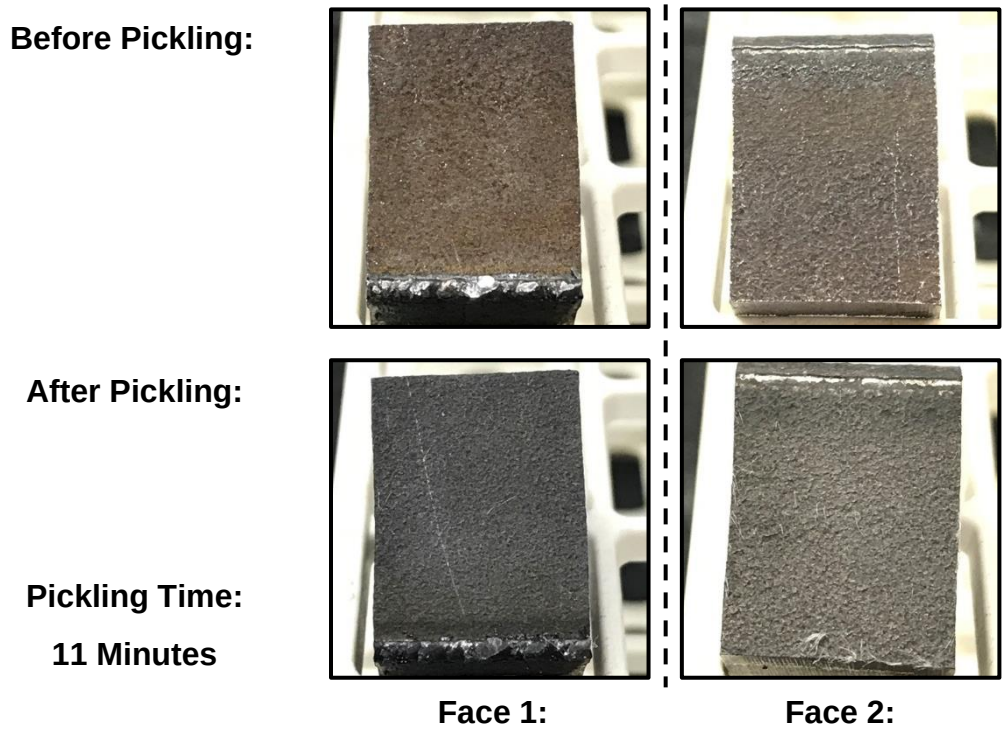


Figure D-63: Solution 0.7A125F regenerated to 7% acid – Coupon 1 Photos

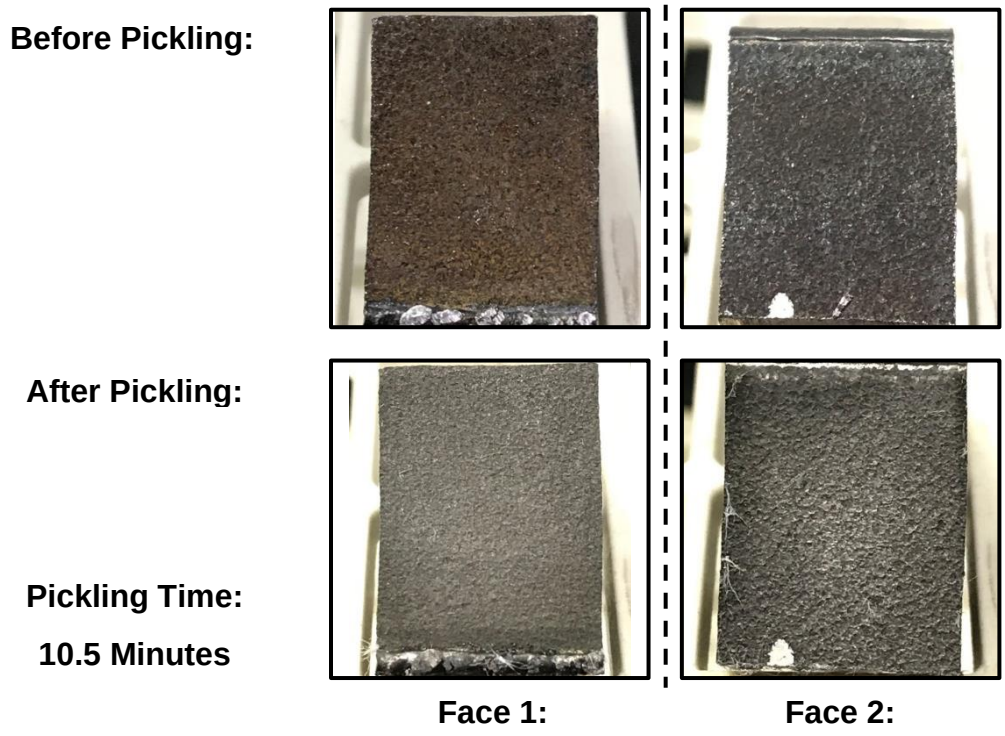


Figure D-64: Solution 0.7A125F regenerated to 7% acid – Coupon 2 Photos

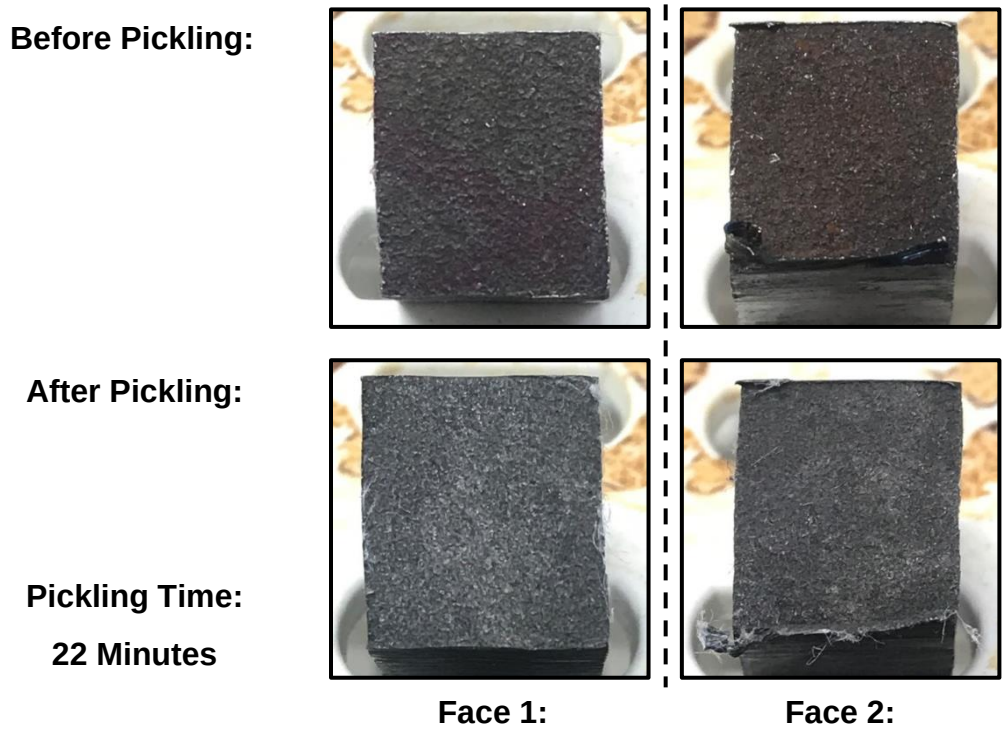


Figure D-65: Solution 2.6A114F – Coupon 1 Photos

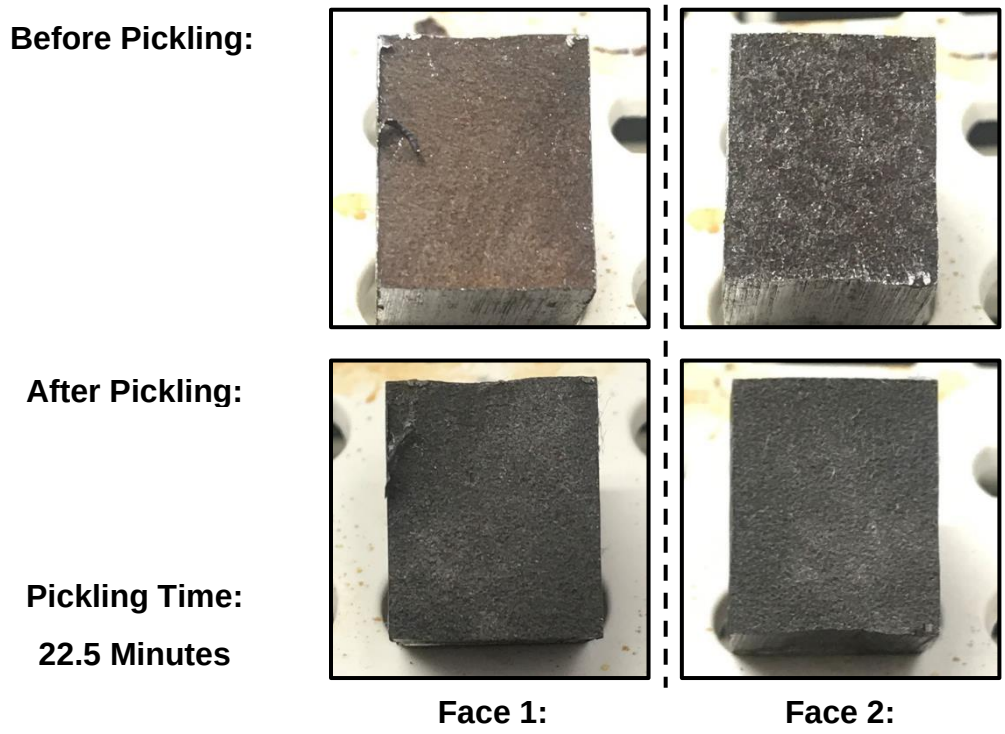


Figure D-66: Solution 2.6A114F – Coupon 2 Photos

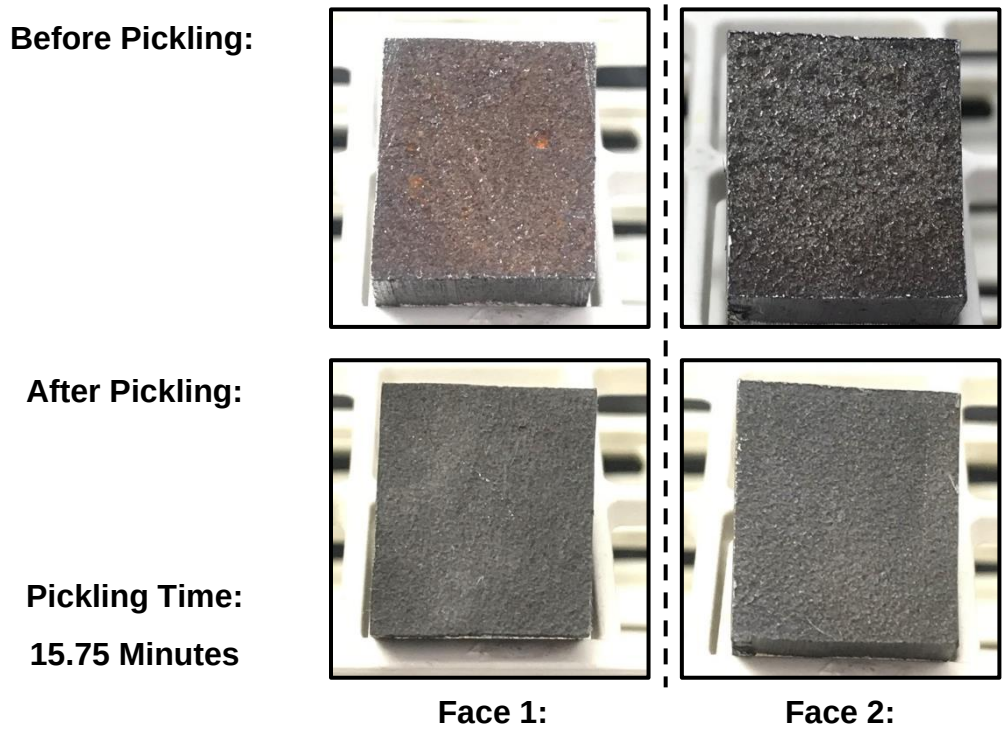


Figure D-67: Solution 2.6A114F regenerated to 4% acid – Coupon 1 Photos

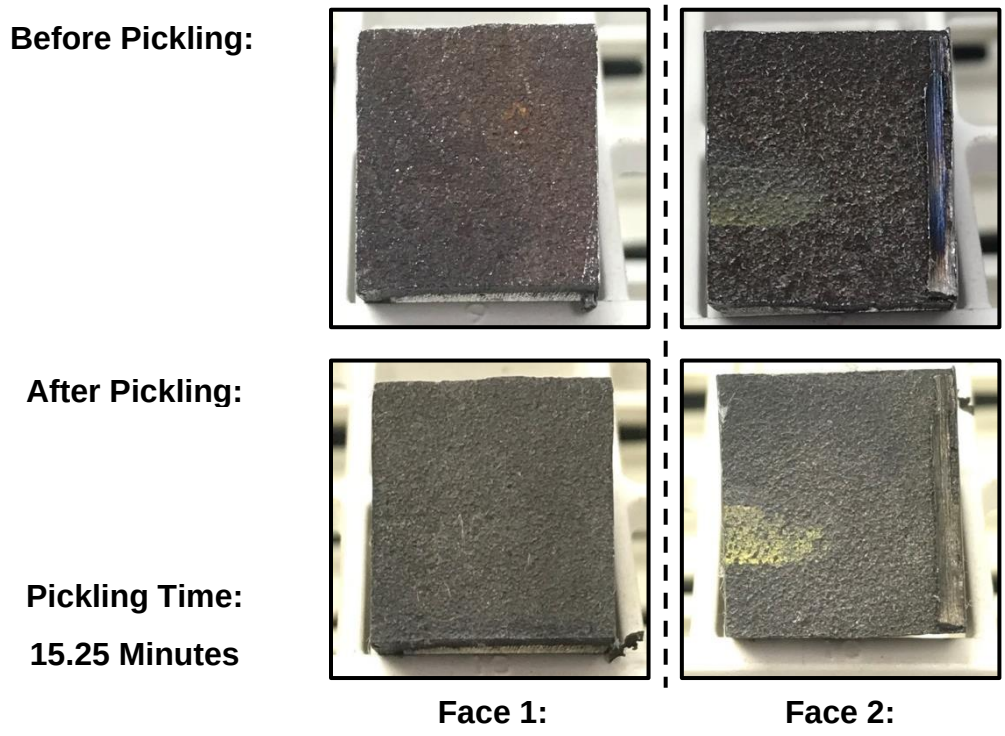


Figure D-68: Solution 2.6A114F regenerated to 4% acid – Coupon 2 Photos

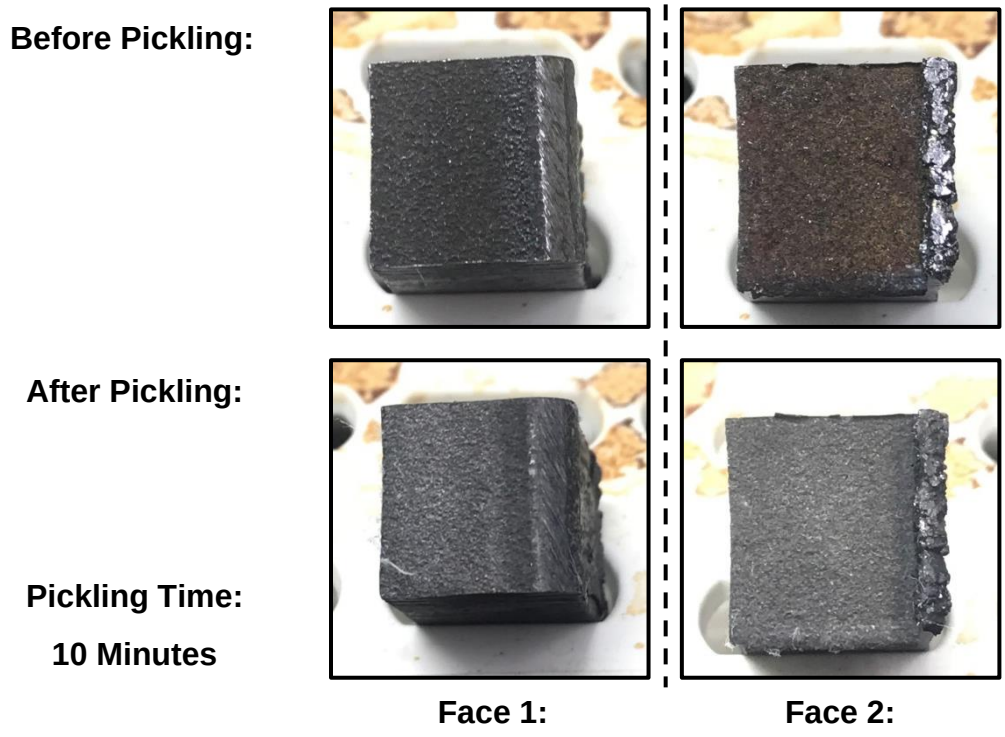


Figure D-69: Solution 2.6A114F regenerated to 7% acid – Coupon 1 Photos

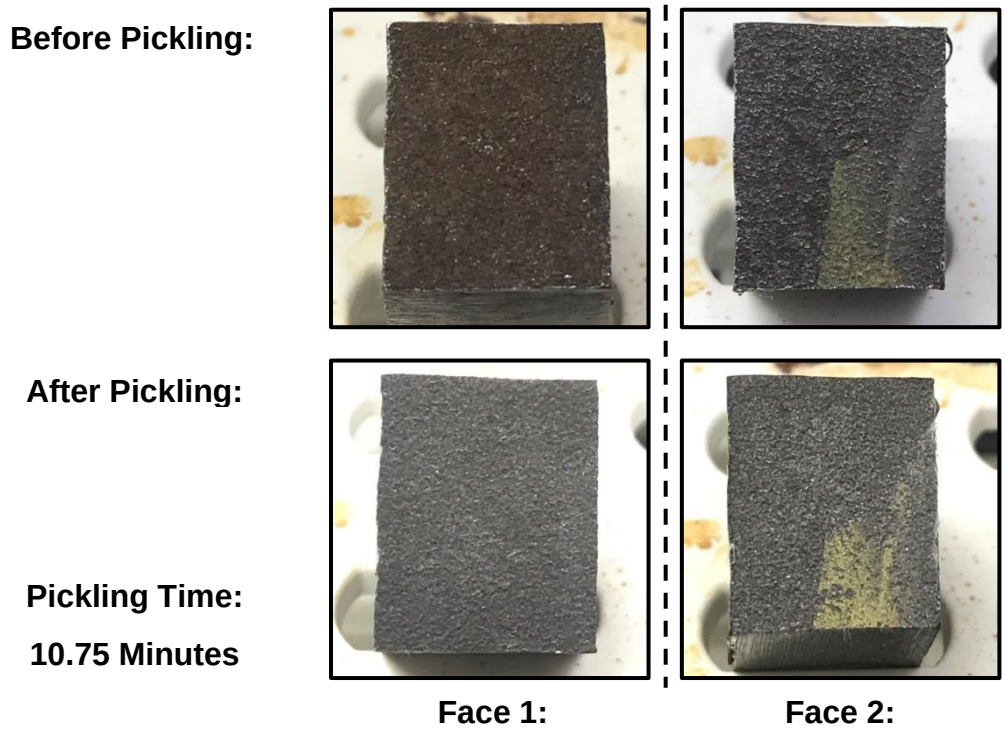


Figure D-70: Solution 2.6A114F regenerated to 7% acid – Coupon 2 Photos

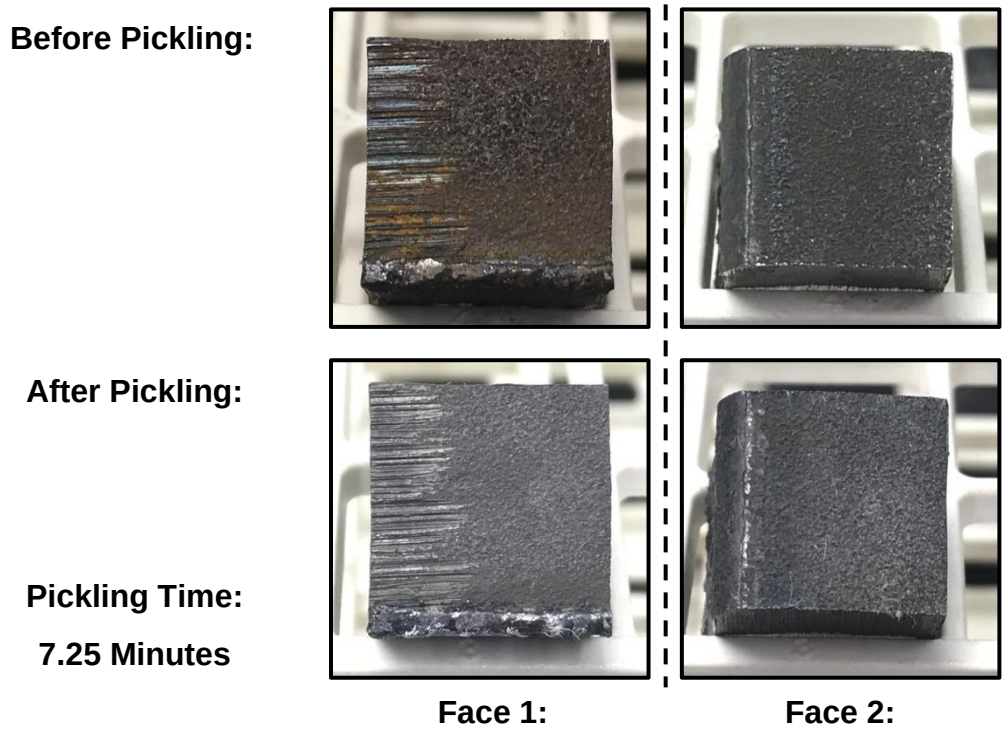


Figure D-71: Solution 2.6A114F regenerated to 9% acid – Coupon 1 Photos

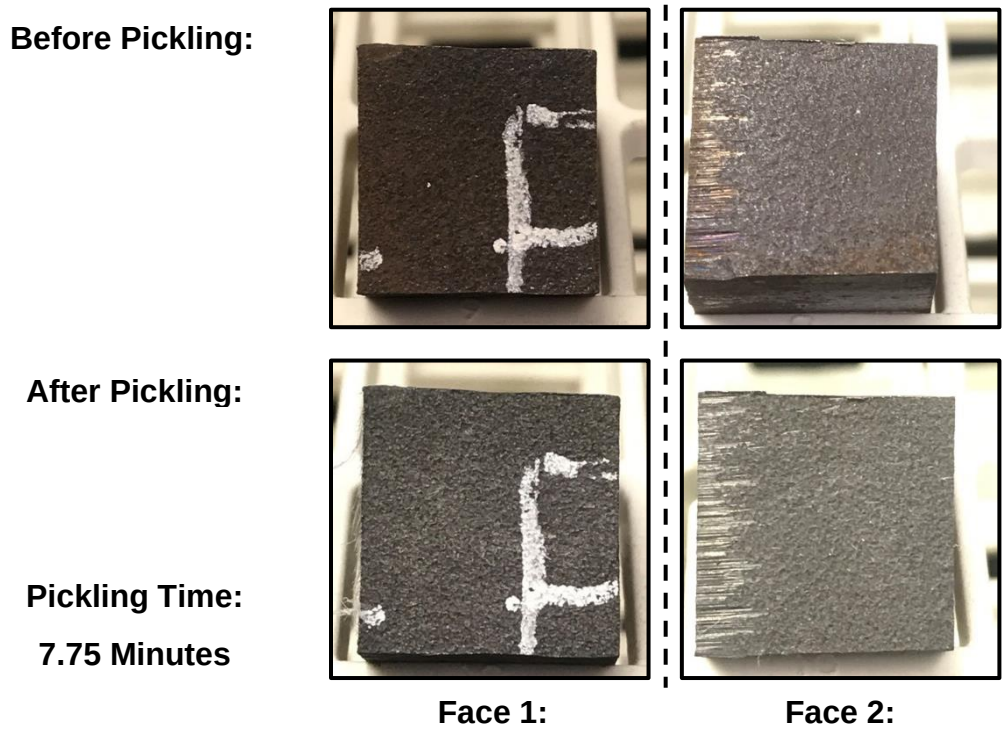


Figure D-72: Solution 2.6A114F regenerated to 9% acid – Coupon 2 Photos

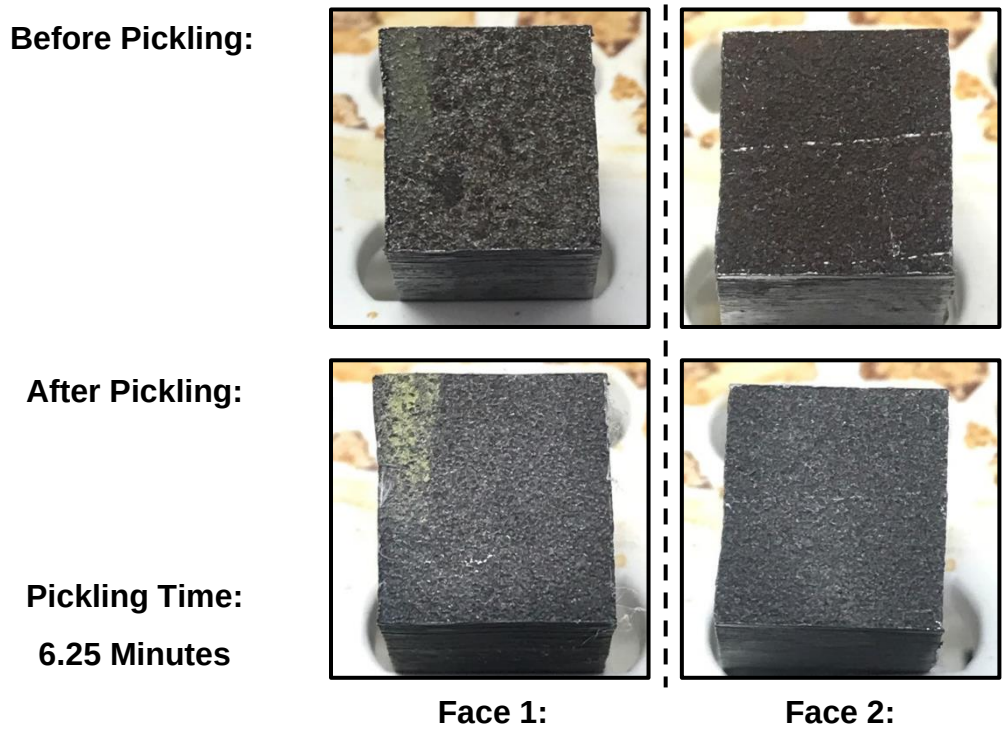


Figure D-73: Solution 2.6A114F regenerated to 12% acid – Coupon 1 Photos

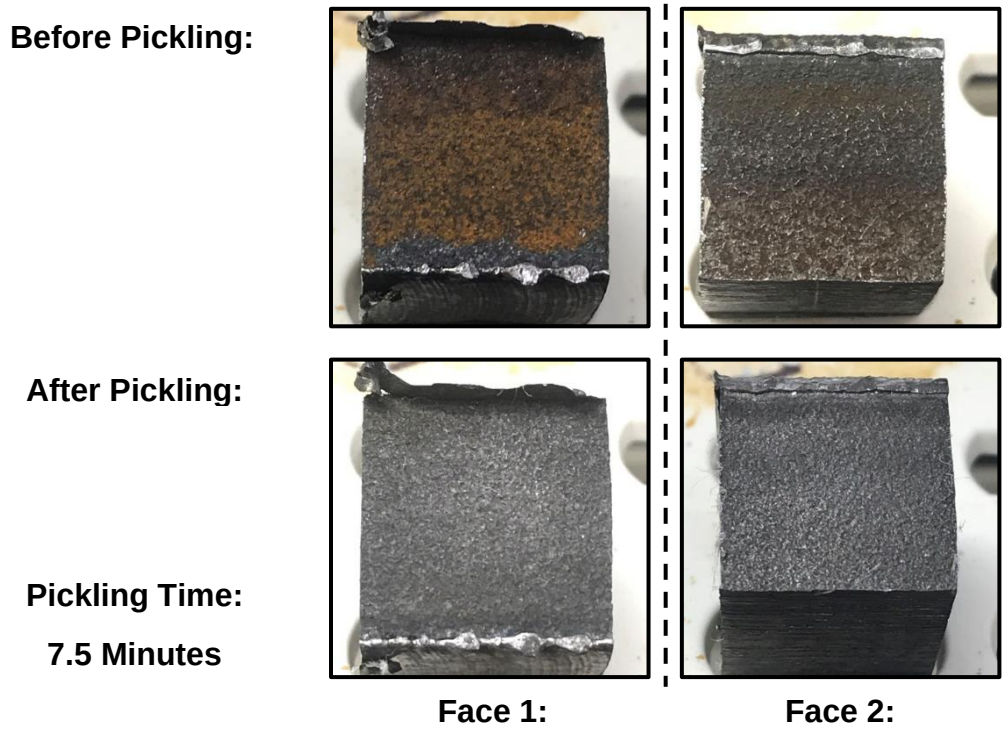


Figure D-74: Solution 2.6A114F regenerated to 12% acid – Coupon 2 Photos

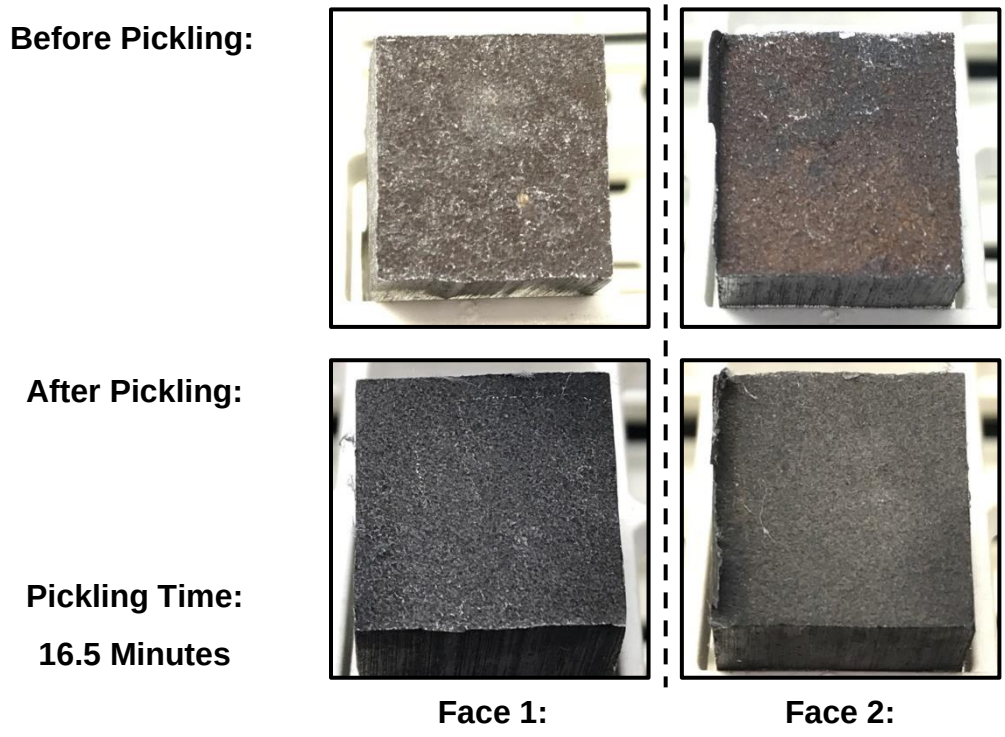


Figure D-75: Solution 4A103F – Coupon 1 Photos

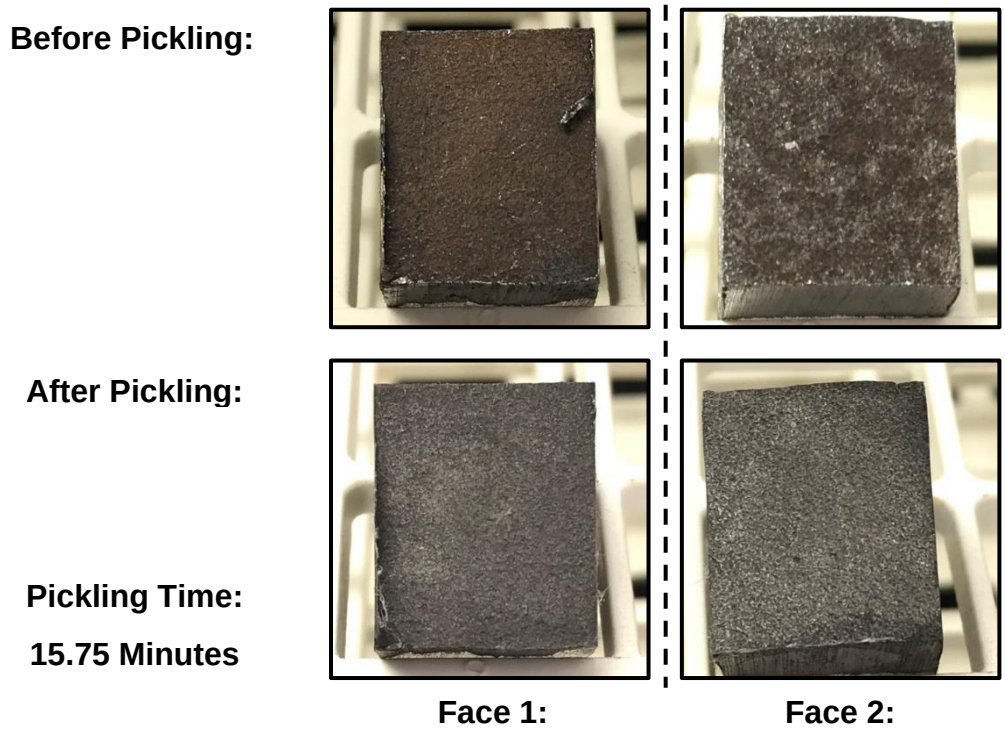


Figure D-76: Solution 4A103F – Coupon 2 Photos

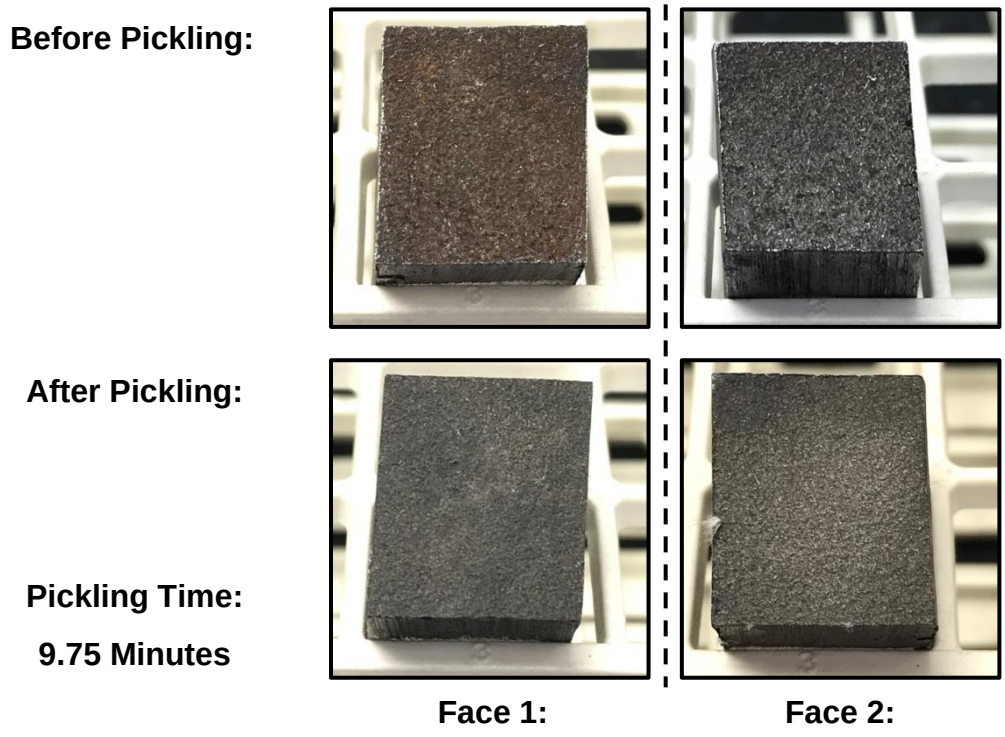


Figure D-77: Solution 4A103F regenerated to 7% acid – Coupon 1 Photos

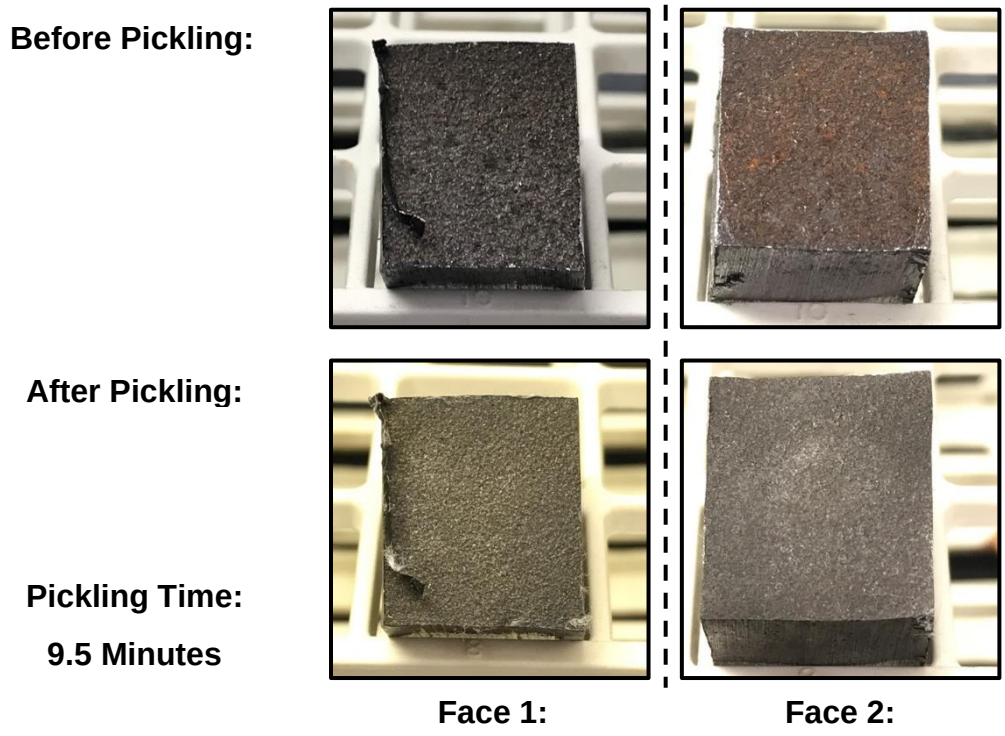


Figure D-78: Solution 4A103F regenerated to 7% acid – Coupon 2 Photos

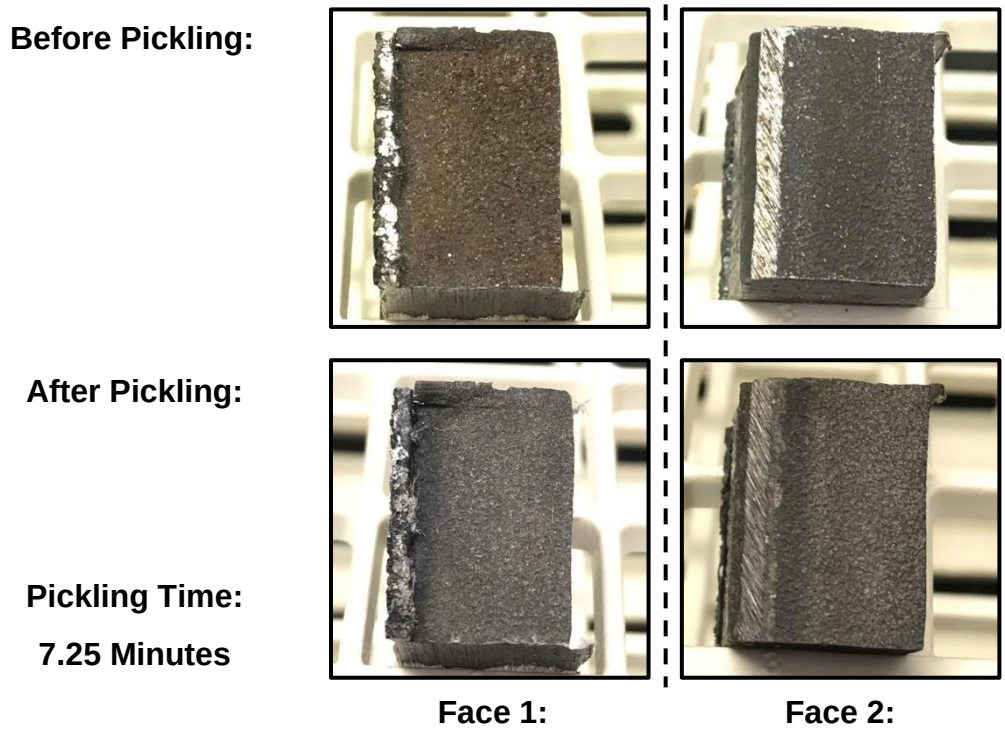


Figure D-79: Solution 4A103F regenerated to 9% acid – Coupon 1 Photos

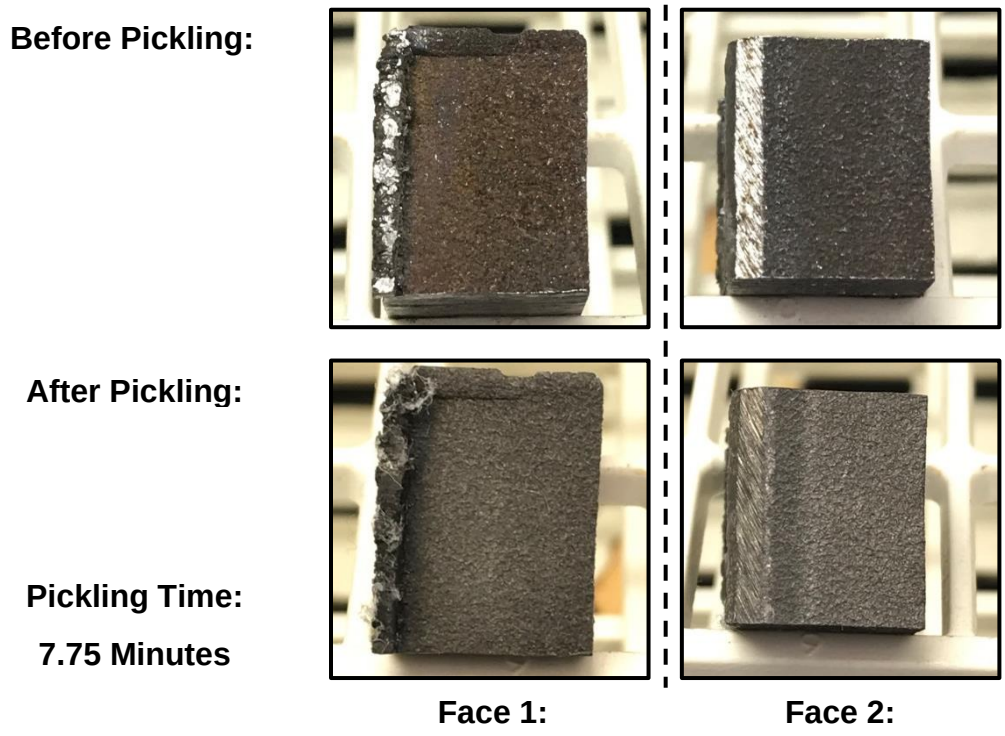


Figure D-80: Solution 4A103F regenerated to 9% acid – Coupon 2 Photos

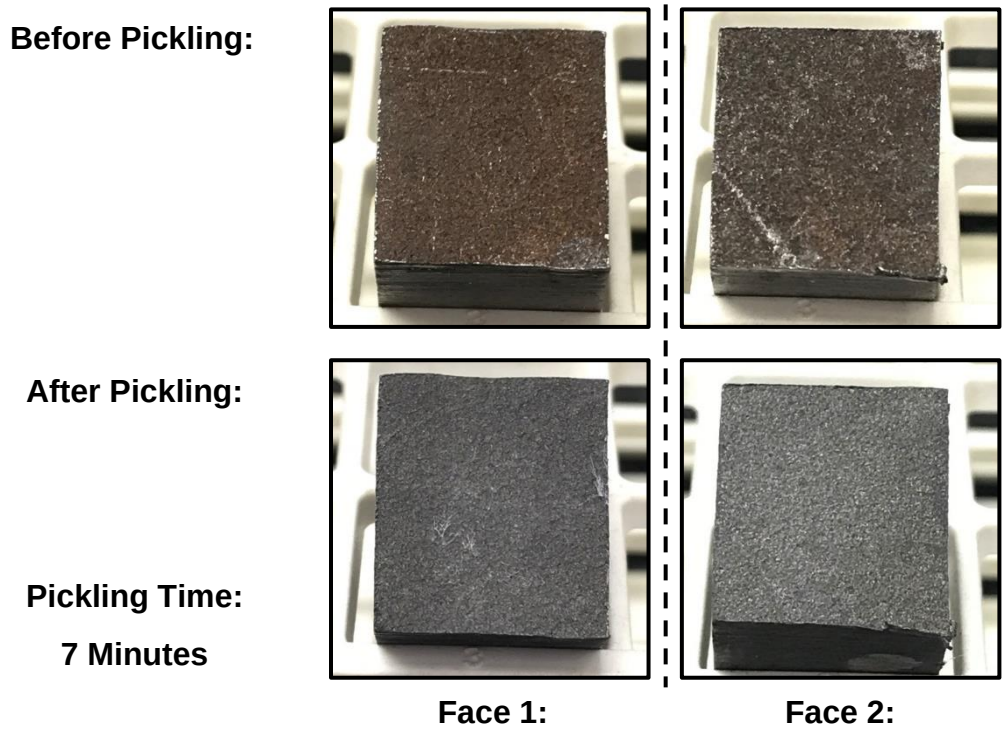


Figure D-81: Solution 4A103F regenerated to 12% acid – Coupon 1 Photos

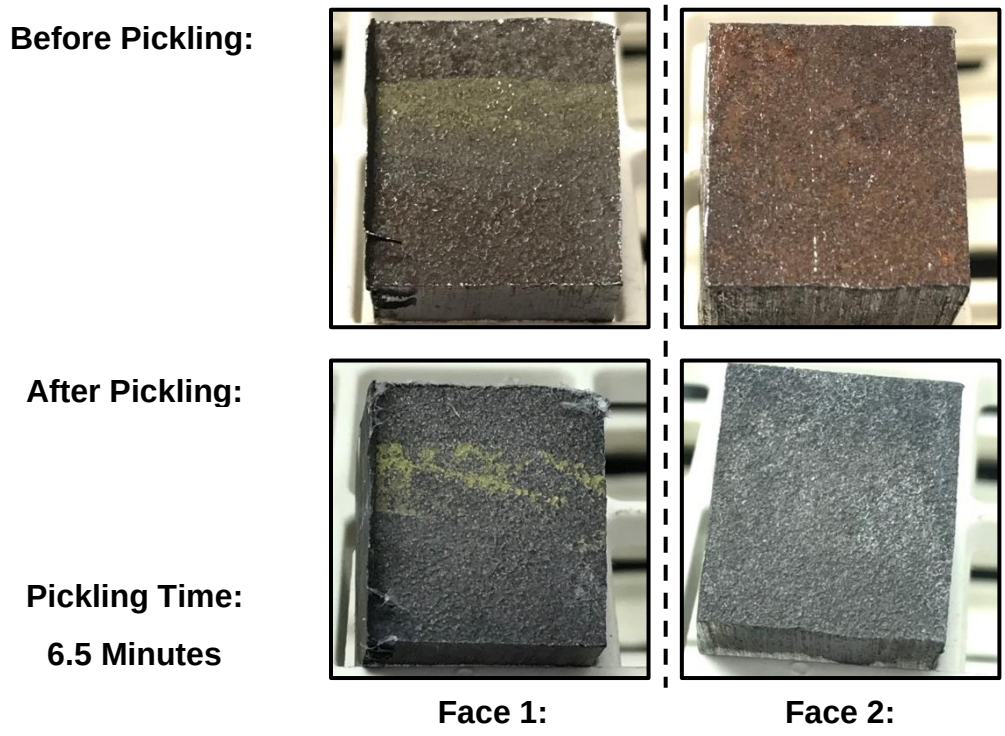


Figure D-82: Solution 4A103F regenerated to 12% acid – Coupon 2 Photos

Saturation/Solubility Limit Tests

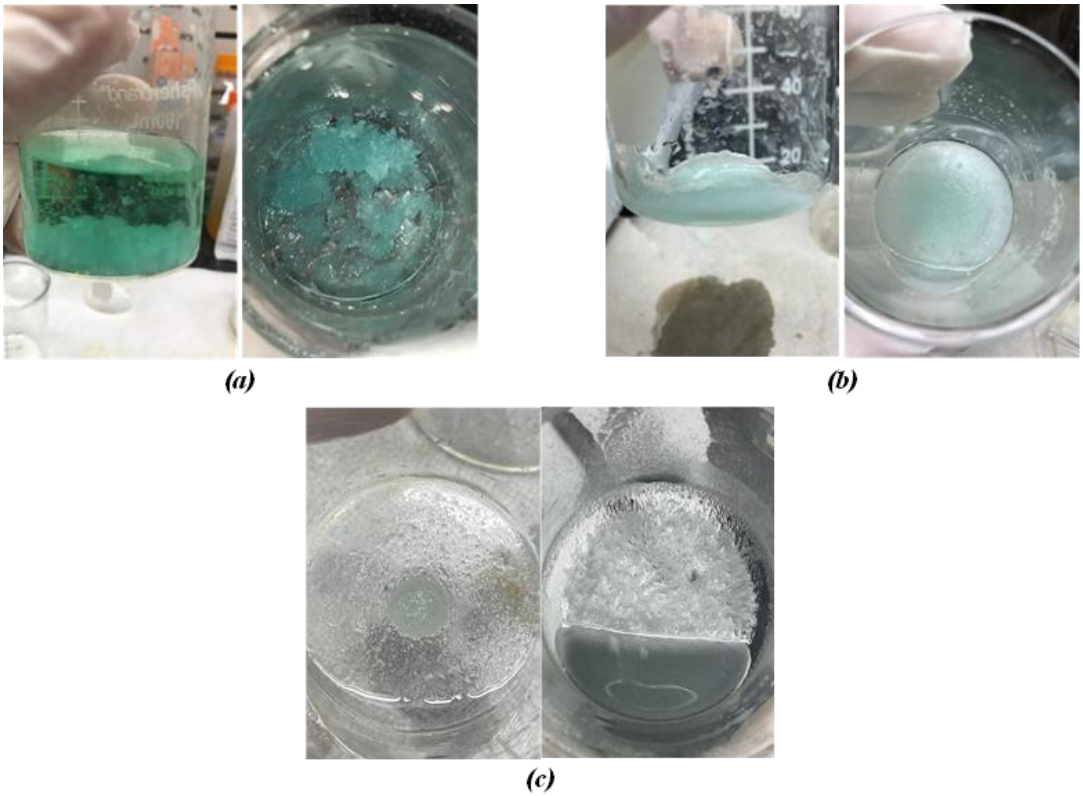


Figure D-83: Iron (II) Sulfate precipitates formed from saturation test solutions: a.) 1A182F – heptahydrate formed; b.) 5A159F – appearances of both hydrates; c.) 9A137F – monohydrate formed

APPENDIX E – TASK 3 TEST RESULTS

Table E-1: Solution data for hydrochloric acid pickling solutions with low zinc concentrations

Initial Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)	Zinc Conc. (g/L)	Combined Metal Concentration (g/L)
2A104FZ	1.7	16.9	92.6	11.7	104.2
4A83FZ	4.3	44.1	74.0	9.5	83.4
8A52FZ	7.9	82.6	45.9	6.0	51.9
3A165FZ	2.8	28.9	146.2	18.7	165.0
5A151FZ	4.6	47.4	134.2	17.1	151.3

Table E-2: Solution data for sulfuric acid pickling solutions with low zinc concentrations

Initial Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)	Zinc Conc. (g/L)	Combined Metal Concentration (g/L)
2.5A81FZ	2.5	25.9	71.5	9.3	80.8
5A63FZ	5.2	55.9	56.1	7.3	63.4
8A46FZ	7.9	85.9	40.7	5.3	46.0
4A104FZ	4.5	47.6	92.2	12.0	104.2
2.6A116FZ	2.6	27.6	102.5	13.3	115.8

Table E-3: Solution data for hydrochloric acid pickling solutions with high zinc concentrations

Initial Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)	Zinc Conc. (g/L)	Combined Metal Concentration (g/L)
2A111FZ	1.7	16.9	51.2	59.6	110.8
4A88FZ	4.3	44.1	40.8	47.4	88.1
8A54FZ	8.0	82.6	24.3	30.1	54.4
3A175FZ	2.9	28.9	81.1	93.7	174.8
5A160FZ	4.6	47.4	74.1	85.4	159.6

Table E-4: Solution data for sulfuric acid pickling solutions with high zinc concentrations

Initial Solution	Acid Conc. (%)	Acid Conc. (g/L)	Iron Conc. (g/L)	Zinc Conc. (g/L)	Combined Metal Concentration (g/L)
2.5A86FZ	2.5	25.9	39.9	46.3	86.2
5A68FZ	5.2	55.9	31.3	36.3	67.7
8A49FZ	7.9	85.9	22.8	26.7	49.4
4A111FZ	4.5	47.6	51.2	60.0	111.2
2.6A124FZ	2.6	27.6	56.9	66.7	123.6

Table E-5: Coupon mass changes from pickling for hydrochloric acid pickling solutions with low zinc concentrations

2A104FZ Coupon 1		**2A104FZ Coupon 2**		**4A83FZ Coupon 1**		**4A83FZ Coupon 2**		**8A52FZ Coupon 1**		**8A52FZ Coupon 2**	
Mass Before (g)	36.81	Mass Before (g)	43.38	Mass Before (g)	44.79	Mass Before (g)	39.07	Mass Before (g)	57.07	Mass Before (g)	36.18
Mass After (g)	36.69	Mass After (g)	43.27	Mass After (g)	44.68	Mass After (g)	38.99	Mass After (g)	56.96	Mass After (g)	36.05
Loss (g)	0.12	Loss (g)	0.11	Loss (g)	0.11	Loss (g)	0.08	Loss (g)	0.11	Loss (g)	0.13

3A165FZ Coupon 1		**3A165FZ Coupon 2**		**5A151FZ Coupon 1**		**5A151FZ Coupon 2**	
Mass Before (g)	43.68	Mass Before (g)	36.55	Mass Before (g)	38.21	Mass Before (g)	45.62
Mass After (g)	43.56	Mass After (g)	36.43	Mass After (g)	38.11	Mass After (g)	45.5
Loss (g)	0.12	Loss (g)	0.12	Loss (g)	0.1	Loss (g)	0.12

Table E-6: Coupon mass changes from pickling for sulfuric acid pickling solutions with low zinc concentrations

2.5A81FZ Coupon 1		2.5A81FZ Coupon 2		5A63FZ Coupon 1		5A63FZ Coupon 2		8A46FZ Coupon 1		8A46FZ Coupon 2	
`Mass Before (g)	39.26	Mass Before (g)	38.47	Mass Before (g)	48.99	Mass Before (g)	47.38	Mass Before (g)	61.65	Mass Before (g)	41.15
Mass After (g)	39.1	Mass After (g)	38.32	Mass After (g)	48.87	Mass After (g)	47.18	Mass After (g)	61.54	Mass After (g)	41.07
Loss (g)	0.16	Loss (g)	0.15	Loss (g)	0.12	Loss (g)	0.2	Loss (g)	0.11	Loss (g)	0.08

4A104FZ Coupon 1		4A104FZ Coupon 2		2.6A116FZ Coupon 1		2.6A116FZ Coupon 2	
Mass Before (g)	41.66	Mass Before (g)	39.79	Mass Before (g)	44.51	Mass Before (g)	39.2
Mass After (g)	41.55	Mass After (g)	39.68	Mass After (g)	44.42	Mass After (g)	39.12
Loss (g)	0.11	Loss (g)	0.11	Loss (g)	0.09	Loss (g)	0.08

Table E-7: Coupon mass changes from pickling for hydrochloric acid pickling solutions with high zinc concentrations

2A111FZ Coupon 1		2A111FZ Coupon 2		4A88FZ Coupon 1		4A88FZ Coupon 2		8A54FZ Coupon 1		8A54FZ Coupon 2	
Mass Before (g)	49.34	Mass Before (g)	45.83	Mass Before (g)	46.45	Mass Before (g)	51.2	Mass Before (g)	47.44	Mass Before (g)	49.84
Mass After (g)	49.31	Mass After (g)	45.8	Mass After (g)	46.43	Mass After (g)	51.16	Mass After (g)	47.41	Mass After (g)	49.82
Loss (g)	0.03	Loss (g)	0.03	Loss (g)	0.02	Loss (g)	0.04	Loss (g)	0.03	Loss (g)	0.02

3A175FZ Coupon 1		3A175FZ Coupon 2		5A160FZ Coupon 1		5A160FZ Coupon 2	
Mass Before (g)	50.34	Mass Before (g)	49.14	Mass Before (g)	65.57	Mass Before (g)	51.2
Mass After (g)	50.32	Mass After (g)	49.12	Mass After (g)	65.52	Mass After (g)	51.17
Loss (g)	0.02	Loss (g)	0.02	Loss (g)	0.05	Loss (g)	0.03

Table E-8: Coupon mass changes from pickling for sulfuric acid pickling solutions with high zinc concentrations

2.5A86FZ Coupon 1		2.5A86FZ Coupon 2		5A68FZ Coupon 1		5A68FZ Coupon 2		8A49FZ Coupon 1		8A49FZ Coupon 2	
Mass Before (g)	44.51	Mass Before (g)	31.41	Mass Before (g)	41.78	Mass Before (g)	31.18	Mass Before (g)	45.41	Mass Before (g)	45.22
Mass After (g)	44.35	Mass After (g)	31.27	Mass After (g)	41.64	Mass After (g)	31.06	Mass After (g)	45.33	Mass After (g)	45.16
Loss (g)	0.16	Loss (g)	0.14	Loss (g)	0.14	Loss (g)	0.12	Loss (g)	0.08	Loss (g)	0.06

4A111FZ Coupon 1		4A111FZ Coupon 2		2.6A124FZ Coupon 1		2.6A124FZ Coupon 2	
Mass Before (g)	41.11	Mass Before (g)	39.59	Mass Before (g)	36.02	Mass Before (g)	31.92
Mass After (g)	41.07	Mass After (g)	39.56	Mass After (g)	36.01	Mass After (g)	31.91
Loss (g)	0.04	Loss (g)	0.03	Loss (g)	0.01	Loss (g)	0.01

APPENDIX F – TASK 3 TEST PHOTOS

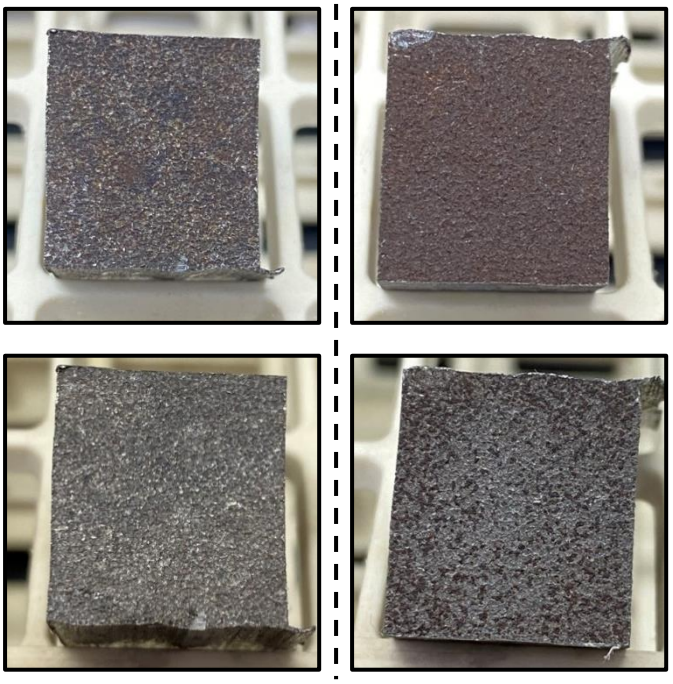
Low Zinc Concentration Tests – Hydrochloric Acid

Before Pickling:

After Pickling:

Pickling Time:

48 Minutes



Face 1: **Face 2:**

Figure F-1: Solution 2A104FZ – Coupon 1 Photos

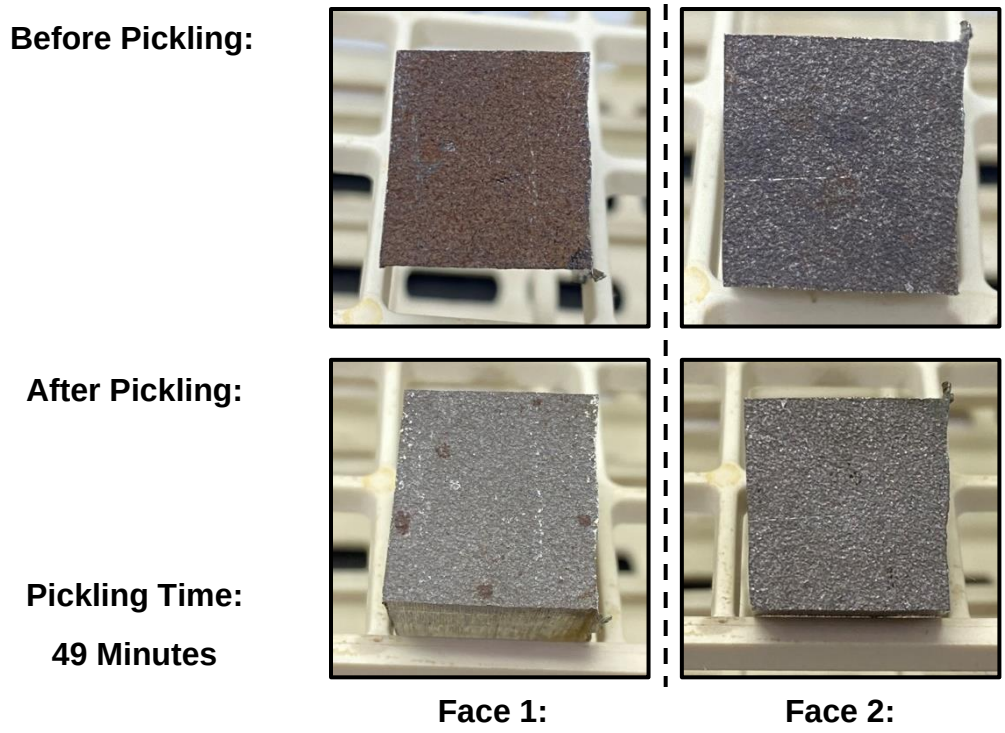


Figure F-2: Solution 2A104FZ – Coupon 2 Photos

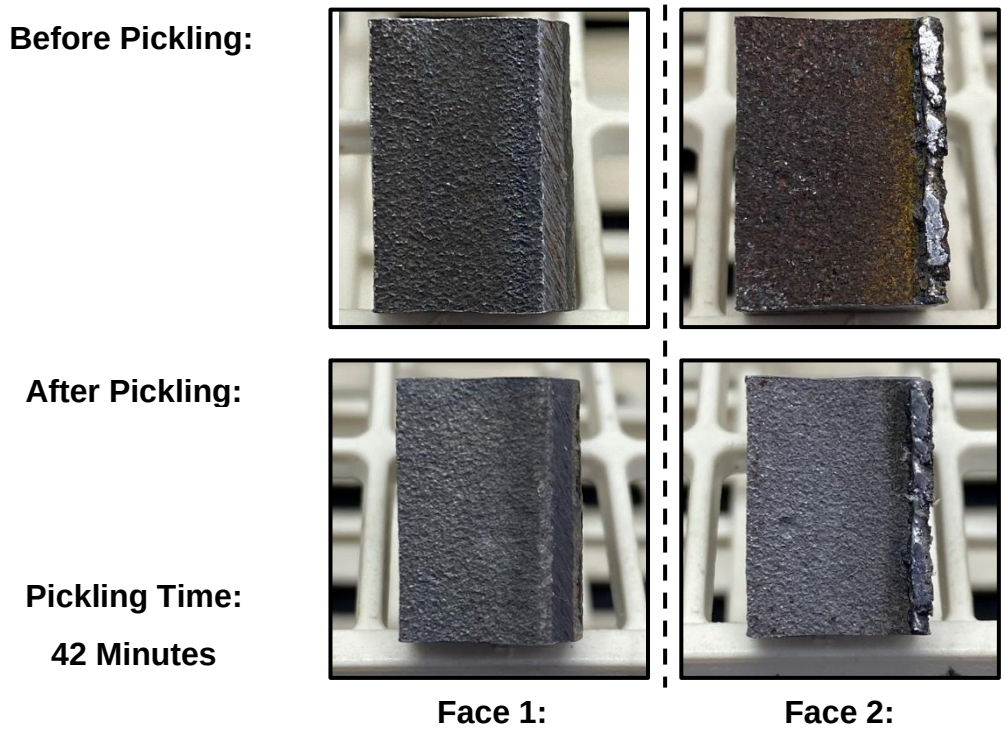


Figure F-3: Solution 2A104FZ second test – Coupon 1 photos

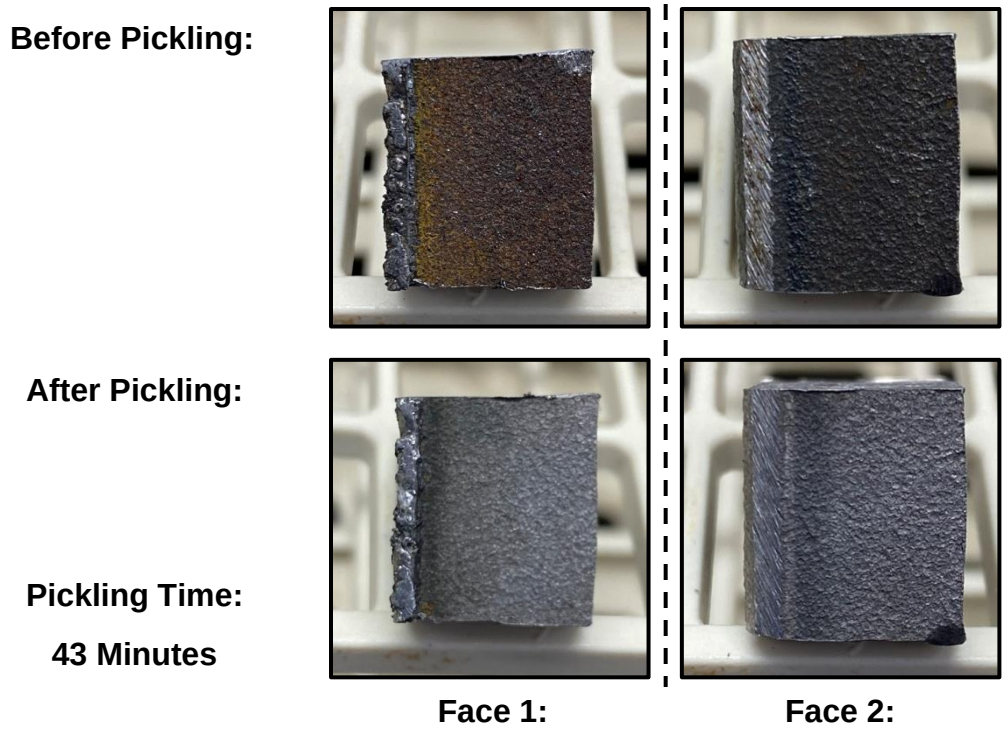


Figure F-4: Solution 2A104FZ second test – Coupon 2 photos

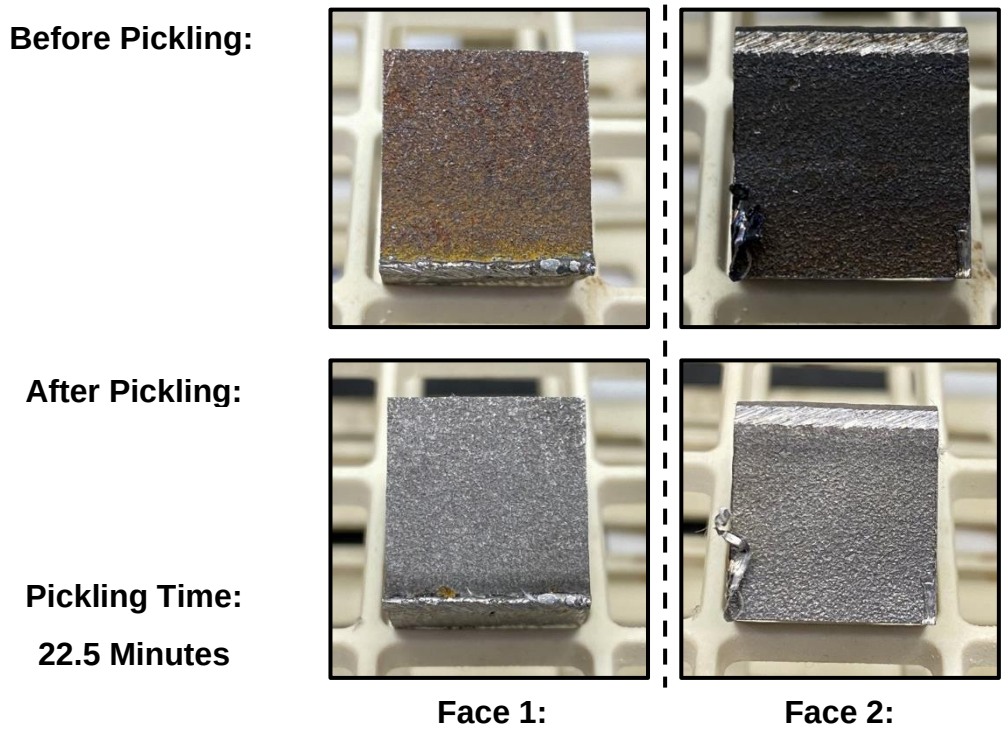


Figure F-5: Solution 4A83FZ – Coupon 1 Photos

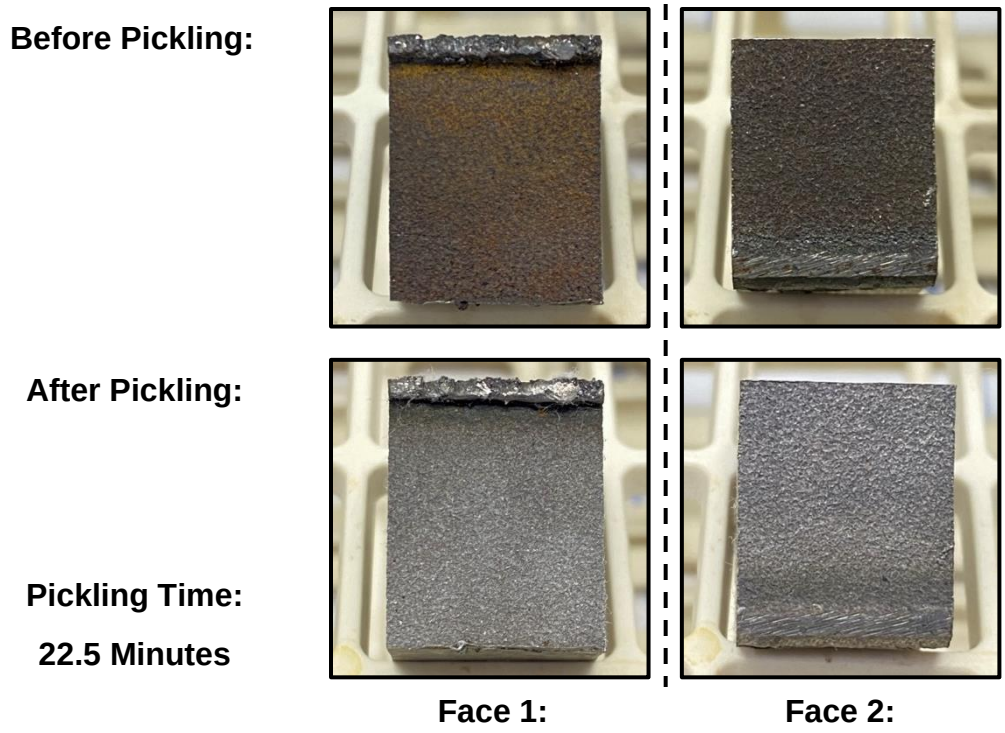


Figure F-6: Solution 4A83FZ – Coupon 2 Photos

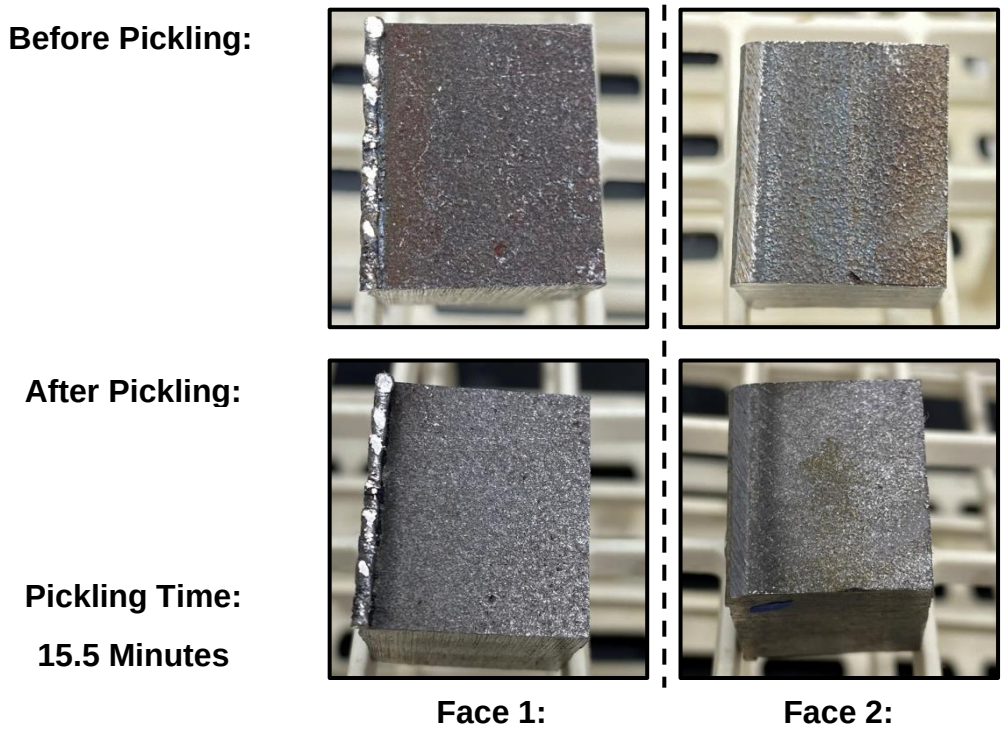


Figure F-7: Solution 8A52FZ – Coupon 1 Photos

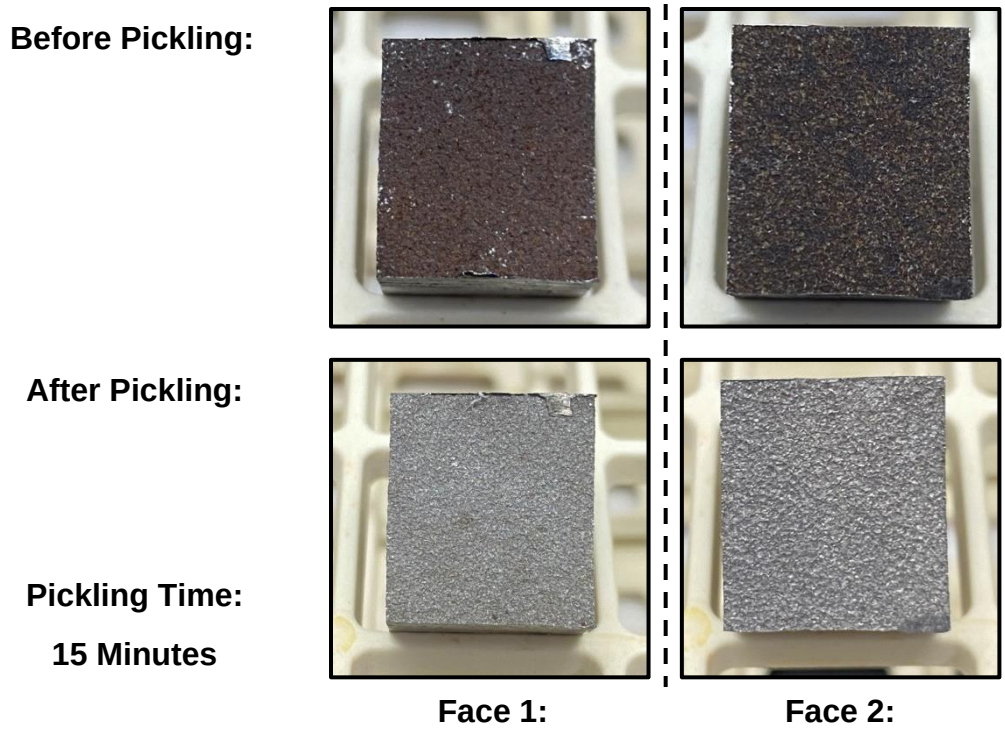


Figure F-8: Solution 8A52FZ – Coupon 2 Photos

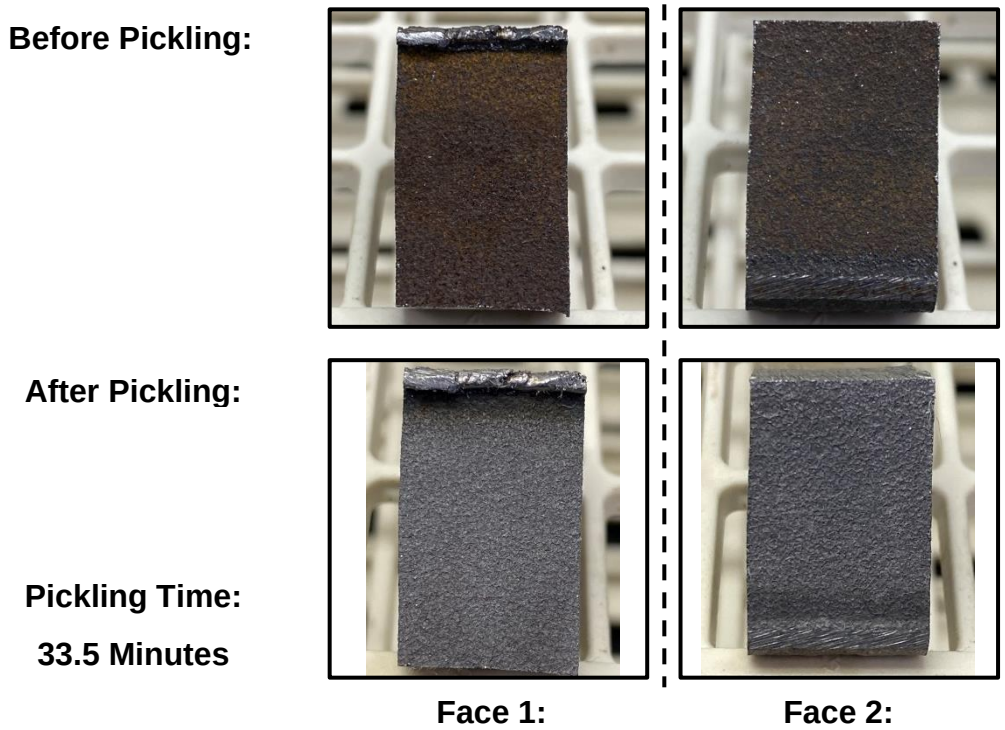


Figure F-9: Solution 3A165FZ – Coupon 1 Photos

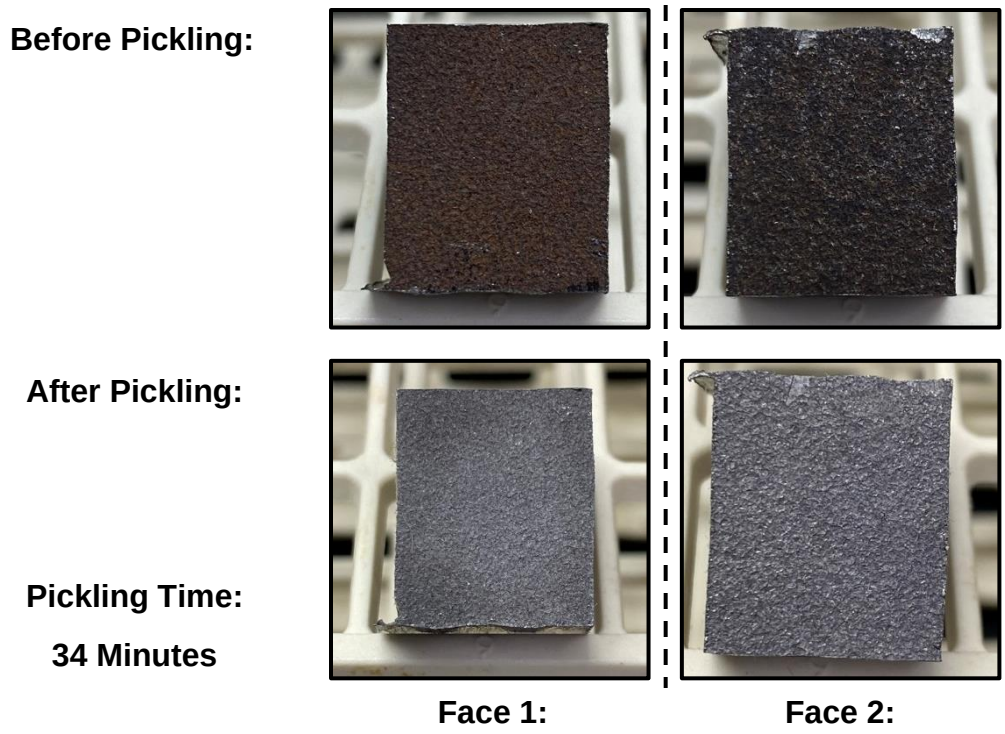


Figure F-10: Solution 3A165FZ – Coupon 2 Photos

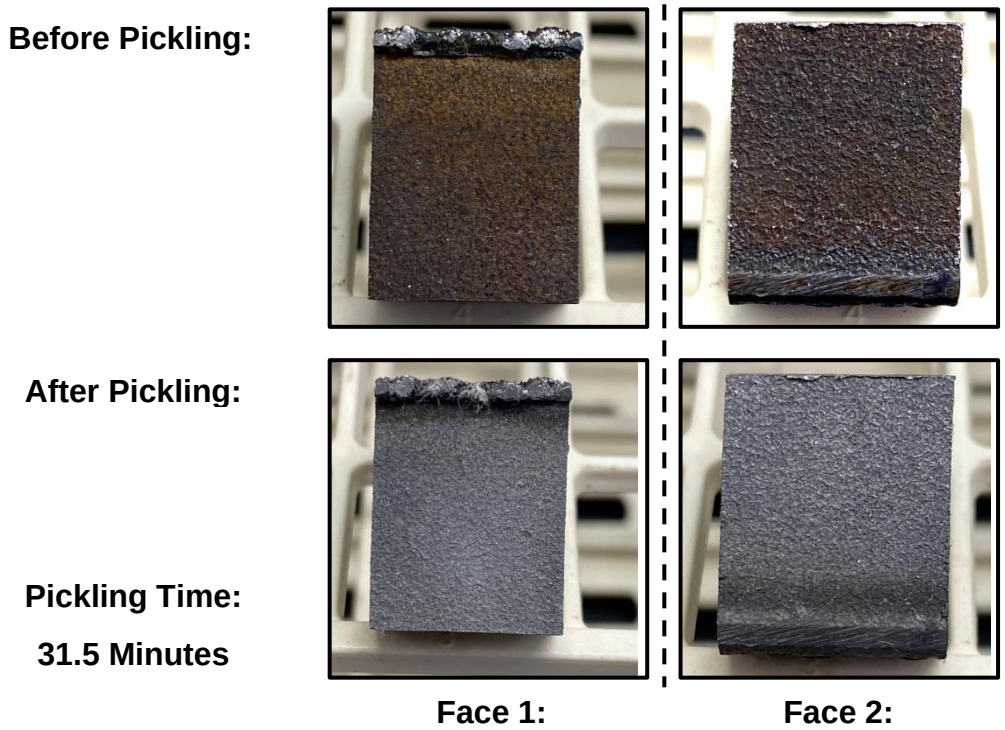


Figure F-11: Solution 5A151FZ – Coupon 1 Photos

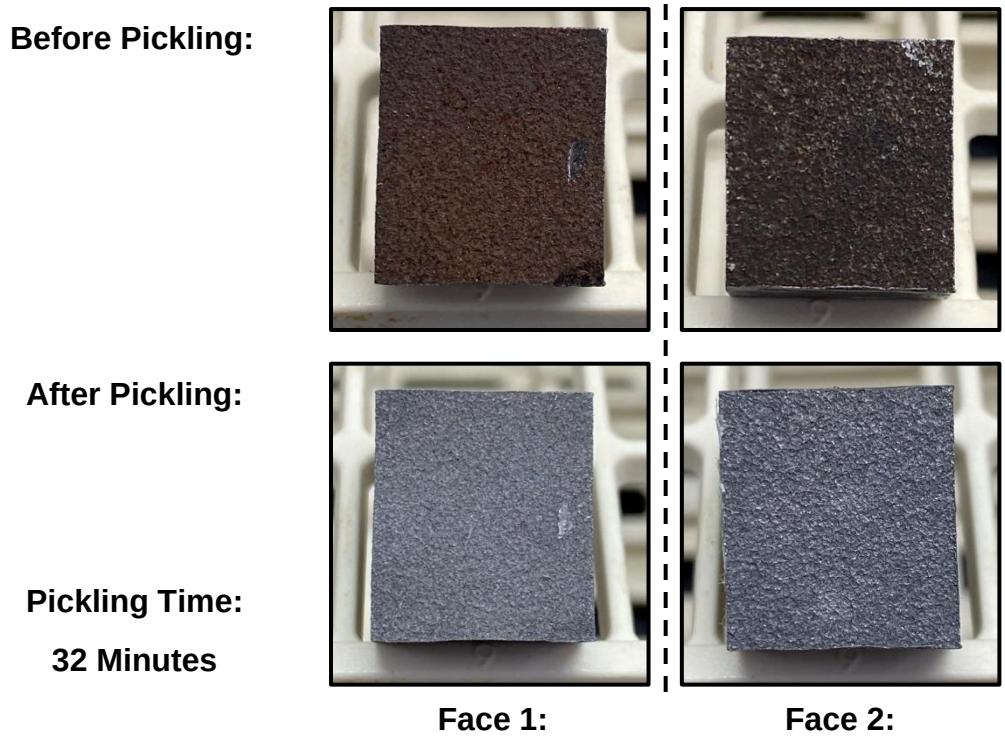


Figure F-12: Solution 5A151FZ – Coupon 2 Photos

Low Zinc Concentration Tests – Sulfuric Acid

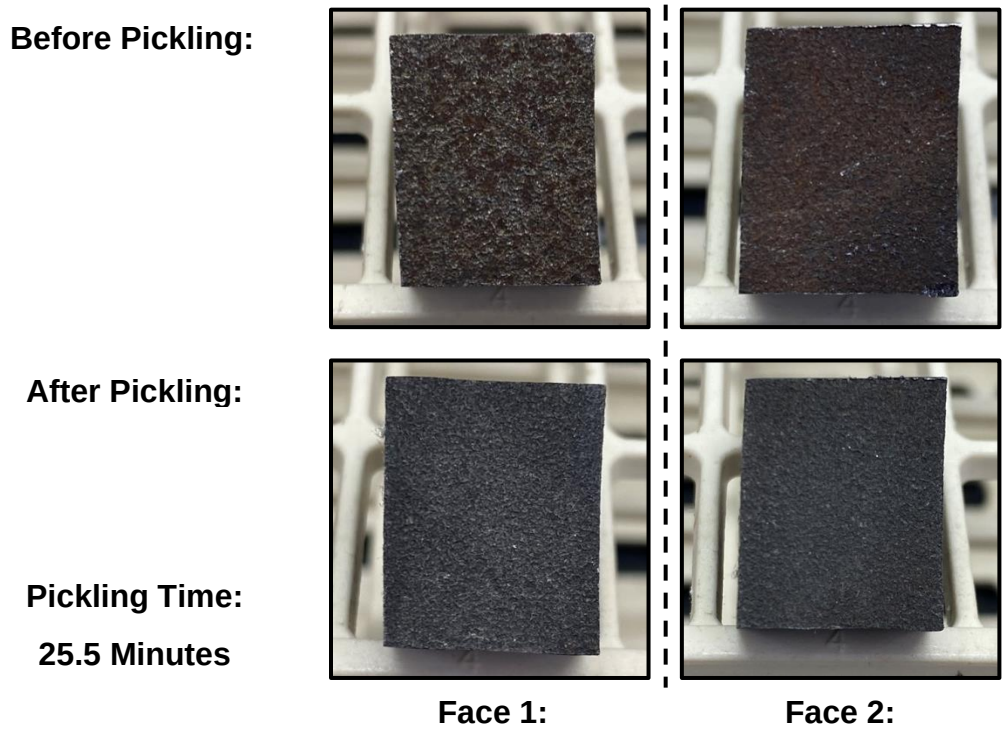


Figure F-13: Solution 2.5A81FZ – Coupon 1 Photos

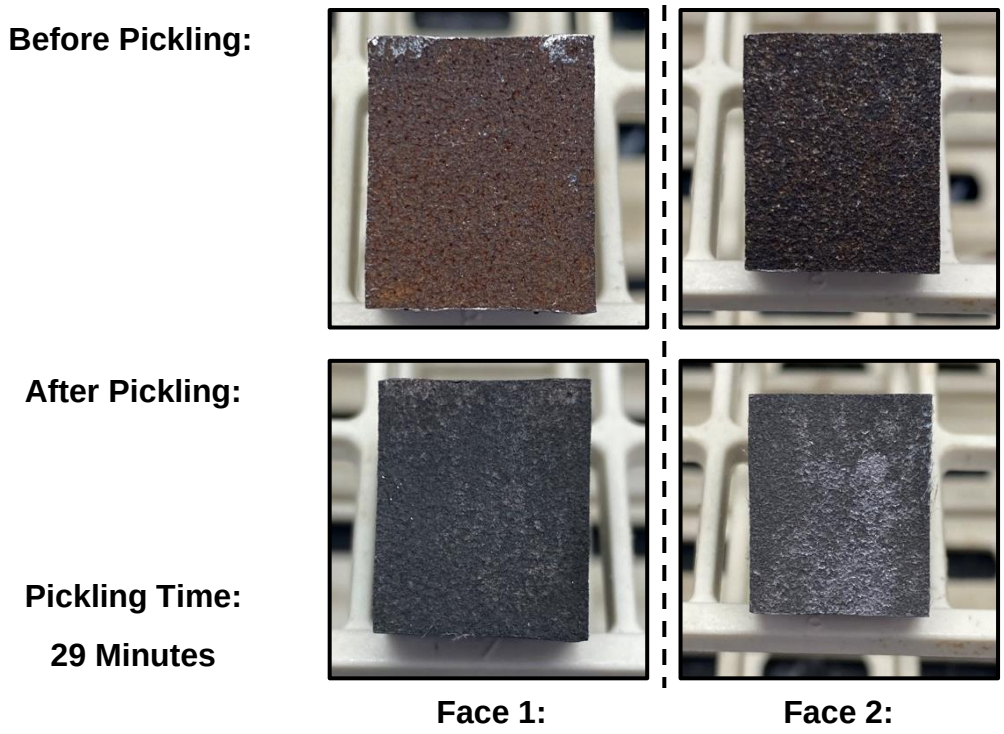


Figure F-14: Solution 2.5A81FZ – Coupon 2 Photos

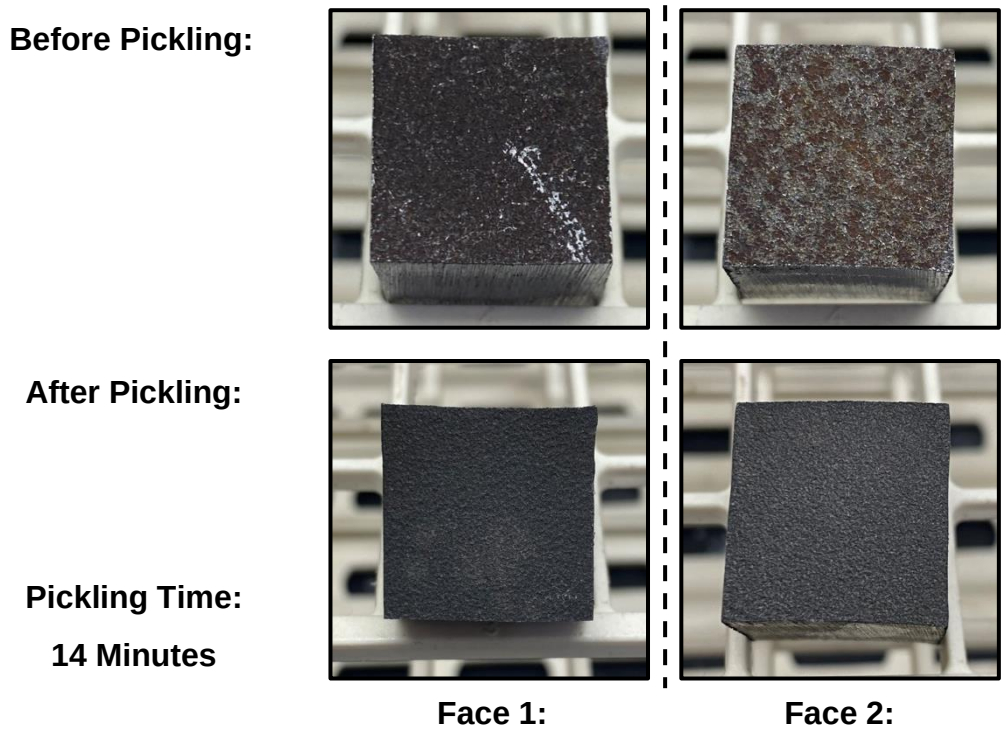


Figure F-15: Solution 5A63FZ – Coupon 1 Photos

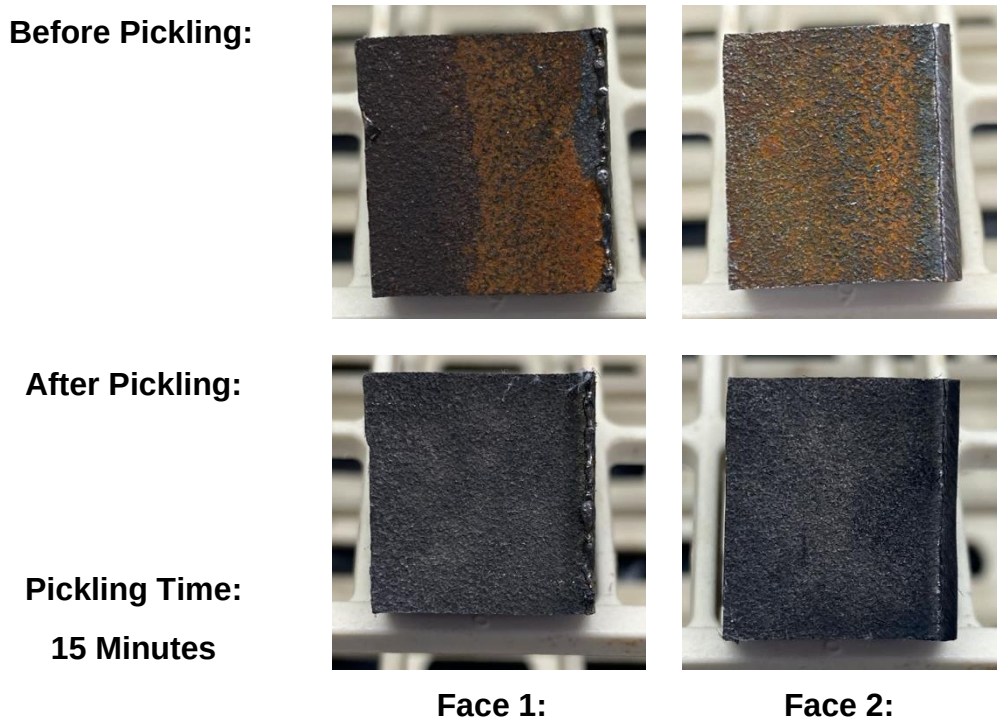


Figure F-16: Solution 5A63FZ – Coupon 2 Photos

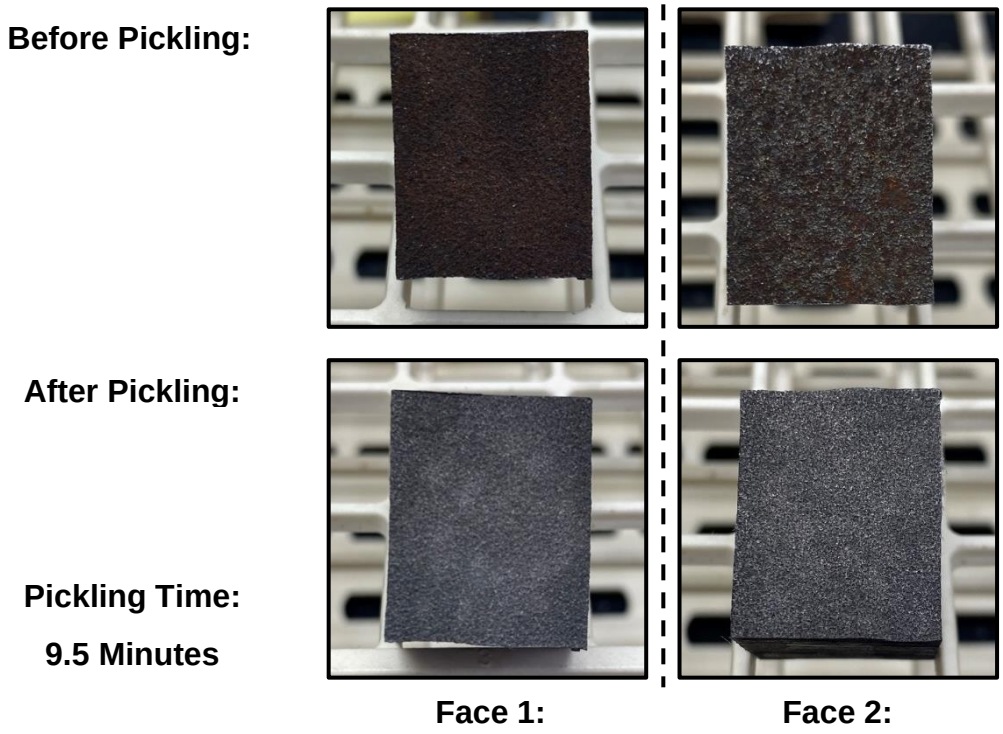


Figure F-17: Solution 8A46FZ – Coupon 1 Photos

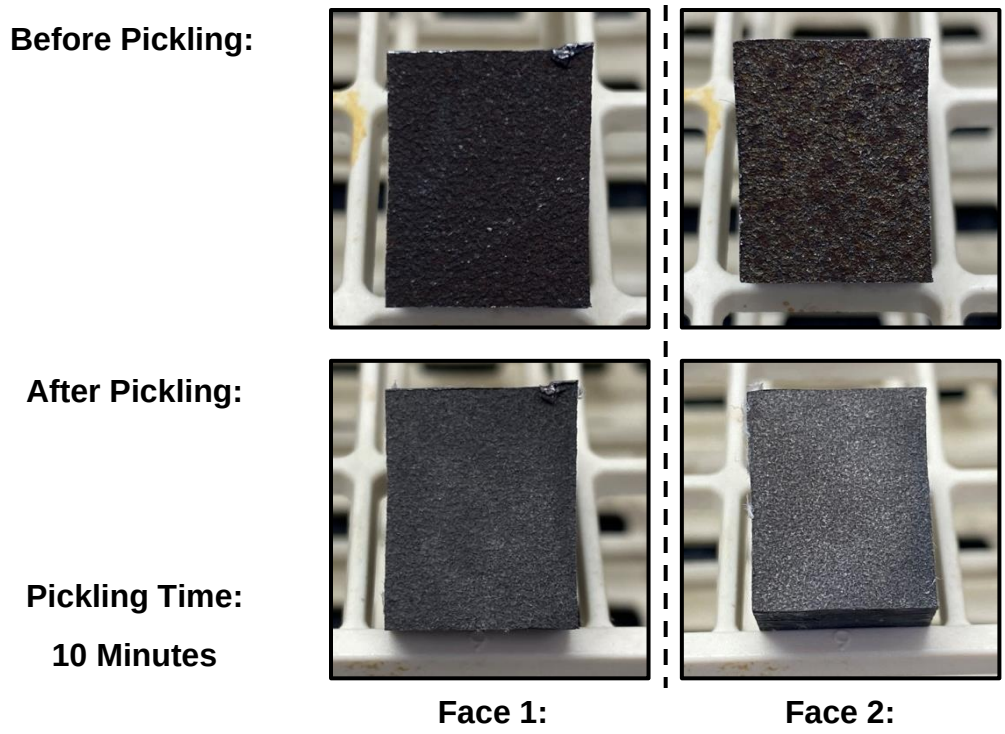


Figure F-18: Solution 8A46FZ – Coupon 2 Photos

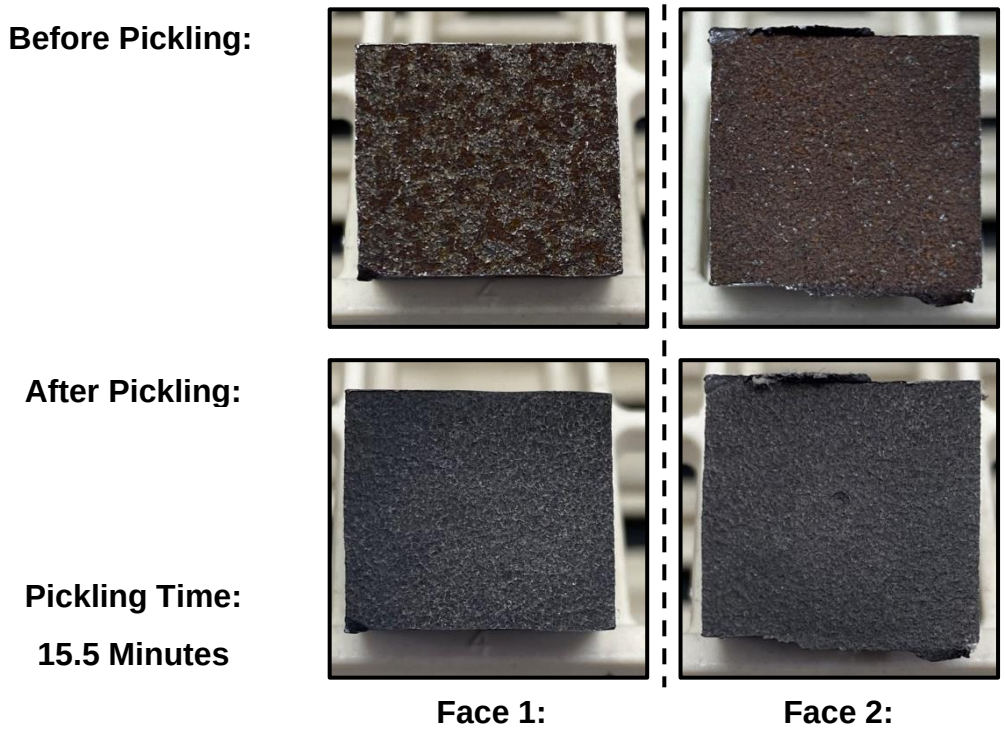


Figure F-19: Solution 4A104FZ – Coupon 1 Photos

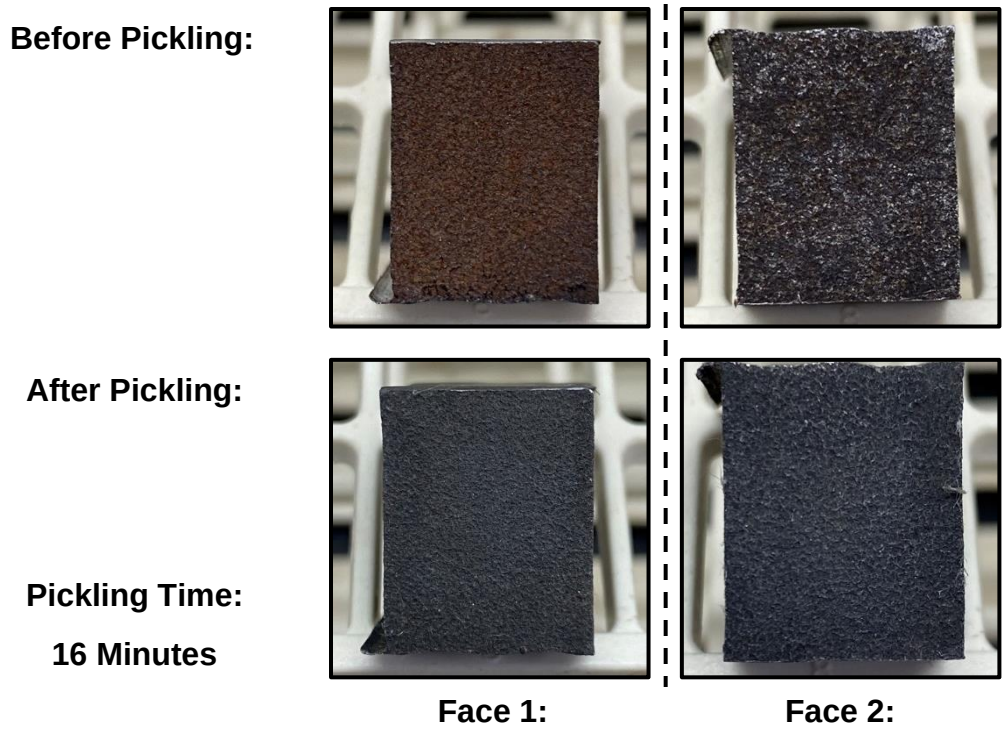


Figure F-20: Solution 4A104FZ – Coupon 2 Photos

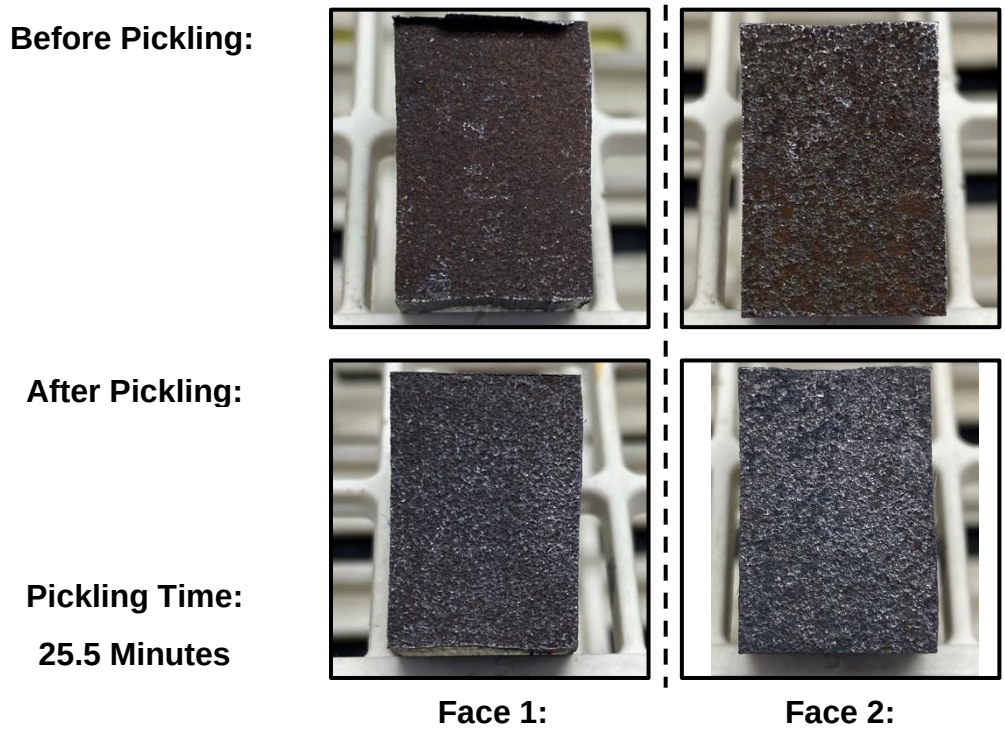


Figure F-21: Solution 2.6A116FZ – Coupon 1 Photos

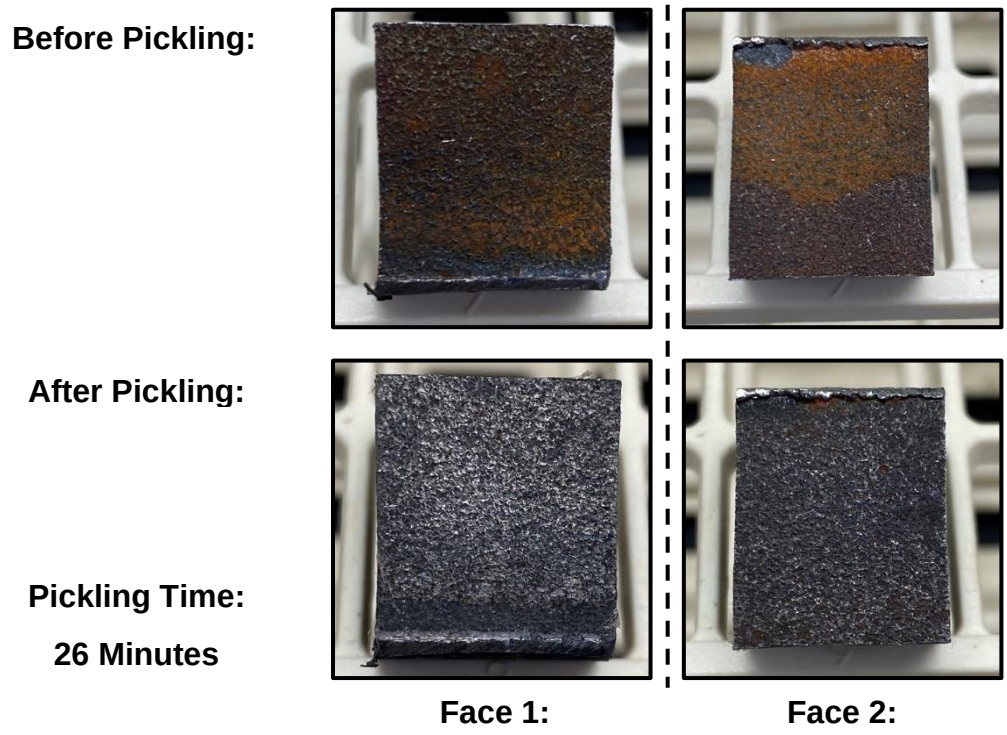


Figure F-22: Solution 2.6A116FZ – Coupon 2 Photos

High Zinc Concentration Tests – Hydrochloric Acid

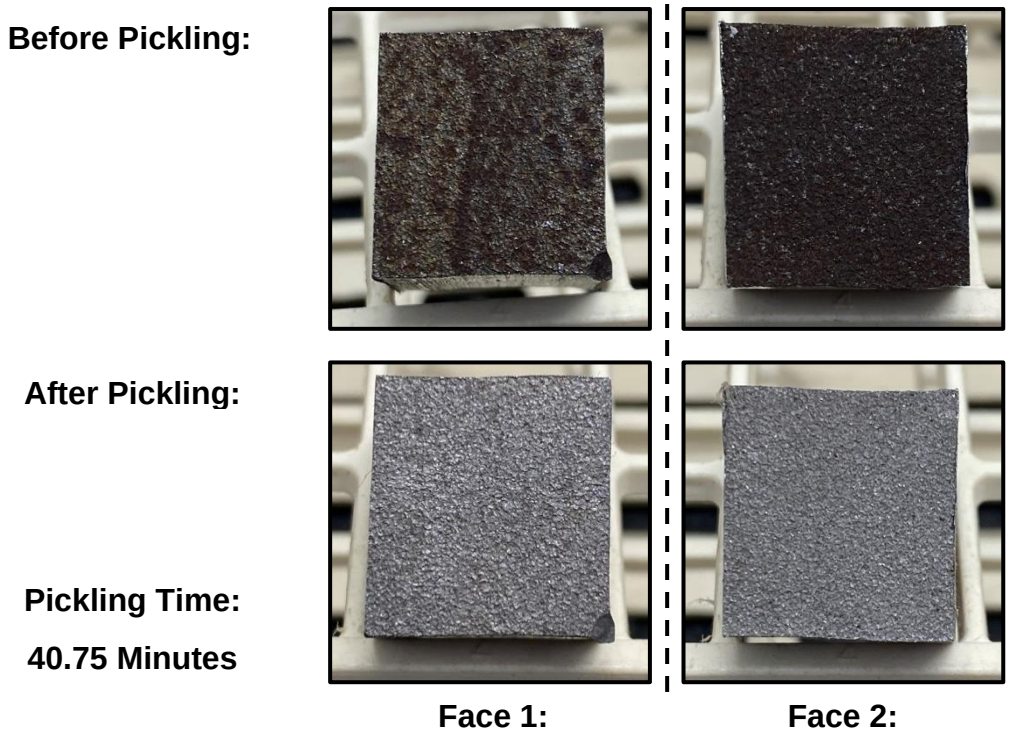


Figure F-23: Solution 2A111FZ – Coupon 1 Photos

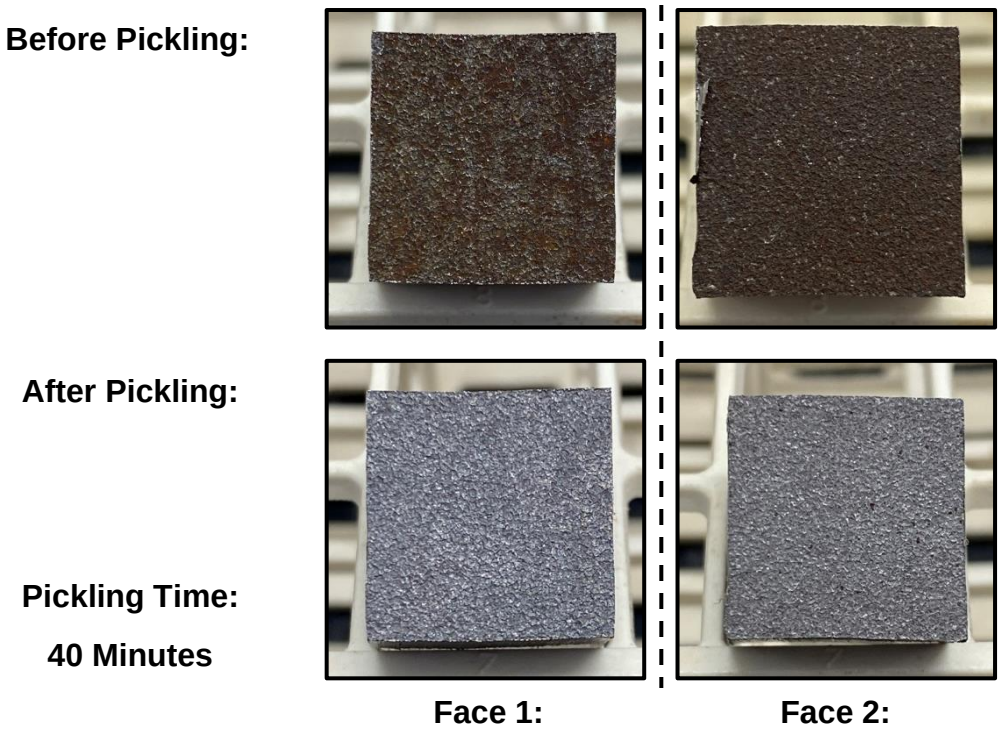


Figure F-24: Solution 2A111FZ – Coupon 2 Photos

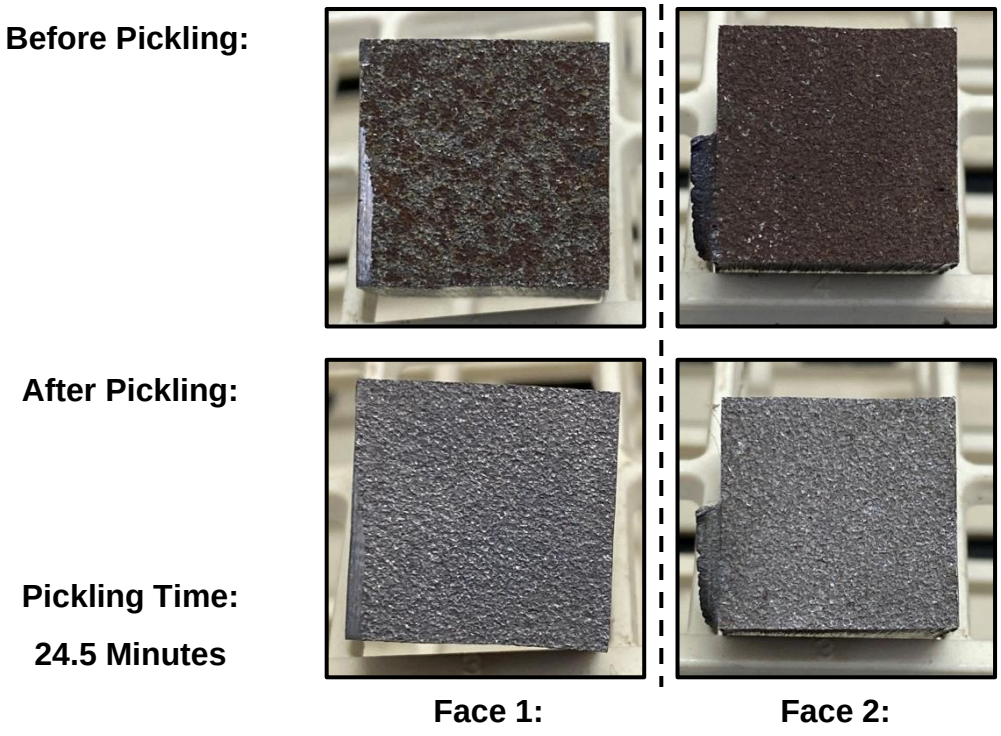


Figure F-25: Solution 4A88FZ – Coupon 1 Photos

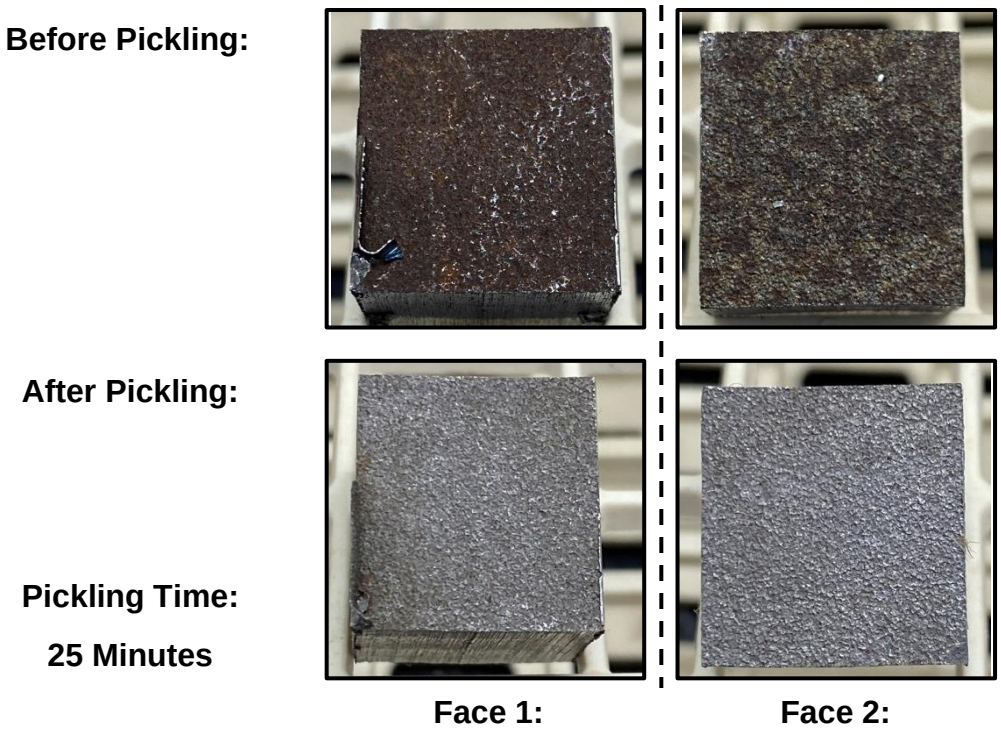


Figure F-26: Solution 4A88FZ – Coupon 2 Photos

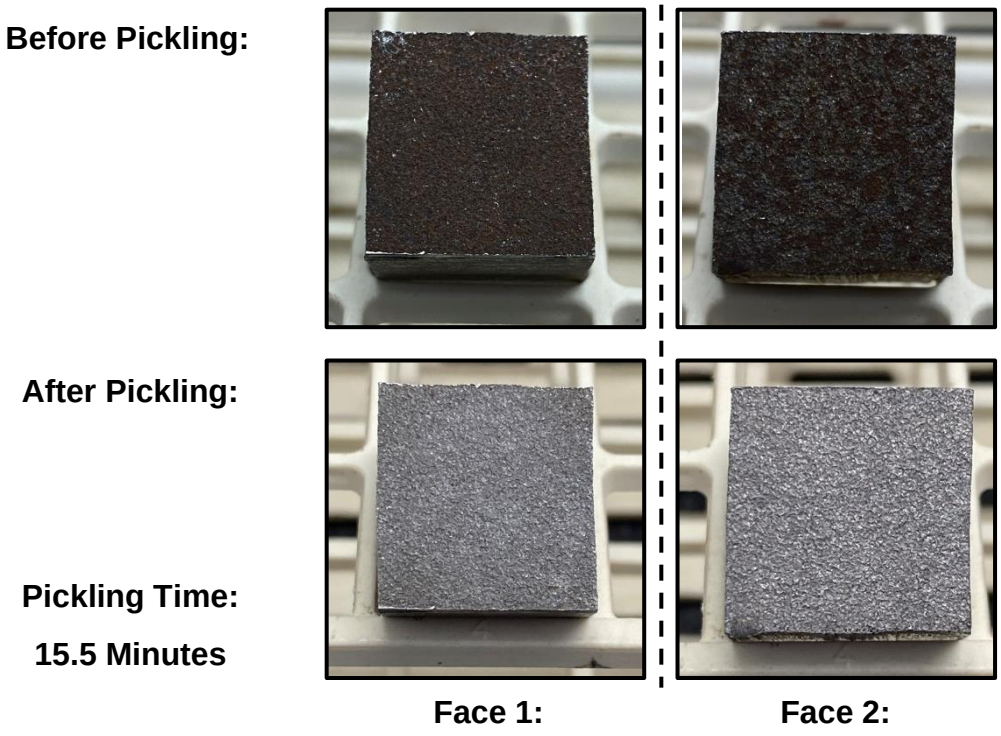


Figure F-27: Solution 8A54FZ – Coupon 1 Photos

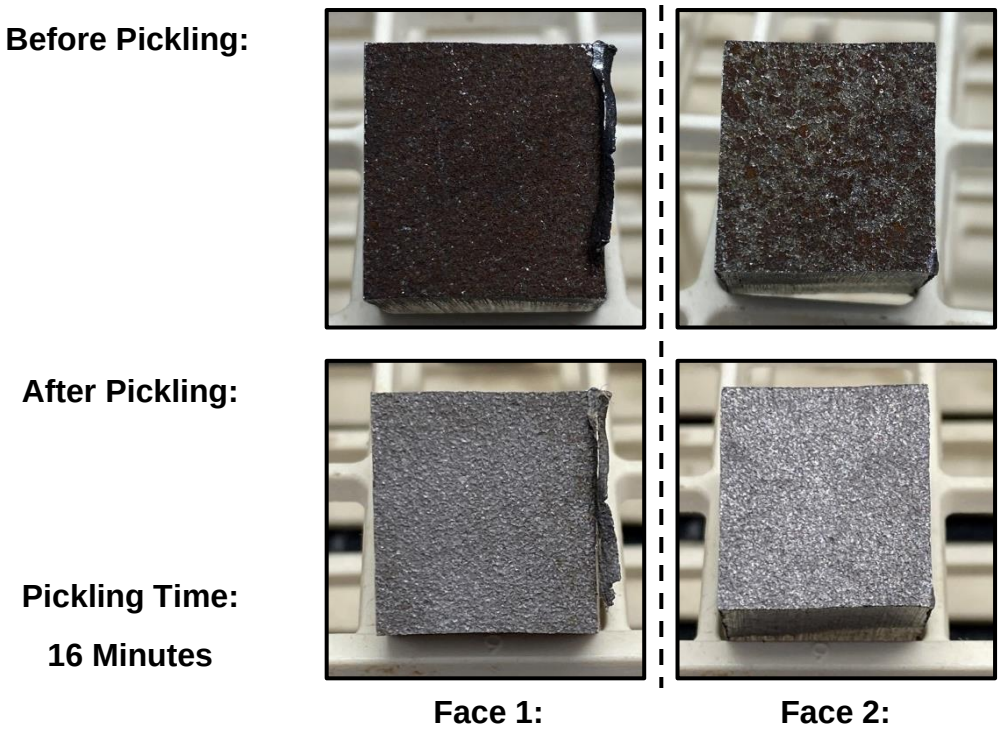


Figure F-28: Solution 8A54FZ – Coupon 2 Photos

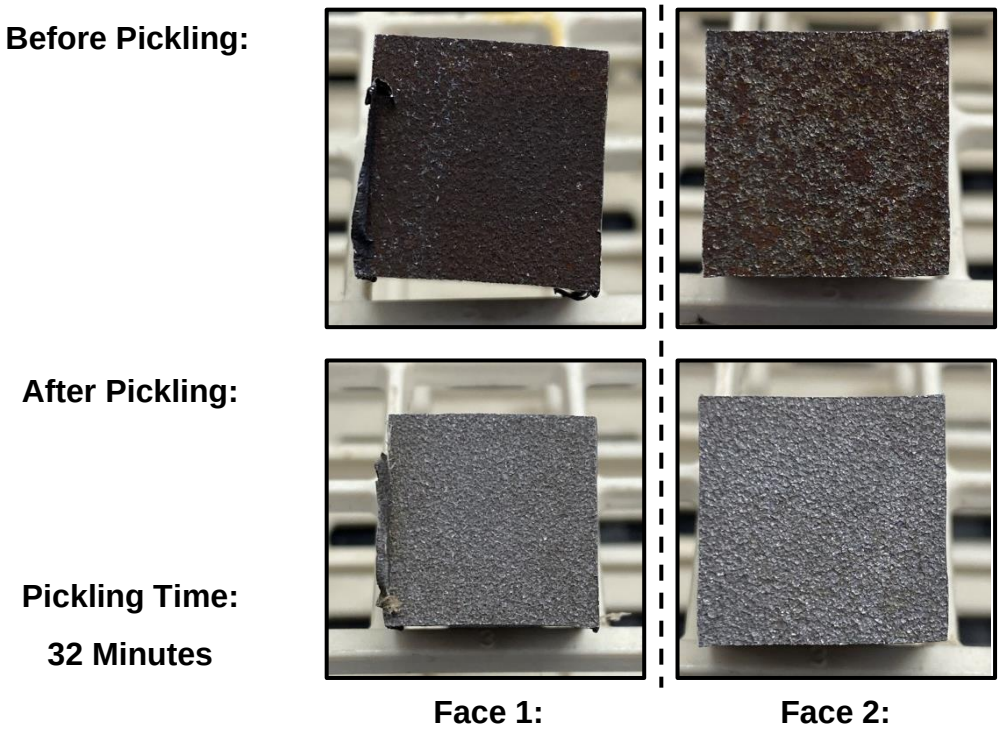


Figure F-29: Solution 3A175FZ – Coupon 1 Photos

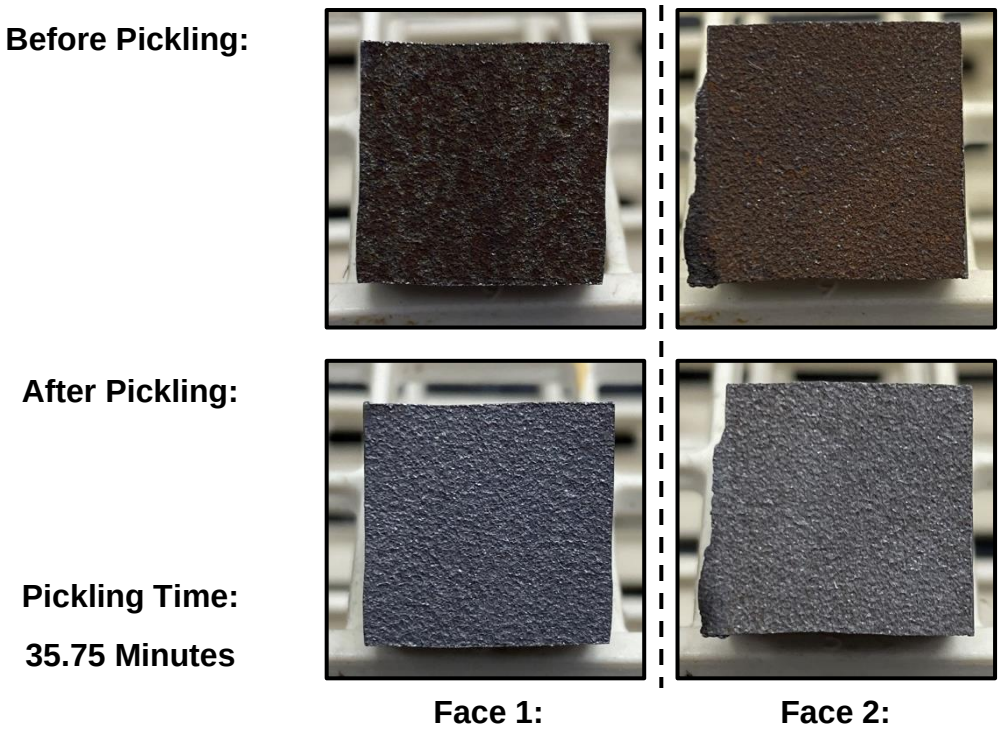


Figure F-30: Solution 3A175FZ – Coupon 2 Photos

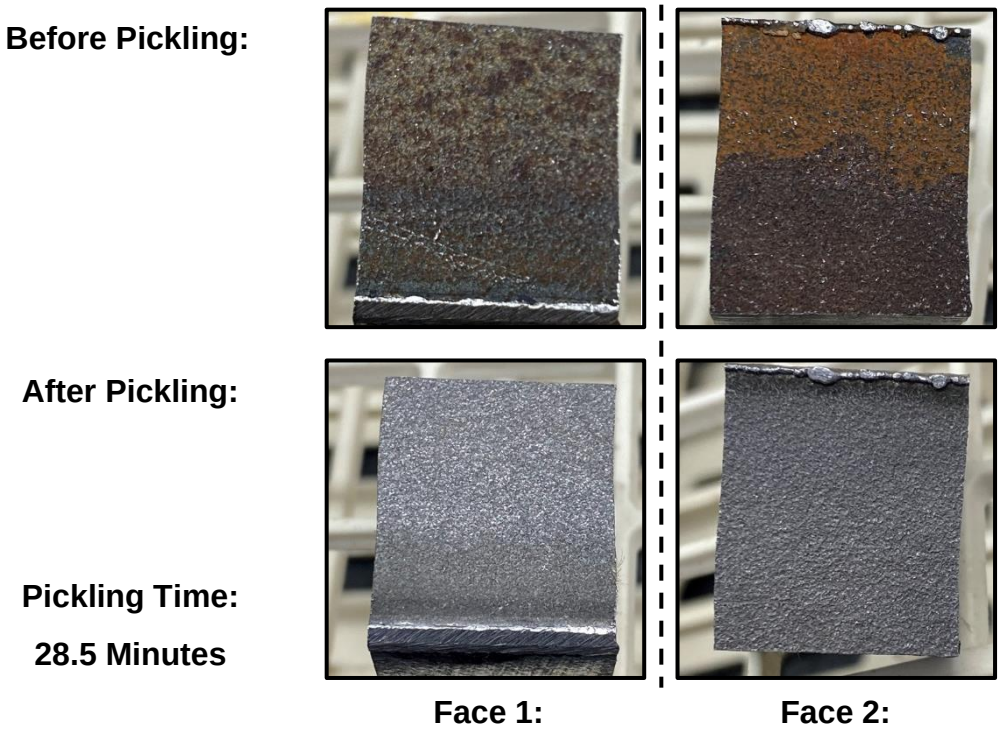


Figure F-31: Solution 5A160FZ – Coupon 1 Photos

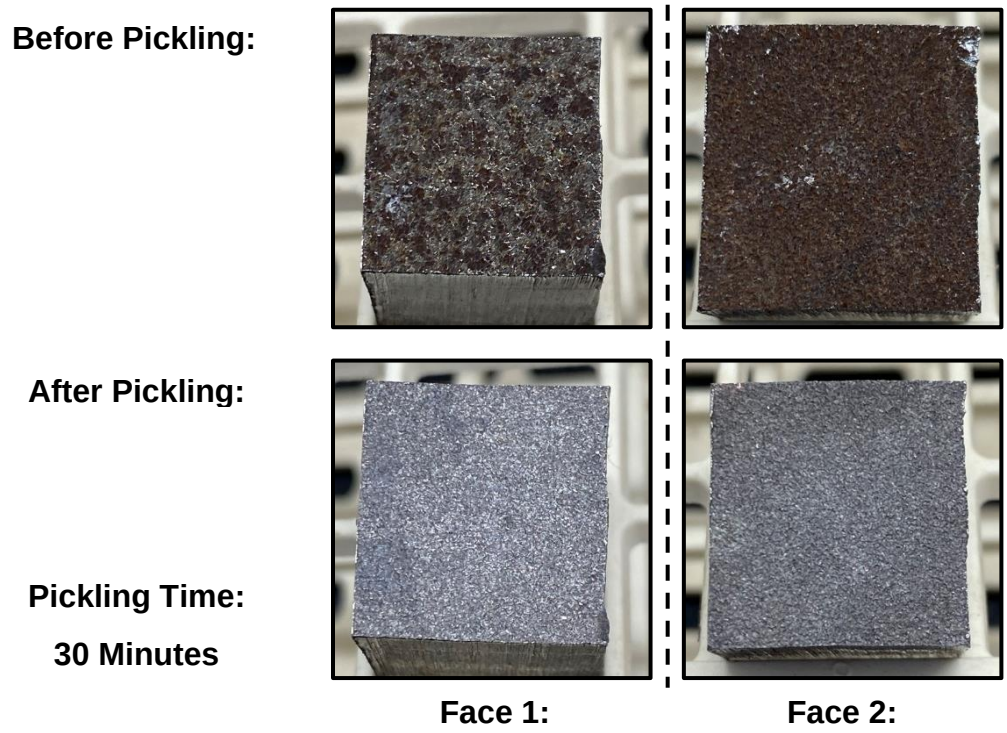


Figure F-32: Solution 5A160FZ – Coupon 2 Photos

High Zinc Concentration Tests – Sulfuric Acid

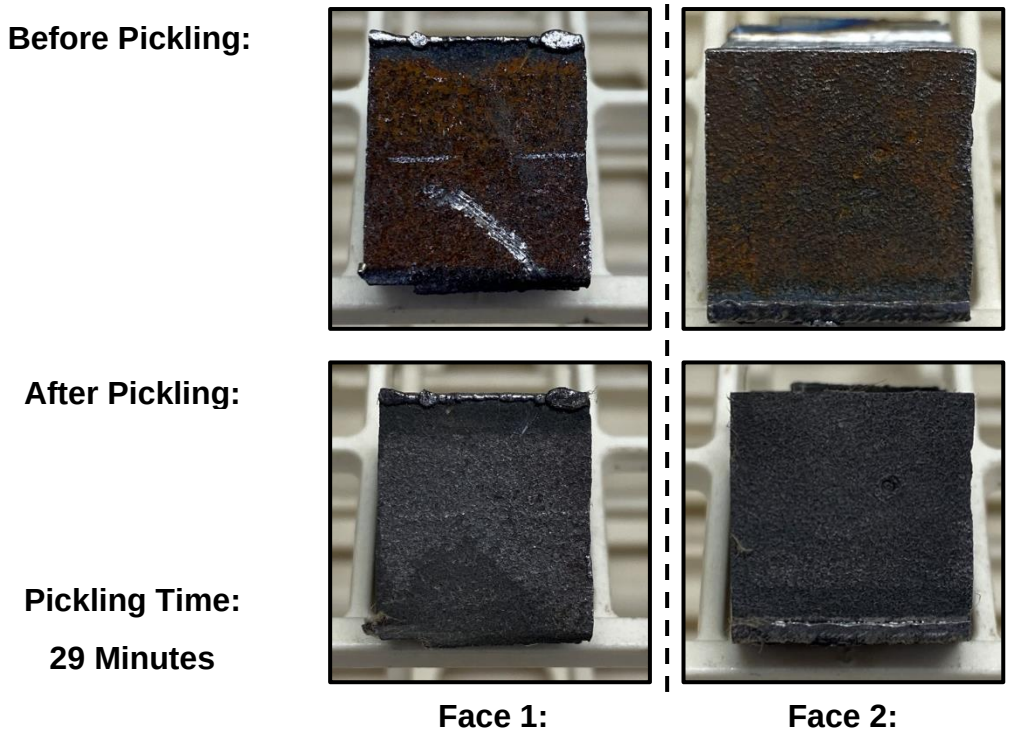


Figure F-33: Solution 2.5A86FZ – Coupon 1 Photos

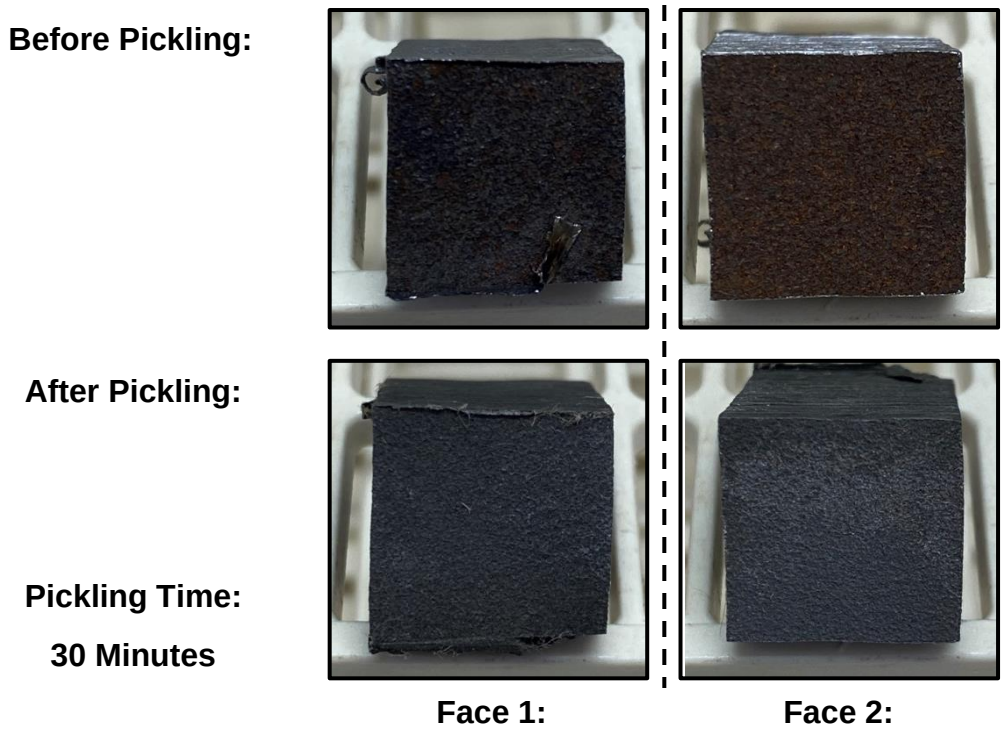


Figure F-34: Solution 2.5A86FZ – Coupon 2 Photos

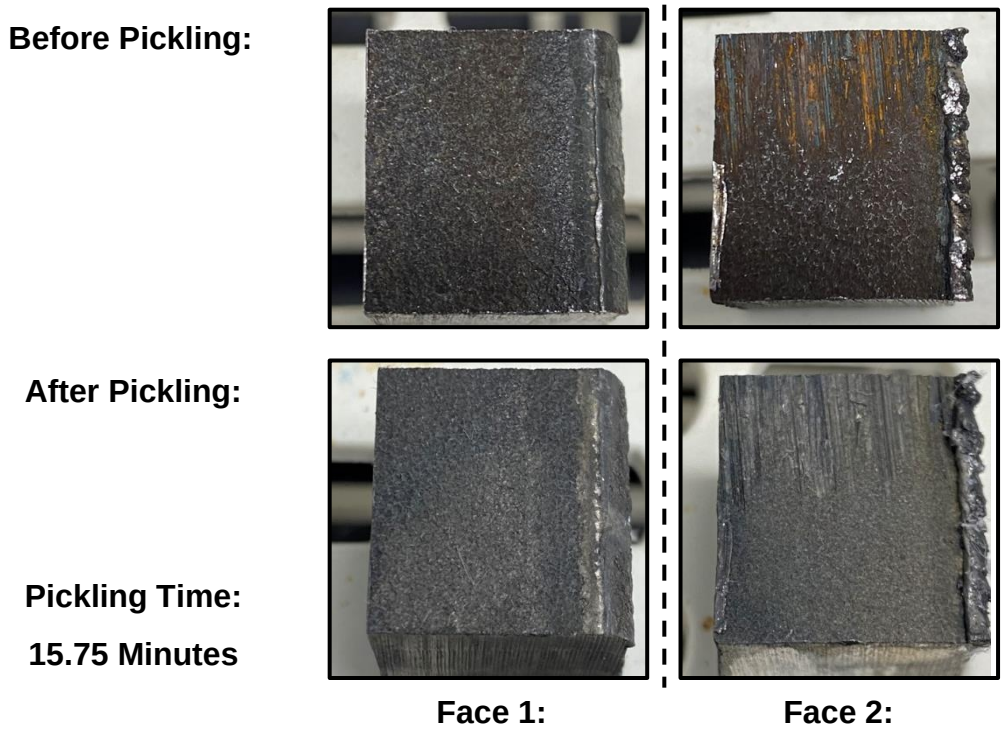


Figure F-35: Solution 5A68FZ – Coupon 1 Photos

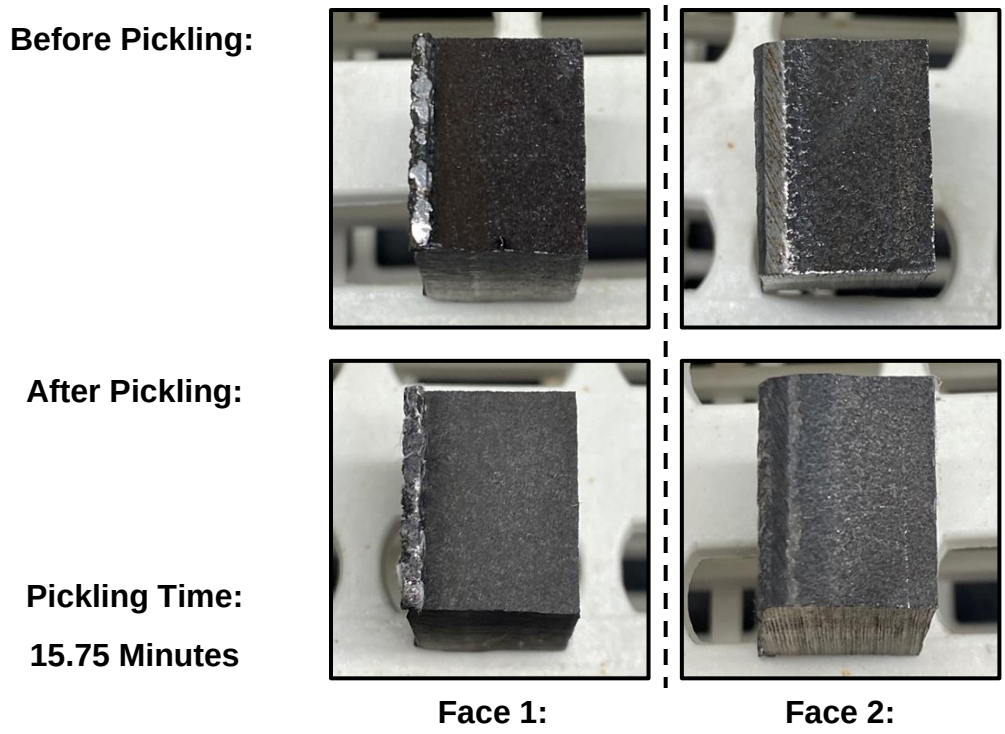


Figure F-36: Solution 5A68FZ – Coupon 2 Photos

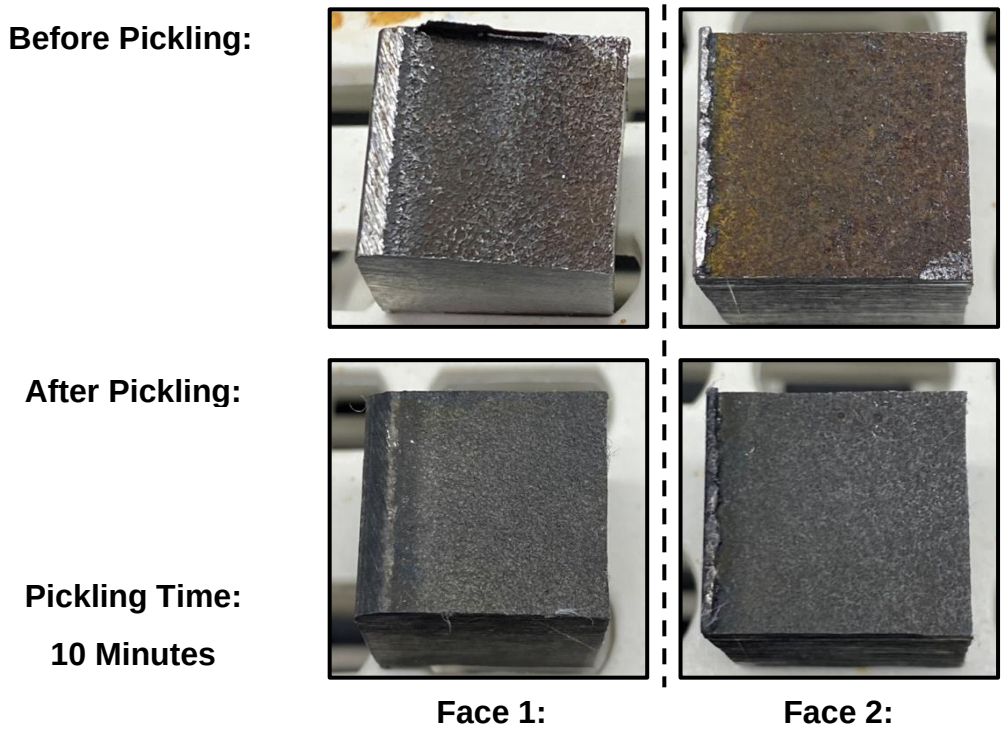


Figure F-37: Solution 8A49FZ – Coupon 1 Photos

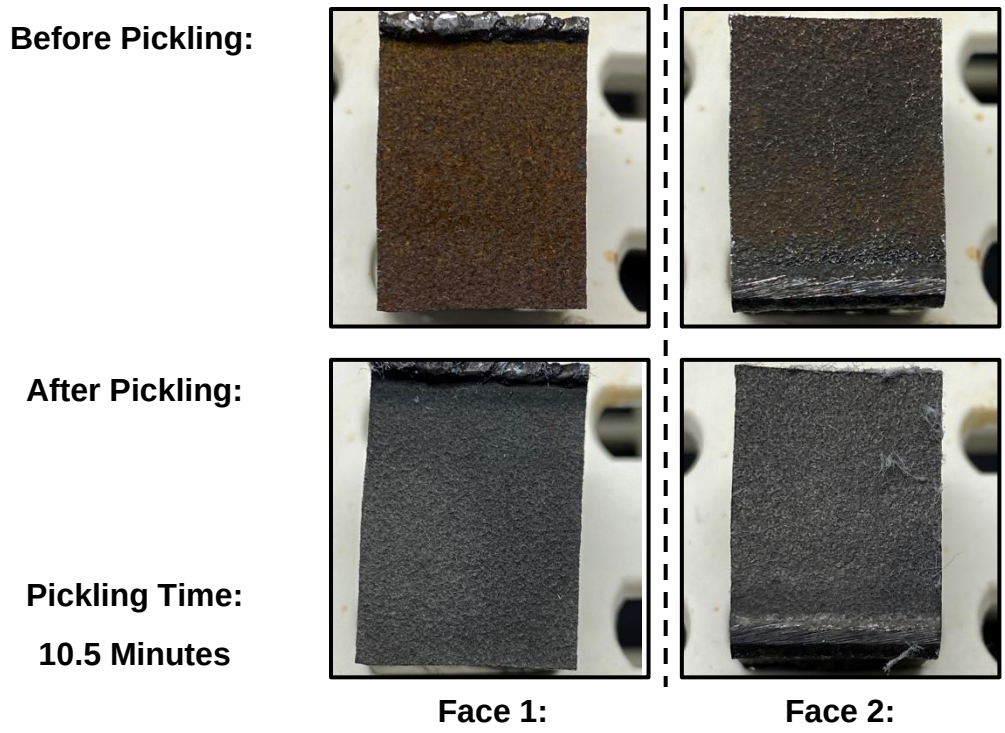


Figure F-38: Solution 8A49FZ – Coupon 2 Photos

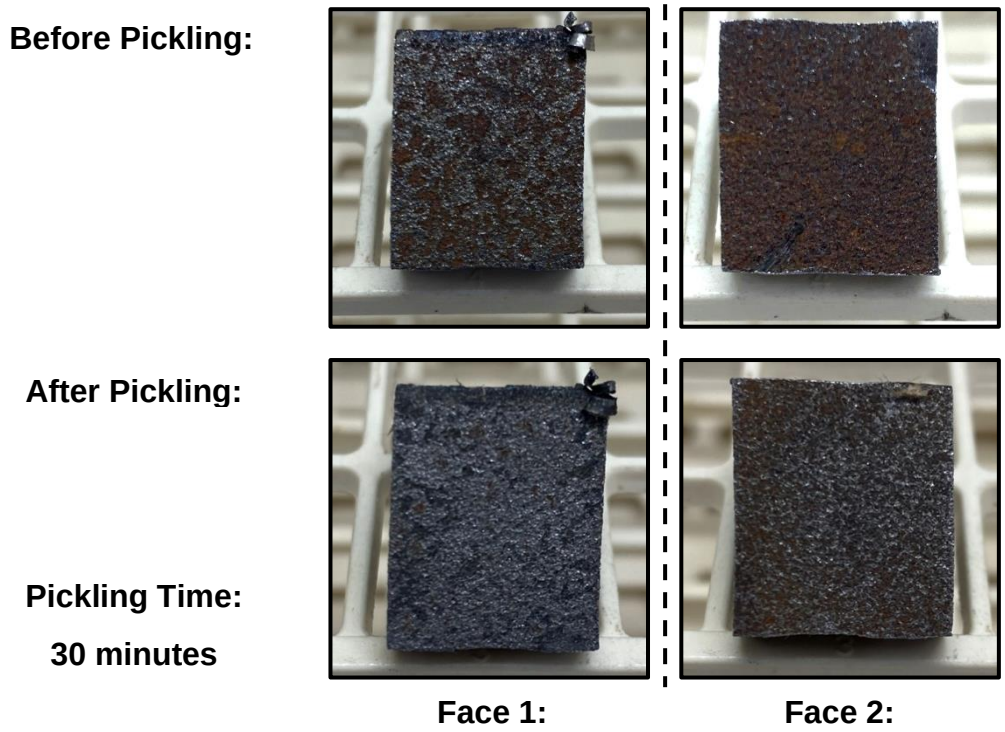


Figure F-39: Solution 4A111FZ – Coupon 1 Photos

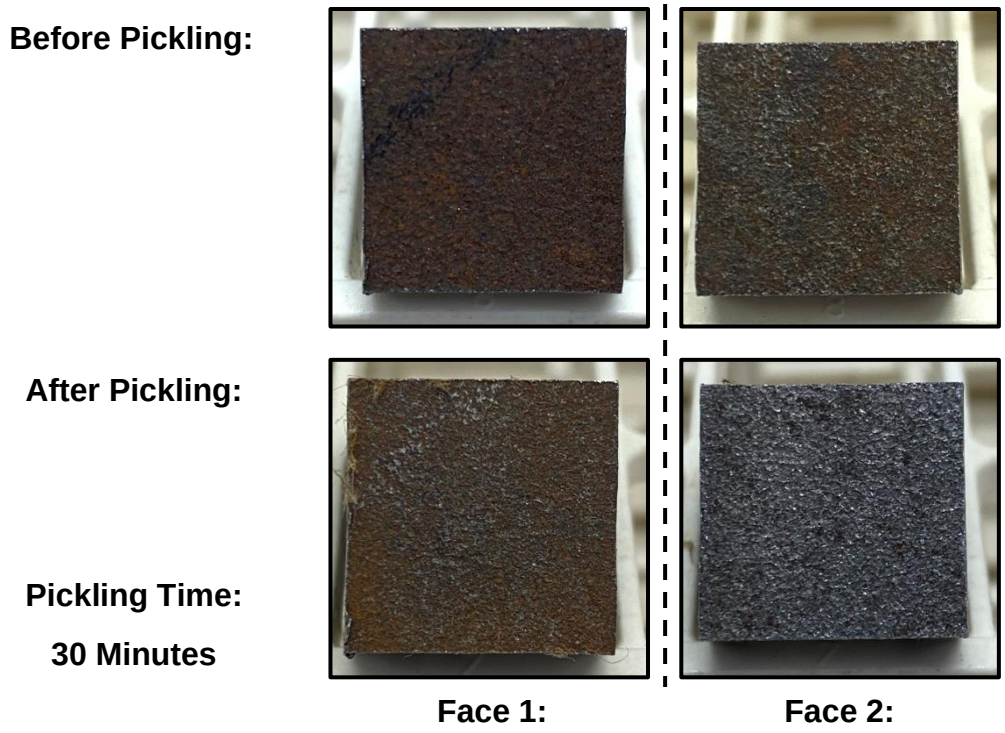


Figure F-40: Solution 4A111FZ – Coupon 2 Photos

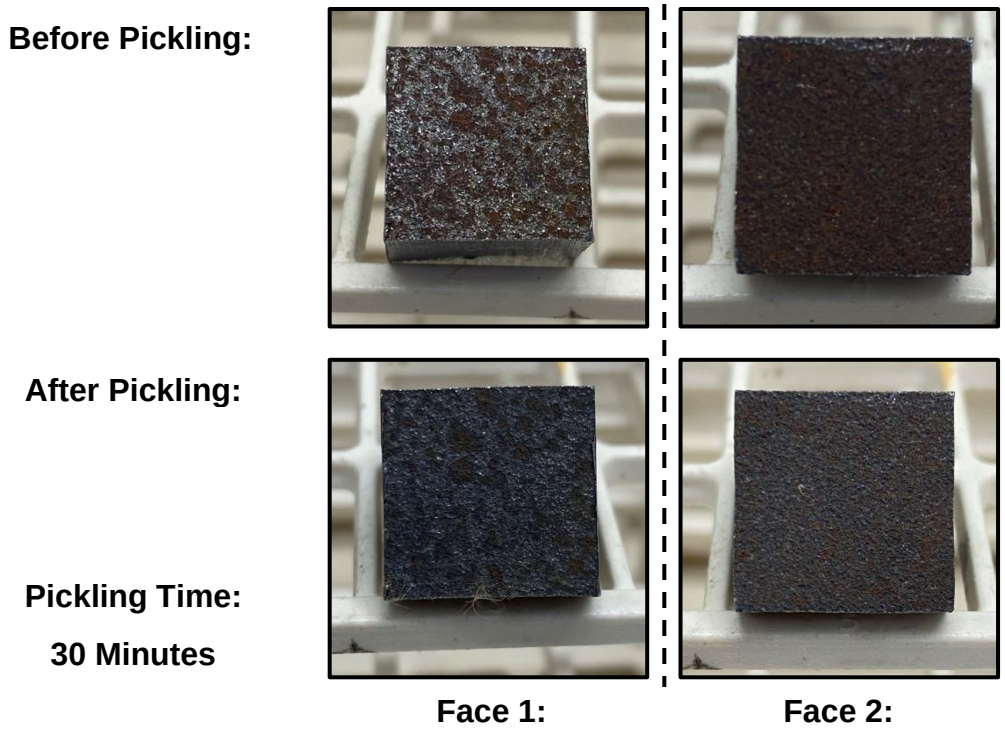


Figure F-41: Solution 2.6A124FZ – Coupon 1 Photos

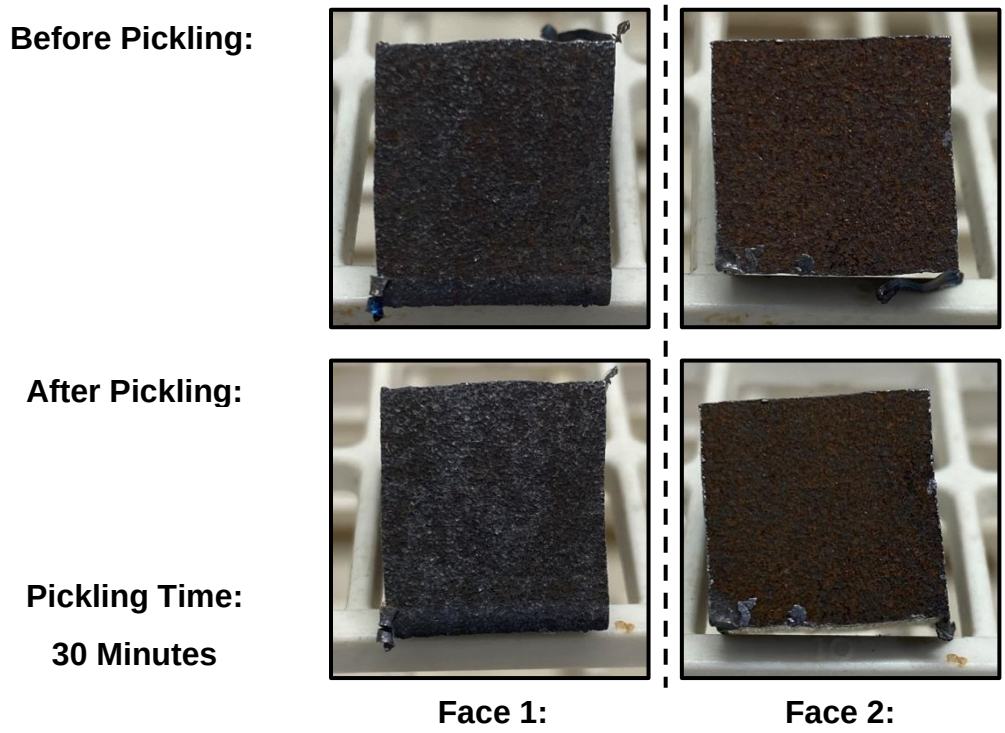


Figure F-42: Solution 2.6A124FZ – Coupon 2 Photos