

A Comparative Study of Molecular Reaction Surface Technology (MRST) Against Conventional Methods of Corrosion Treatment by Electrochemical Impedance Spectroscopy (EIS) and Qualitative Analysis (QA) CLS-CLS-18B-100

Nelson Cheng¹ PhD (Honoris Causa) Patrick Moe¹ BSc, Grad Dip. M.Sc.
Magna International Pte Ltd¹

Joe Ong², Samuel Vernon Ong², Andy Teo Rui Yi², Soh Wee Wen²
Singapore Polytechnic School of Chemical and Life Science²

Abstract

The present research studies on the Molecular Reaction Surface Technology (MRST) against other conventional forms of corrosion treatment on carbon steel using electrochemical impedance spectroscopy (EIS). The first aim was to understand what advantages MRST presented over other current forms of corrosion treatment. The second aim was to understand the effect of each corrosion treatment method on the metal surface and to discover if any of these methods were able to passivate the surface of the metal to prevent it from future corrosion. In this research, a I/E Tafel plot is utilised to obtain the transfer current of the electrochemical cell to determine the corrosion rate of the carbon steel specimens. The corrosion rates of the carbon steel specimens serve as a comparison to the effectiveness of the various corrosion treatment methods and to discover if any surface passivation had occurred on the metal surface after treatment. The present research is able to discuss the similarities between MRST and other commercial and common methods of corrosion treatment and highlights some key findings that should be further studied in future research.

Keywords

MRST; EIS, Chelating, Metal Loss, Rust, Corrosion

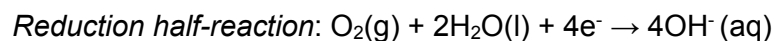
Introduction

2.0 Corrosion

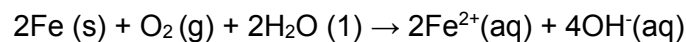
2.1 Corrosion and Its Problems ^{[3][4][5][6]}

Corrosion, also known as rusting, is a chemical or electrochemical degradation of metals that happens due to interactions the environment. It is an oxidation-reduction process that destroys iron exposed to moisture in air. The reaction causes damage to many equipment which results in large costs for many companies to conduct maintenance and repair works. When ferrous metals are exposed to O₂ and H₂O, a reaction will take place over time which forms rust in a reaction described as follows:

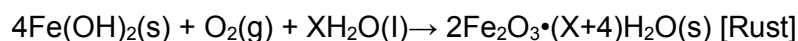
Iron is first oxidized to iron (II) ions, Fe²⁺ and oxygen from the air is reduced to hydroxide ions (OH⁻). The oxidation-reduction reaction takes place via two separate, but simultaneous half-reactions as shown:



Combining the half reactions from the first step, it gives a balanced chemical equation for the overall reaction between iron, oxygen and water.



Next, iron (II) hydroxide reacts further with oxygen and water to form hydrated iron (III) oxide (Fe₂O₃•_n H₂O), which is a flaky, reddish-brown solid known as rust.



2.2 Corrosion Prevention ^[7]

2.2.1. Inhibitors

Inhibitors are chemicals that react with the metal surface by interrupting chemical reactions that cause corrosion. Inhibitors work by adsorbing themselves onto the metal surface and forming a protective film, which passivates the metal. Inhibitors are applied as a solution or as a protective coating by dispersion techniques.

Changing the anodic or cathodic polarization behaviour, decreasing the diffusion of ions to the metal surface or increasing the electrical resistance of the metal will inhibit

the process of corrosion. They can also be applied to metals as corrective actions to counter unexpected corrosion.

2.2.2. Plating

Electroplating: A thin layer of metal (most often nickel, tin or chromium) is deposited on the substrate metal in an electrolytic bath. The bath consists of the water solution containing salts of the metal to be deposited.

Electroless: A coating metal (cobalt or nickel), is deposited on the substrate metal using a chemical reaction in this non-electric plating method.

Hot Dipping: The metal is placed in a molten bath of protective coating, giving the metal a thin layer coating

Mechanical Plating: Metal powder and glass beads are cold welded onto a substrate metal and then soaked in treated aqueous solution and is applied by using zinc or cadmium.

2.2.3. Coatings

Metals are coated with paints, organic or polymer coating to protect the metal surface from being exposed to the environment.

2.3 Corrosion Treatment ^[8]

Corrosion treatment is the process of remove the rust from metals that are susceptible to corrosion or have corroded. There are a few methods that can be used to remove rust from the metal, ranging from chemical, physical and electrical methods.

Strong acid/alkali solutions are able to remove light rust in a short amount of time through chemical reactions with the ferrous oxide in rust to produce another iron complex which is removed by filtration of the solution after treatment. These chemicals require proper procedures when handling and preparing diluted solutions for use. They are highly corrosive and toxic to the user and extra precaution must be taken. Furthermore, acids readily react with metals and will undergo unwanted reaction with unreacted metal, leading to metal loss which can be detrimental for some parts, where too much loss in metal will cause part failure. Acids also cause hydrogen embrittlement, which make the metal more susceptible to corrosion if unprotected. Both acidic and alkaline solutions must be neutralised after use, and extended use will cause part deterioration.

Electrolysis utilises a controlled DC current to remove the rust. As with acidic and alkaline solutions, electrolysis produces waste that must be neutralised before disposal. It is one of the fastest methods of rust removal, however it is also corrosive and toxic to users hence strict procedures must be followed.

Another method of corrosion treatment is the use of aqueous solutions. These chemicals are pH neutral and are completely safe to handle and use. The metal part is soaked into the solution until fully treated and removed and dried. This method although slower, produces waste that is still safe and can be disposed directly into drain systems without any further need for neutralisation or chemical treatment.

2.4 Disadvantages of Common Rust Removal Techniques ^[9]

2.4.1. Sand Blasting

Sand blasting requires a complex set up and is usually unable to completely remove rust on the substrate. It also does not work well on surfaces that are painted, in which to do so, the paint must be removed from the substrate in order to use this technique. Certain set ups can also produce gas which can gather at the ceiling and cause breathing difficulties within the room hence this method must be carried out in a well-ventilated room.

2.4.2. Electrolysis Pressure Washing

Electrolysis pressure washing can be harmful for the environment as it will harm the plants and other organisms in nearby water bodies due to the process being carried out in the environment where the water is mixed with another substance or chemical. It also damages fragile surfaces and does not provide protection against reoccurring corrosion.

2.4.3. Chemical Removal

Chemical removal is a much faster alternative in comparison to the other two techniques above. However, precautions and close observations must be taken to ensure that the metal is not left in the acid for too long, whereby failure to do so will lead to part deterioration. Dealing with acids also poses a serious hazard to the user where acid spillage is a risk. Corrosive fumes will be produced when preparing the acid solution, hence users must prepare the chemicals in a fume hood.

2.5 Application of Electrochemical Impedance Spectroscopy (EIS) in Analysis of Corrosion Treatment

2.5.1 Polarisation resistance (R_p)

Polarisation resistance is a measure of the resistance of the material to corrosion and it measures the amount of metal being corroded at a certain time. This can also be defined as the effective resistance imposed at the electrode surface by a measurable rate of electron transfer process.

An electrode is polarised when its potential is forced away from its value at corrosion potential. Therefore, when R_p is high, the specimen is able to resist corrosion and when R_p is low, the specimen is corroding and does not have any corrosion resistance. [10]

2.5.2 Ways to obtain R_p

Measurement and determination of polarisation resistance is based on the linearity of the polarisation curves near the potential E_{corr} .

$$R_p = \left(\frac{\Delta E}{\Delta i} \right)_{\Delta E \rightarrow 0}$$

R_p is related to I_{corr} and is defined as the ratio between applied voltage, change in potential and change in current. I_{corr} is the transfer current of the electrochemical system. When the applied voltage is constant, and the current value is small, R_p is higher. A specimen would undergo less corrosion if the current flow is limited, whereas a larger current value would give a lower R_p which would suggest more corrosion since the current flow is greater. [10]

2.5.3 Tafel Plot

Tafel equation in electrochemical kinetics relates the rate of an electrochemical reaction to the overpotential. For an electrochemical reaction, the polarisation curves usually show linear behaviour of E vs $\log(i)$. The anodic and cathodic polarisation linear curves are both extrapolated to E_{corr} to obtain I_{corr} . Tafel plot presents the relationship between current (A) versus potential (V). Corrosion density is determined from both graphs and can be substituted into an equation to calculate the corrosion rate of the metal specimen.

$$\text{Corrosion rate} = k \left(\frac{a \cdot i_{\text{corr}}}{nD} \right)$$

Where,

a = atomic weight of the metal

i_{corr} = corrosion density, $\mu\text{A}/\text{cm}^2$

n = number of electron charges (Fe)

D = Density, g/cm³

k = constant depending on the unit of corrosion rate, mm/yr = 0.00327

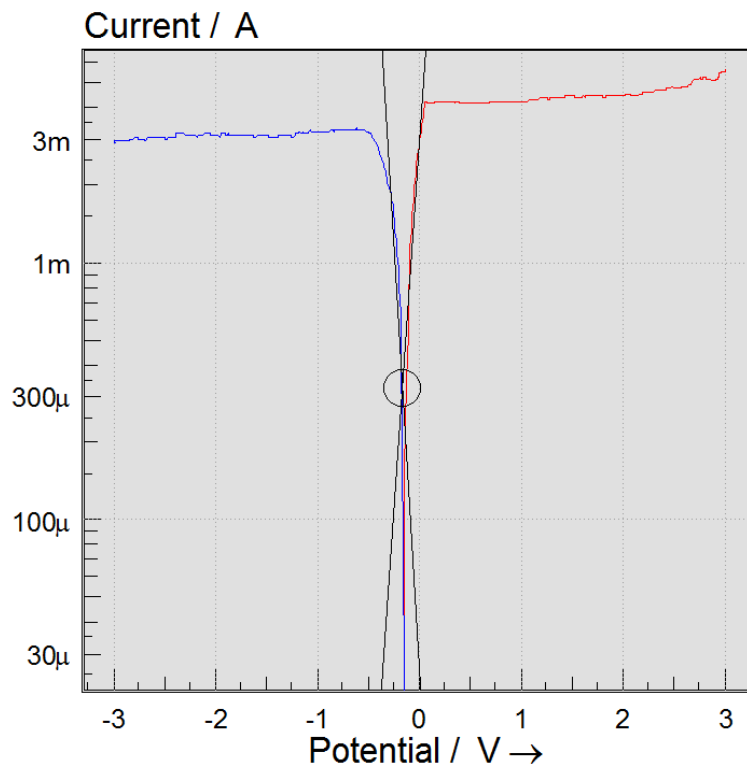


Figure 1: EIS Tafel Plot of Carbon Steel

As seen above, the graph is plotted as current (A) versus potential (V). Once the tangents were drawn for cathodic and anodic curve, the value for I_{corr} can be obtained at the E_{corr} value, which is the intersection of the two tangents. To determine corrosion density before obtaining corrosion rate, the exposed area of the metal specimen to the electrolyte must be measured as this value is not determined by the graph generated by the EIS programme.

A Tafel plot analysis tool provides a quick estimation of corrosion rate and the polarisation resistance. The corrosion rate is calculated from the estimated corrosion density.

The present research requires us to determine the corrosion rates of steel to understand the effectiveness of the various corrosion treatment methods studied. Hence, electrochemical impedance spectroscopy (EIS) is used under the Tafel plot to obtain the I_{corr} value which will allow us to determine the corrosion rates of the metal and observe if there is resistance in corrosion of the metal after treatment. Referring to the equation to calculate corrosion rate; a , n , D and k values are all constant variables. Hence, I_{corr} values are directly related to corrosion rate, where higher I_{corr} value indicates lower R_p , and more susceptibility to corrosion. ^[11]

A stress corrosion process is always changing with time and cannot be stable. Hence, obtaining a stable result is prone to errors. Small changes in the system are assumed to be quasi-stable for good experimental data to be obtained.

2.6 Stereo Microscopy in Analysis of Surface Morphology of Carbon Steel Specimens

Stereo Microscopy is used in this experiment to analyse the surface morphology of the carbon steel specimens. Stereo Microscope provides us with the ability to see the small and greater details found within the compound of the steel specimens. The images seen will be in three-dimensional view instead of flat images. The following pictures as shown below consist of both 'Clean' steel and rusted steel.

2.7 Molecular Reaction Surface Technology (MRST)

Vapro 812 (Neutral pH Rust Remover) – Solution E

Vapro 812 is an organic rust remover with a neutral pH. Vapro 812 removes rust on ferrous and non-ferrous metals through the chelation of ferrous ions on the surface of the metal. Vapro 812 is biodegradable and safe for the environment, humans and the metal. Furthermore, Vapro 812 does not cause hydrogen embrittlement, which is a form of corrosion that is induced due to the absorption of hydrogen by the metal surface. Vapro 812 is a fully organic solution and is an ideal replacement for common rust removers in cases where chemical waste disposal is unavoidable. Usage of Vapro 812 does not require further rinsing or neutralisation after application.

The application of MRST in Vapro 812 is in the reaction of iron (Fe^{3+}) ions in the stable oxide complex (rust) and the rust remover. As mentioned under Vapro 887, rust is an iron oxide, most commonly hydrated iron (III) oxide.

Vapro 812 is a chelating agent which removes rust from the surface of the ferrous metal by chelation of Fe^{3+} ions from $\text{Fe}(\text{OH})_3$. The chemical structure of Vapro 812 binds to the Fe^{3+} ion to form a six-membered ring chelate suspended in solution. Vapro 812 attacks only Fe^{3+} ions which can only be found on the surface of the metal in $\text{Fe}(\text{OH})_3$, hence avoiding any loss of metal through unwanted reaction with the metal itself.

Chelation and Chelating Agents

Chelating agents are compounds that bind to metal ions through multiple bonds to form chelates, which are complex ring-like structures. Chelating agents consist of either bidentate or polydentate ligands which are able to bind to the metal ion at multiple sites to form ring structures that include the metal ion and the ligand atoms involved in bonding. This process of chelation extracts the metal ion into the solution of chelating agent by binding the metal ion to form a new complex.

An example to illustrate the reaction mechanism of a polydentate chelating agent is used to explain how Vapro 812 works to remove rust.

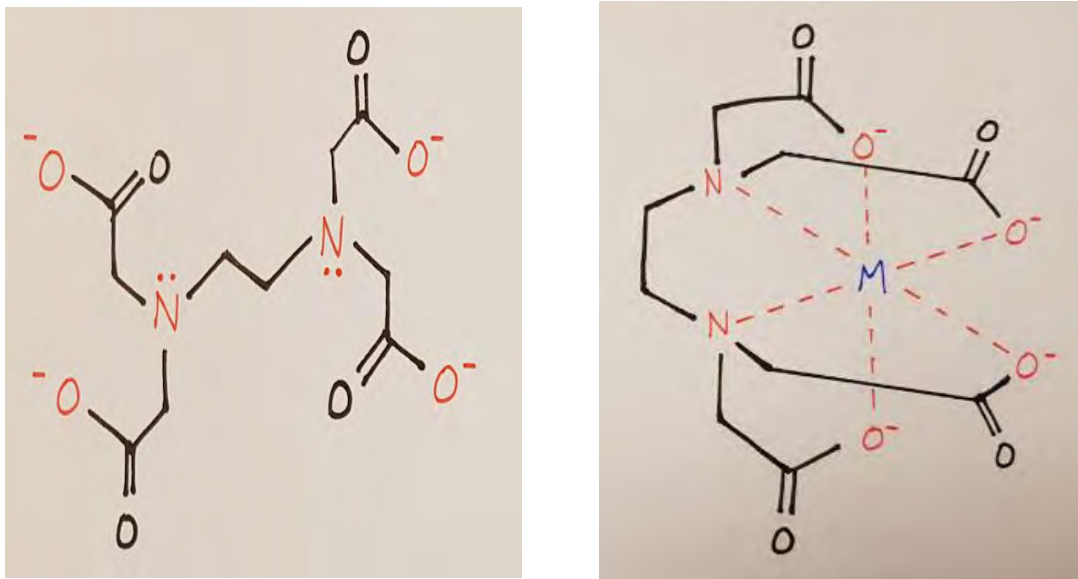


Figure 2 & 3: Chemical drawing of EDTA⁴⁻

Ethylenediaminetetraacetic Acid (EDTA) produces EDTA⁴⁻ ions, which are polydentate ligands that bind to metal ions at the atoms that are highlighted in red. There is a total of 6 binding sites, similar to Vapro 812. As EDTA⁴⁻ attacks a metal ion and bonds with it, it creates a metal-EDTA complex that has a 6-membered ring structure, as seen by the bonds highlighted in red. Vapro 812 works in a very similar way to remove Fe³⁺ ions from rust on the surface of the metal, specifically targeting only the Fe³⁺ ions due to its polydentate characteristic which prevents it from reacting with other forms of iron ions.

Vapro 887 (Rust Converter) – Solution C

Vapro 887 is a rust converter which protects ferrous metals from further corrosion by converting various forms of rust, including Fe₂O₃ and Fe(OH)₃ into Fe₃O₄, known as iron (II,III) oxide. Fe₃O₄ is a black ferrosferric oxide which remains stable under different environmental conditions. Unlike Vapro 812, Vapro 887 is a milky white emulsion liquid applied through coating a rusted iron surface, in which a black coat of Fe₃O₄ forms on the surface after 15

minutes of application. The black coat of ferrosferric oxide passivates the metal from further corrosion.

3. Materials and Methods

Preparation of Carbon Steel Specimens

The present project conducts its experiments on carbon steel samples. These steel samples are cut into equally sized bars of 3mm thickness and sanded on all surfaces to remove any pre-existing corrosion, surface contaminants and/or passivated layers.

These 'clean' steel specimens are soaked in 5%w/w NaCl solution for 2 hours and then hung in an enclosed laboratory to induce corrosion by chloride ions.

The steel bars are taken down after 2 weeks of hanging, where almost complete surface corrosion is assumed. EIS is conducted for the steel bars and the I/E Tafel slopes are obtained through EIS.

5 batches of 4 specimens each (C, D, E, F, G; 1, 2, 3, 4) were sorted and labelled for the present research.



Figure 4: Hanging of metal specimens after soaking in NaCl solution

Specimen Batch	Treatment Solution
C (1 - 4)	Vapro 887 MRST Rust Converter
D (1 - 4)	Commercially available Acid Based Rust Converter
E (1 - 4)	Vapro 812 Neutral pH MRST Rust Remover
F (1 - 4)	Commercially available Aqueous Rust Remover
G (1 - 4)	10% Hydrochloric Acid solution

Rust Conversion for Carbon Steel Specimens through Coating

A 9cm² area in corroded specimens C1 to C4 and D1 to D4 was coated on one side with rust converter using a brush. 15 minutes drying time was allowed between coats. A second coat was applied on all specimens when the first coat dries. For specimens C1 to C2 and D1 to D2, the procedure was repeated on the other side. Another two coats were applied on C3 to C4 and D3 to D4, before the procedure repeats on the other side. In total, two coats were applied on both sides of specimens C1 to C2 and D1 to D2, while four coats were applied on both sides of specimens C3 to C4 and D3 to D4.

Preparation of HCl solution

A 10% HCl solution was prepared from a 37% HCl stock solution and labelled as solution G.

Rust Removal for Carbon Steel Specimens through Complete Soaking

Four 175ml glass bottles were filled with solution E and the corroded specimens E1 to E4 were immersed in the solution. These specimens were monitored, and the average time taken for complete and visible rust removal was recorded. The same procedure was carried out for the other two solutions, F and G.

EIS of Carbon Steel Specimens after Treatment

EIS was conducted on all corroded specimens and after their respective corrosion treatment methods using the Zahner Zennium Electrochemical Workstation and the ThalesUSB programme distributed by Zahner Elektrik.

The electrochemical cell was assembled as follows. The steel bar specimen was mounted to the working electrode in a three-electrode system. For all tests, the reference electrode used was a saturated calomel electrode (SCE) and the counter electrode was a platinum electrode. The electrolyte used was deionised water. The surface area exposed to the electrolyte was 9cm².

Dynamic I/E scan mode was used, and the parameters were set to run from 3V to -3V potential and a current range of -1.5A to 1.5A at a scan rate of 10 mV/s. The I/E Tafel slope is plotted

during the scan and is passed to the analysis programme and the I_{corr} of the specimen is determined.

A second EIS scan was conducted on specimens C and D 2 weeks after treatment to observe if the converted layer was able to protect the metal specimen from corrosion.

Stereo Microscopy of Carbon Steel Specimens

The carbon steel specimens were observed under reflected light with a Zeiss Stemi 508 stereo microscope at 16x magnification. Both 2D and 2.5D images of the specimen surface were taken using the accompanying software.

Observation of Carbon Steel Specimens after Treatment

The carbon steel specimens were soaked in 5%w/w NaCl solution after treatment for 2 hours and hung again. The specimens were observed daily and the time before first sign of red-brown oxide layer formation is observed and recorded.

4. Results and Discussion

Electrochemical Impedance Spectroscopy

Tafel Plot:

Sample	Transfer Current, I_{corr} (uA)									
	Corroded					Treated				
	1	2	3	4	Avg	1	2	3	4	Avg
C	-	0.205	0.443	-	0.324	0.136	0.275	0.061	0.970	0.361
D	0.161	-	-	-	0.161	0.141	-	-	-	0.141
E	0.064	0.293	0.109	0.173	0.160	449.000	366.000	825.000	884.000	631.000
F	0.293	-	0.038	0.326	0.219	328.000	352.000	340.000	297.000	329.250
G	0.049	0.037	0.031	0.090	0.052	398.000	263.000	445.000	-	368.667

Figure 5: I_{corr} values of metal specimens C – G, 1 – 4, immediately after treatment

(Certain readings have been omitted due to instability in graph, resulting in inability to obtain accurate I_{corr} values)

Figure 6: I/E Tafel slope analysis for sample C1, C2, C3 and C4 corroded.

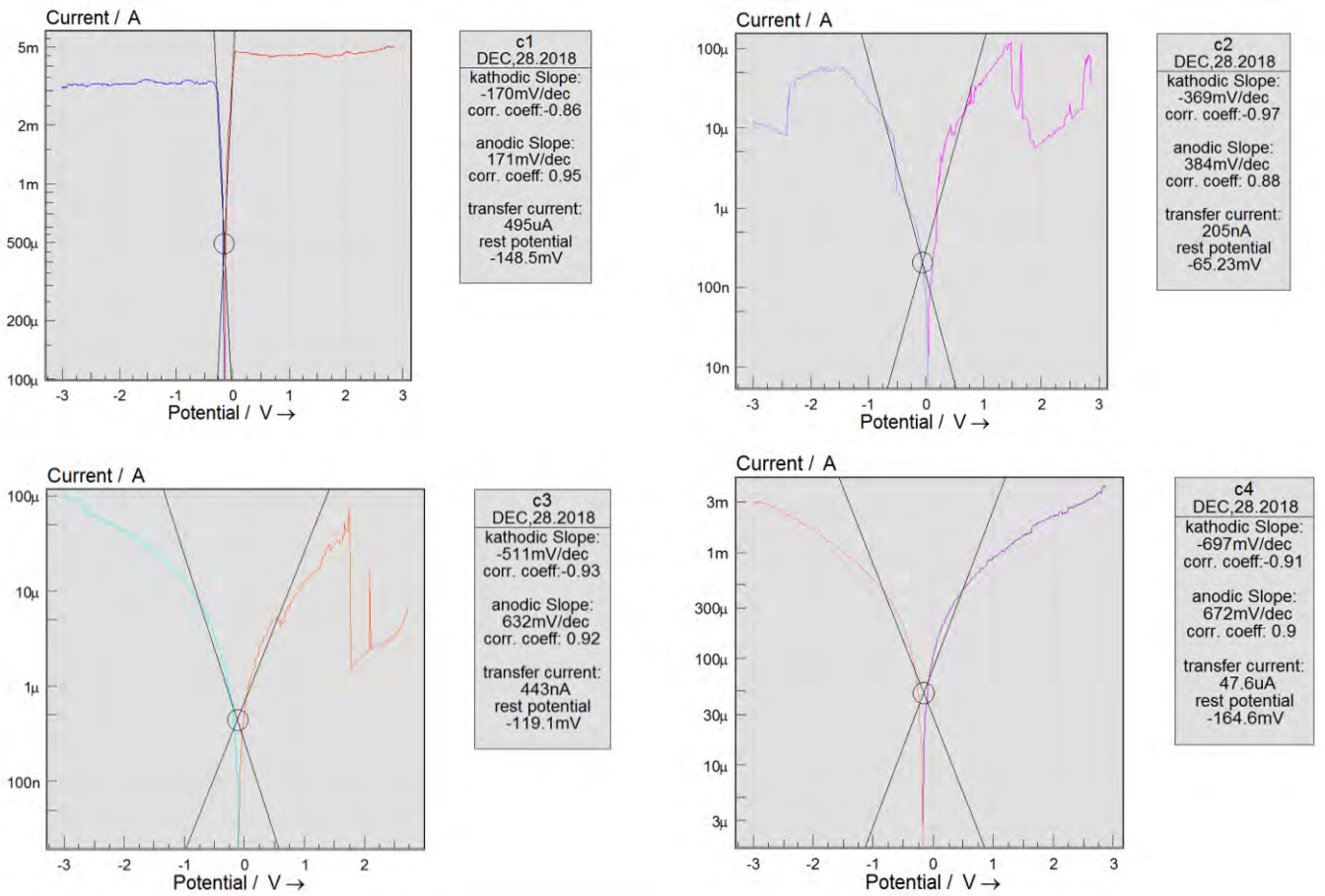
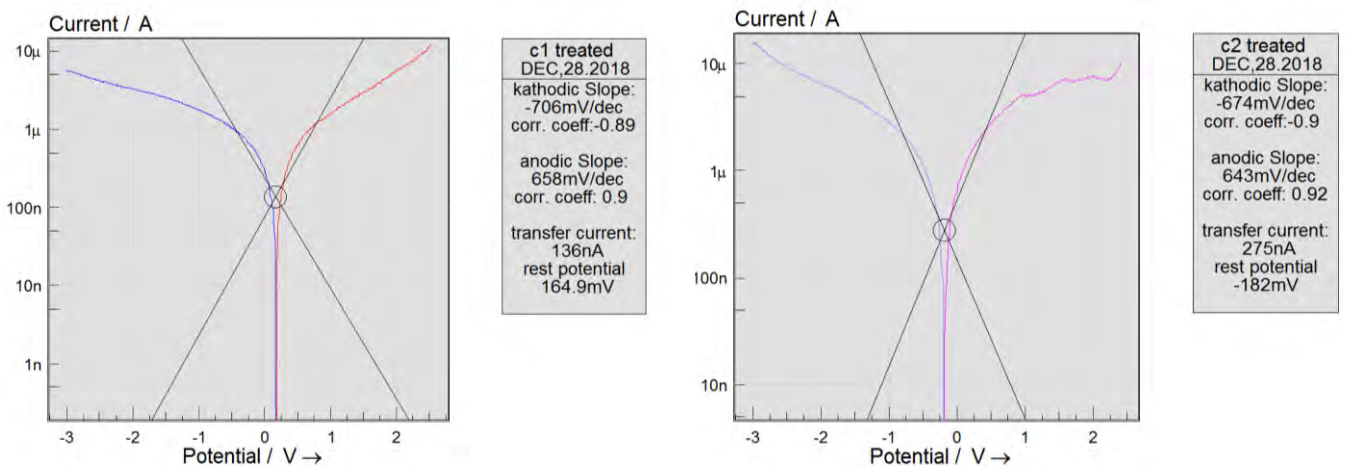
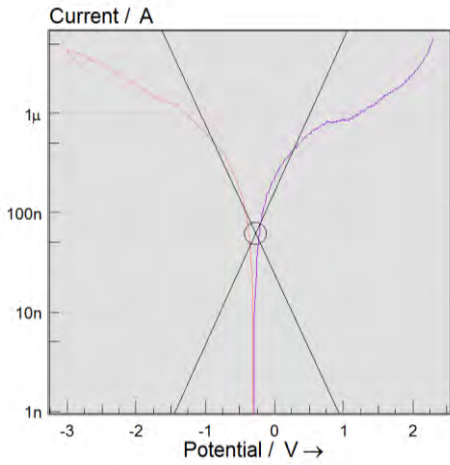


Figure 7: I/E Tafel slope analysis for sample C1, C2, C3 and C4 treated.

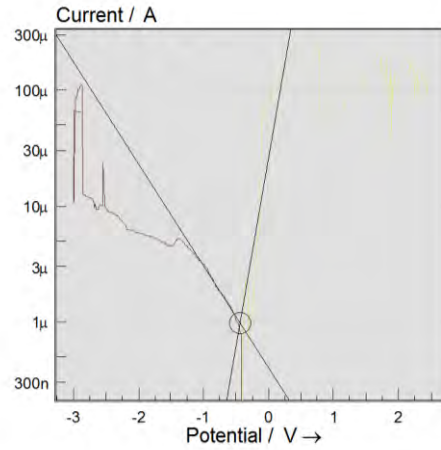




c3 treated
DEC.28.2018
kathodic Slope:
-665mV/dec
corr. coeff:-0.92

anodic Slope:
648mV/dec
corr. coeff: 0.9

transfer current:
61.4nA
rest potential
-273mV

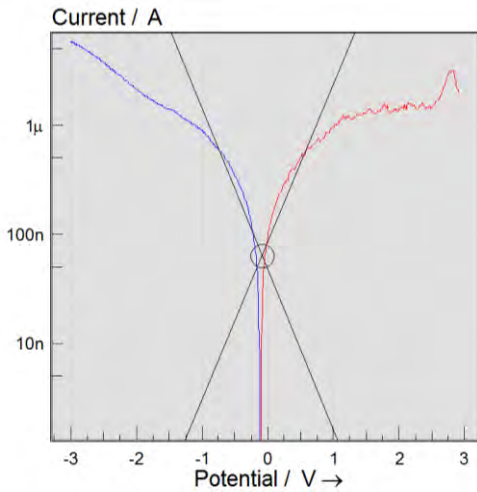


c4 treated
DEC.28.2018
kathodic Slope:
-1.14V/dec
corr. coeff:-0.99

anodic Slope:
308mV/dec
corr. coeff: 0.91

transfer current:
970nA
rest potential
-439.8mV

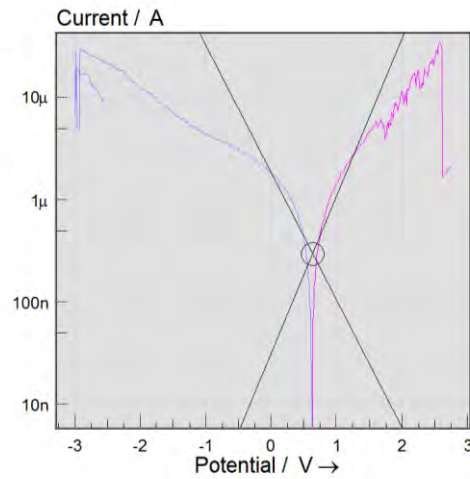
Figure 8: I/E Tafel slope analysis for sample E1, E2, E3 and E4 corroded.



e1
DEC.14.2018
kathodic Slope:
-678mV/dec
corr. coeff:-0.9

anodic Slope:
692mV/dec
corr. coeff: 0.86

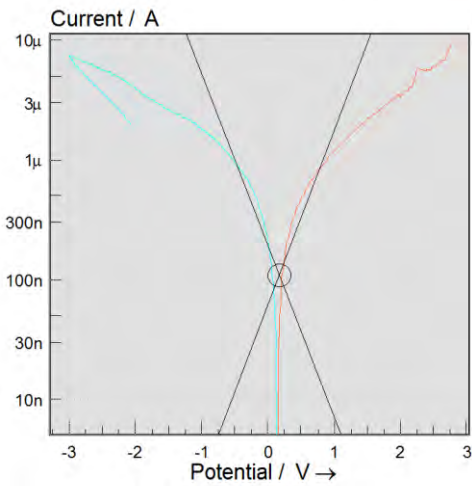
transfer current:
63.5nA
rest potential
-90.66mV



e2
DEC.14.2018
kathodic Slope:
-801mV/dec
corr. coeff:-0.91

anodic Slope:
650mV/dec
corr. coeff: 0.94

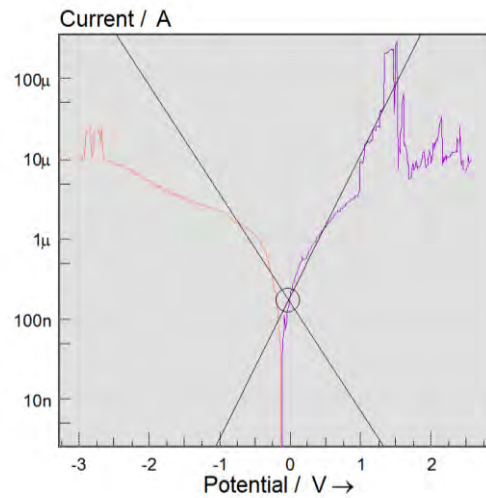
transfer current:
293nA
rest potential
631.2mV



e3
DEC.14.2018
kathodic Slope:
-697mV/dec
corr. coeff:-0.91

anodic Slope:
687mV/dec
corr. coeff: 0.89

transfer current:
109nA
rest potential
166.7mV



e4
DEC.14.2018
kathodic Slope:
-740mV/dec
corr. coeff:-0.89

anodic Slope:
565mV/dec
corr. coeff: 0.95

transfer current:
173nA
rest potential
-26.54mV

Figure 9: I/E Tafel slope analysis for sample E1, E2, E3 and E4 treated

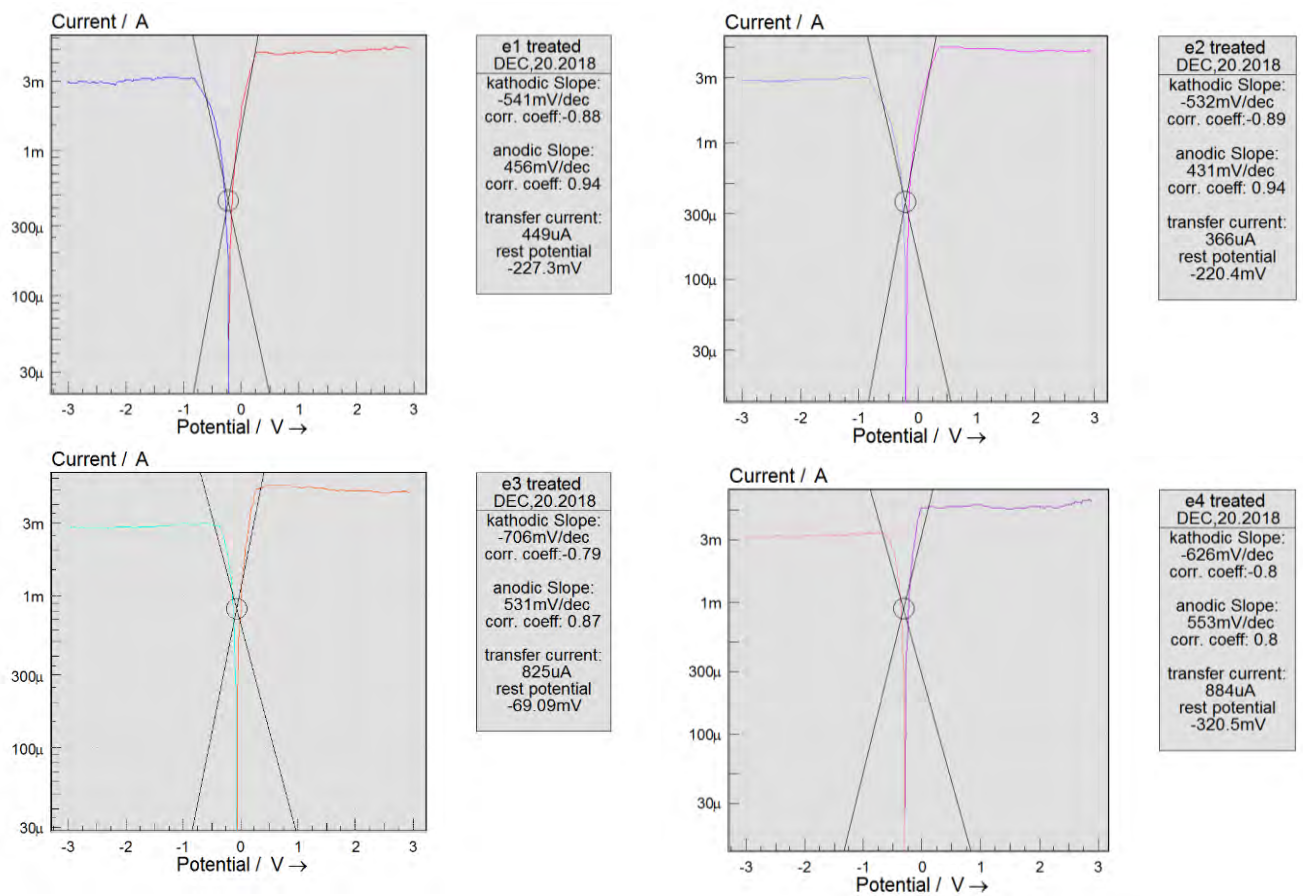
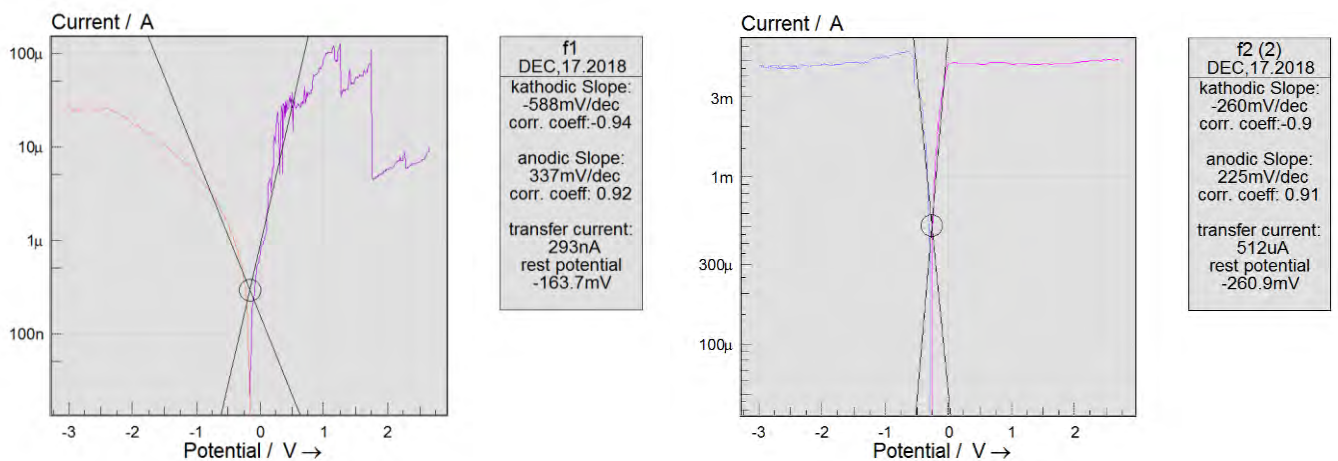
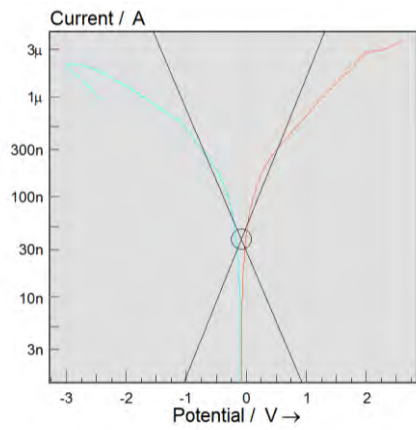
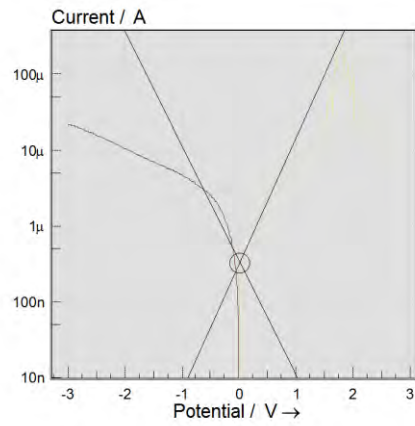


Figure 10: I/E Tafel slope analysis for sample F1, F2, F3 and F4 corroded.



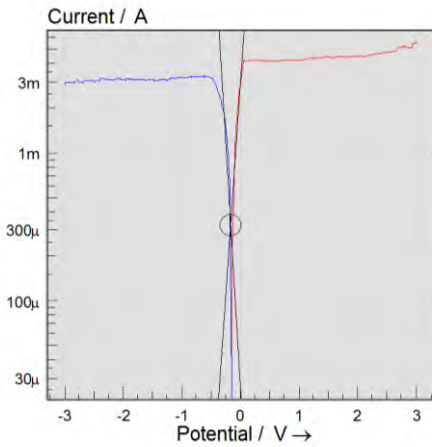


f3
 DEC.17.2018
 cathodic Slope:
 -707mV/dec
 corr. coeff.-0.92
 anodic Slope:
 669mV/dec
 corr. coeff. 0.91
 transfer current:
 37.5nA
 rest potential
 -88.07mV

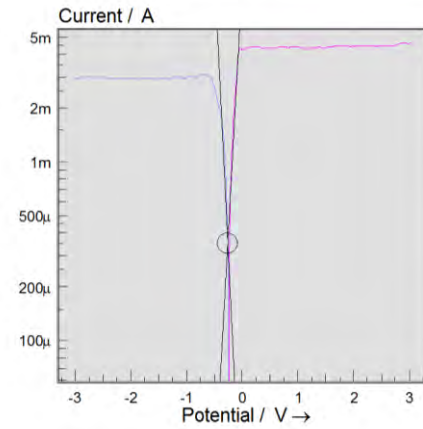


f4
 DEC.28.2018
 cathodic Slope:
 -663mV/dec
 corr. coeff.-0.85
 anodic Slope:
 600mV/dec
 corr. coeff. 0.96
 transfer current:
 326nA
 rest potential
 14.86mV

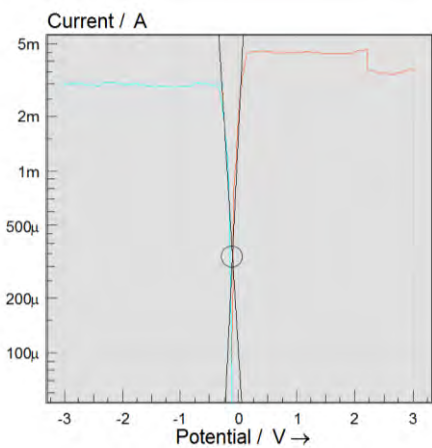
Figure 11: I/E Tafel slope analysis for sample F1, F2, F3 and F4 treated



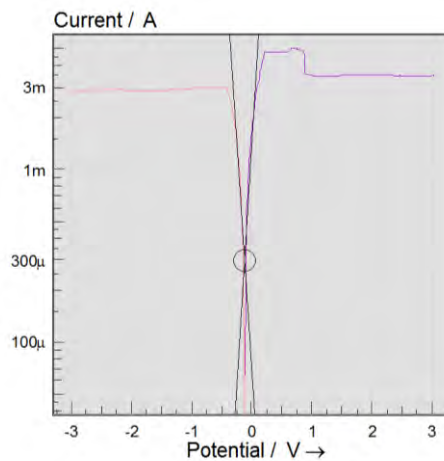
f1 treated
 JAN.04.2019
 cathodic Slope:
 -152mV/dec
 corr. coeff.-0.81
 anodic Slope:
 175mV/dec
 corr. coeff. 0.96
 transfer current:
 328µA
 rest potential
 -170.6mV



f2 treated
 JAN.04.2019
 cathodic Slope:
 -157mV/dec
 corr. coeff.-0.86
 anodic Slope:
 178mV/dec
 corr. coeff. 0.95
 transfer current:
 352µA
 rest potential
 -262.1mV



f3 treated
 JAN.04.2019
 cathodic Slope:
 -195mV/dec
 corr. coeff.-0.94
 anodic Slope:
 152mV/dec
 corr. coeff. 0.92
 transfer current:
 340µA
 rest potential
 -108.2mV



f4 treated
 JAN.04.2019
 cathodic Slope:
 -190mV/dec
 corr. coeff.-0.95
 anodic Slope:
 178mV/dec
 corr. coeff. 0.94
 transfer current:
 297µA
 rest potential
 -121.5mV

Figure 12: I/E Tafel slope analysis for sample G1, G2, G3 and G4 corroded.

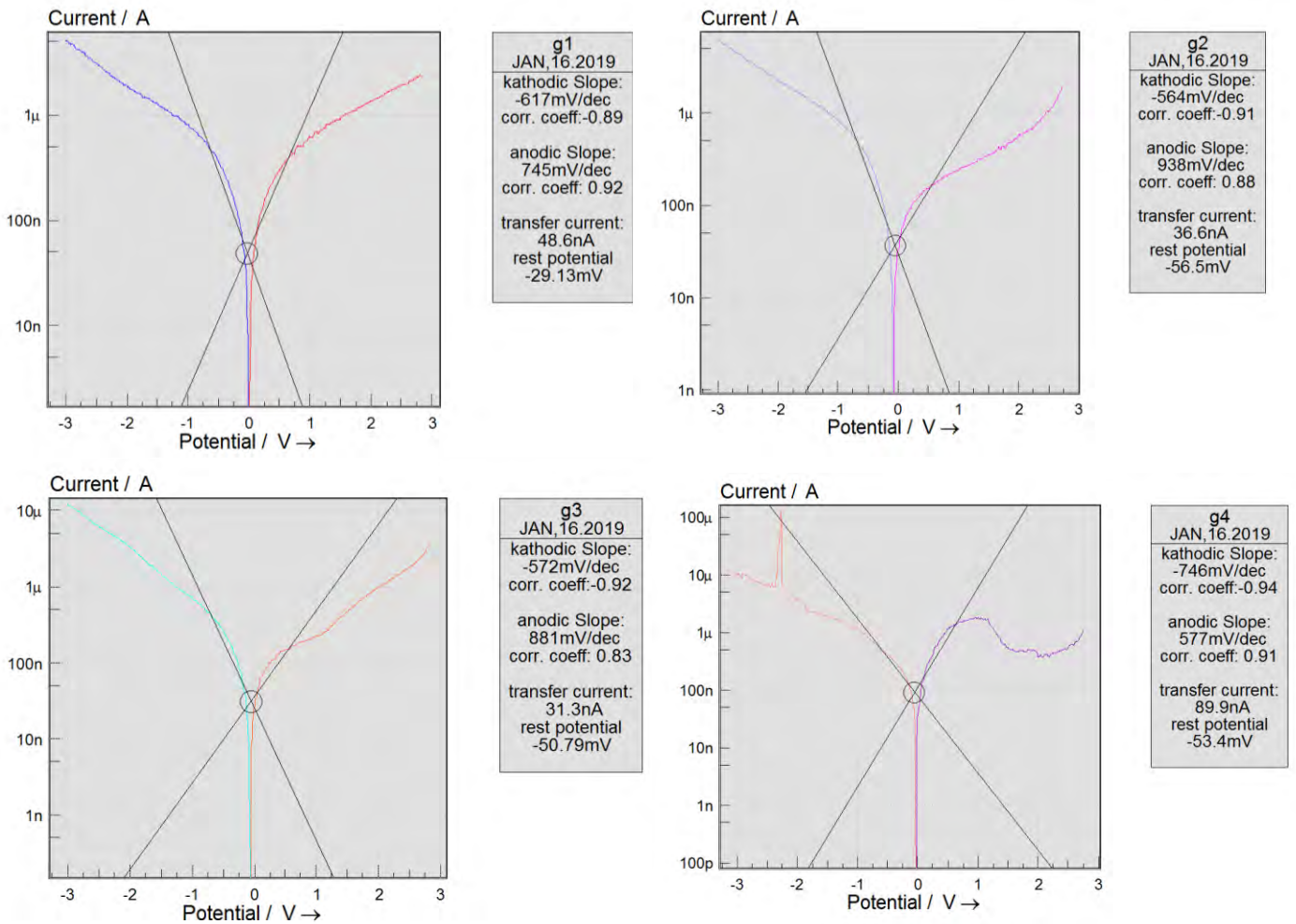
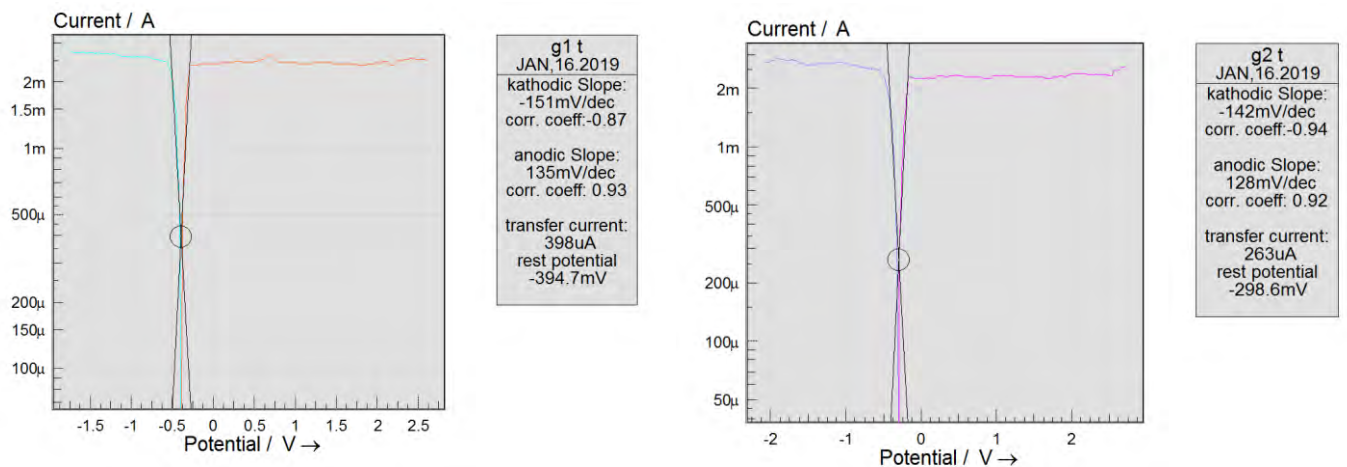


Figure 13: I/E Tafel slope analysis for sample G1 and G2 treated.



As mentioned in theory, the corroded specimens had relatively low and consistent I_{corr} values, which meant that the metal had more resistance to corrosion. This is to be expected as the specimens were almost fully corroded on the metal surface, which meant that any further corrosion would be inhibited and would occur at a much lower rate.

Specimens treated by C and D remained at low I_{corr} values, which indicated that the metal was still resistant to corrosion. Since solution C converts the oxide layer into a stable iron complex, the specimen should be passivated and resistant to corrosion. Hence, the I_{corr} values agree with this and confirms that solution C is able to convert the oxide layer into a passivated layer.

The I_{corr} values of the specimens treated with solutions E, F and G are relatively much higher, with specimens E having a significantly higher I_{corr} average among the three. This meant that the specimens treated with solution E had little to no corrosion resistance after treatment. This could also be an indication that solution E was able to remove rust more effectively compared to solutions F and G as the metal is considered 'cleaner' due to the high susceptibility to corrosion.

Transfer Current (μA)					
Sample	2nd Corrosion				Avg
	1	2	3	4	
C	0.121	0.177	0.048	0.187	0.133
D	6.990	0.610	0.285	0.085	1.992

Figure 14: I_{corr} values of metal specimens C – D, 1 – 4, two weeks after treatment

Looking at the I_{corr} values of C and D, sample D was still undergoing corrosion while sample C had very low corrosion rates, which is due to the stable ferrosferric oxide layer formed during rust conversion.

Qualitative Analysis

Time Taken for Rust Conversion:

Solution	Time Taken (mins)
C (Vapro 887 MRST rust converter)	30
D (Commercially available Acid based rust converter)	70

Time Taken for Complete Rust Removal:

Solution	Time Taken (hours)
E (Vapro 812 Neutral pH MRST rust remover)	5 - 6
F (Commercially available Aqueous rust remover)	> 8
G (Acid solution with 10% HCl)	1.5

Spectro Microscopy:

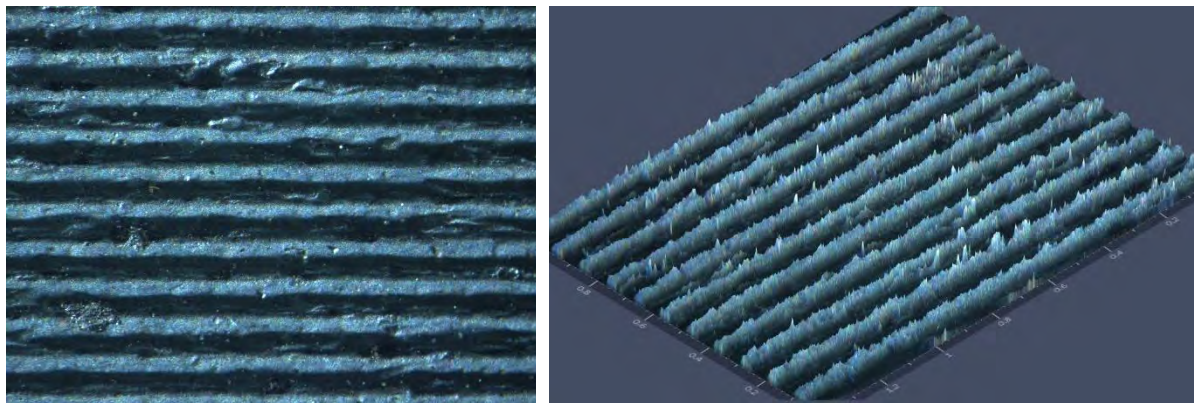


Figure 15 & 16: Sanded carbon steel bar @16x magnification, 2D and 2.5D

Figures 15 & 16 show the surface structure of a sanded carbon steel bar at 16x magnification. The white-blue ridges on the surface indicate the rich presence of iron, which is what carbon steel bar is composed of. The bar is of uniform surface morphology and there are no surface contaminants other than minor surface artefacts. This will serve as the benchmark for comparison with the treated specimens.

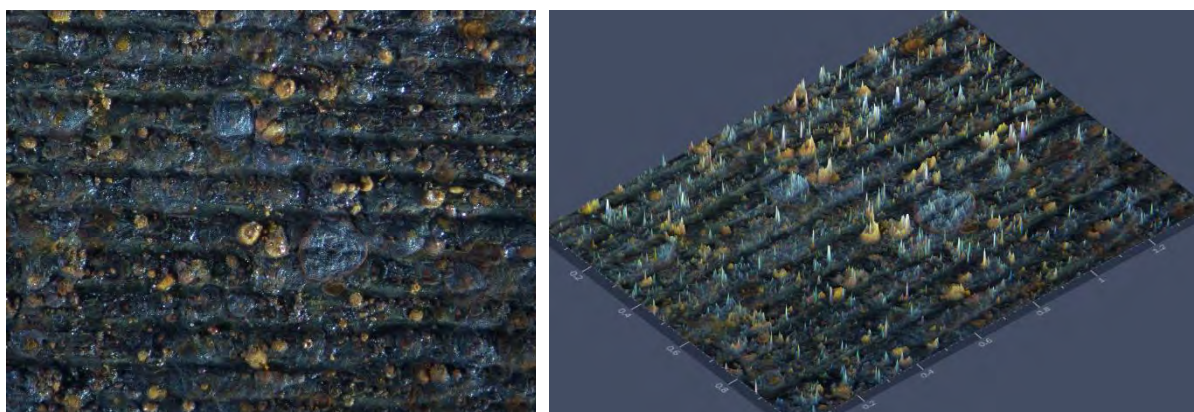


Figure 17 & 18: Corroded carbon steel bar @16x magnification, 2D and 2.5D

Fig 17 & 18 are images of a corroded carbon steel bar specimen. As seen in the images, there is minimal iron content present on the immediate surface of the bar. This is due to the conversion of pure Fe into Fe_2O_3 , which is observed by the presence of large yellow-orange

and red oxides on the surface. Furthermore, some areas appear greenish, which suggest that some $\text{Fe}(\text{OH})_2$ is still being converted into Fe_2O_3 and corrosion is still ongoing.

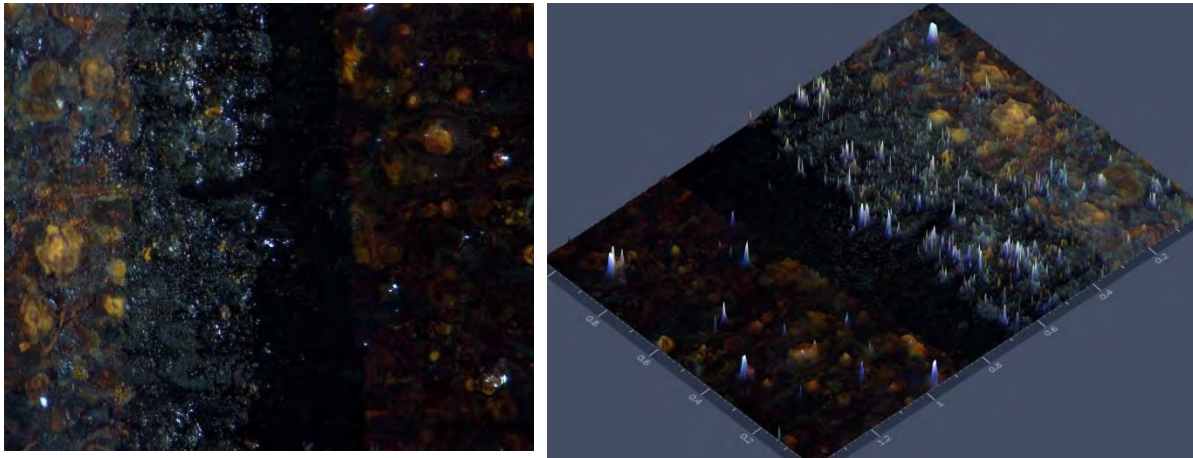


Figure 19 & 20: Specimen C3 after treatment @16x magnification, 2D and 2.5D
The conversion of rust is shown in the images as a black layer of Fe_3O_4 . Very little iron was present in the applied area, which may explain the glossy appearance when the converter was applied. Some rust is also partially visible on the applied area, implying more coats were required to fully convert all the rust.

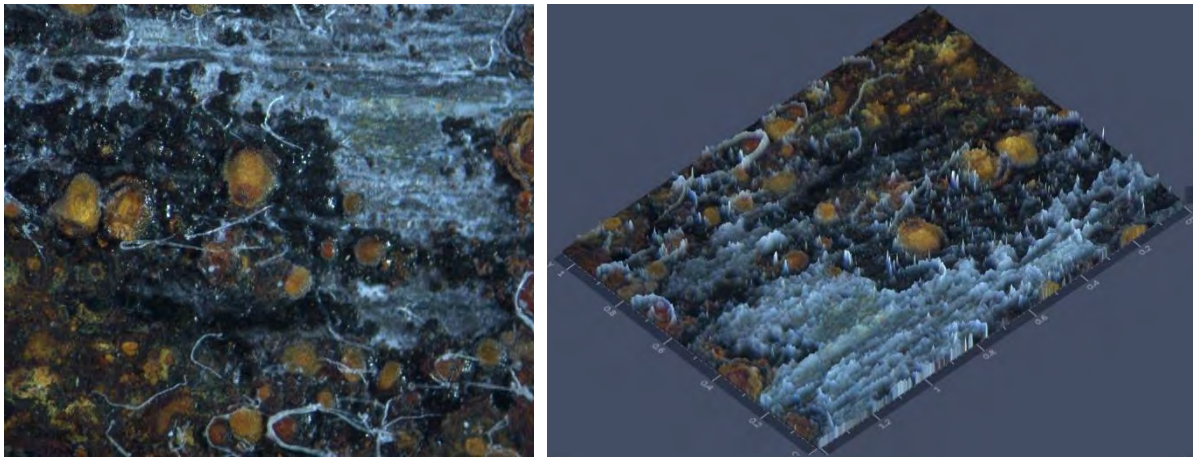


Figure 21 & 22: Specimen D1 after treatment @16x magnification, 2D and 2.5D
The images show the surface of a specimen treated with an acid based rust converter. Instead of converting the Fe_2O_3 into a passivating layer, it appears to have been converted back into iron. Since an acid-based rust converter was used, less iron content is present in the treated area. Furthermore, the treated area remained susceptible to corrosion shortly after treatment, as identified by yellowish-green regions in the treated area. It was noted that surface contaminants (i.e. fibres from industrial paper) are present on the surface and will be ignored.

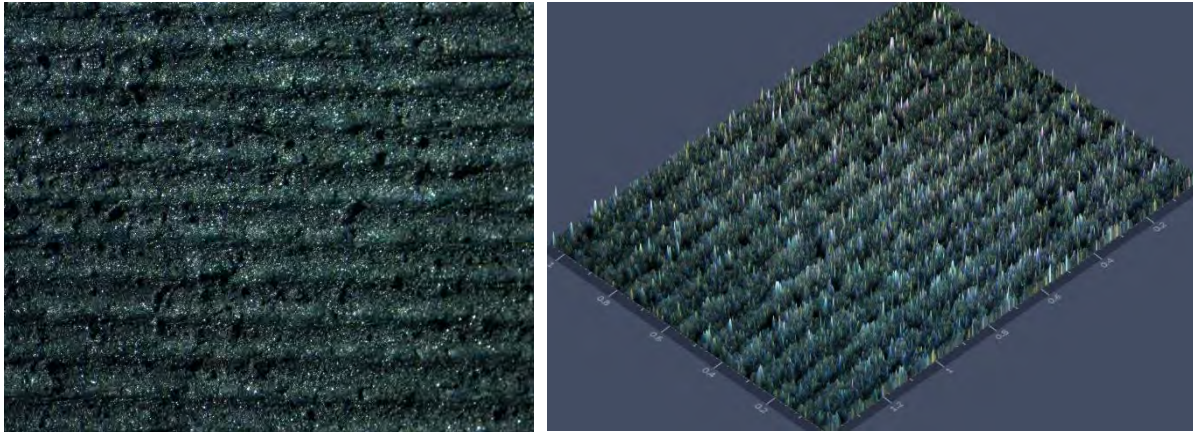


Figure 23 & 24: Specimen E4 after treatment @16x magnification, 2D and 2.5D Solution E, which utilised the MRST technology, was able to effectively remove all Fe_2O_3 from the metal surface. Several pits in the surface of the metal can be observed, which is indication that pitting corrosion had occurred under the layer of oxide. Furthermore, the iron content on the surface of the metal was lesser than the benchmark specimen, which was to be expected as some iron had been lost as Fe_2O_3 that was removed by the solution through the chelation of the Fe^{3+} ions. The surface also appears faintly green, which indicates that although the solution was able to break down and remove the Fe_2O_3 layer, the surface was left unprotected upon removal from the solution.

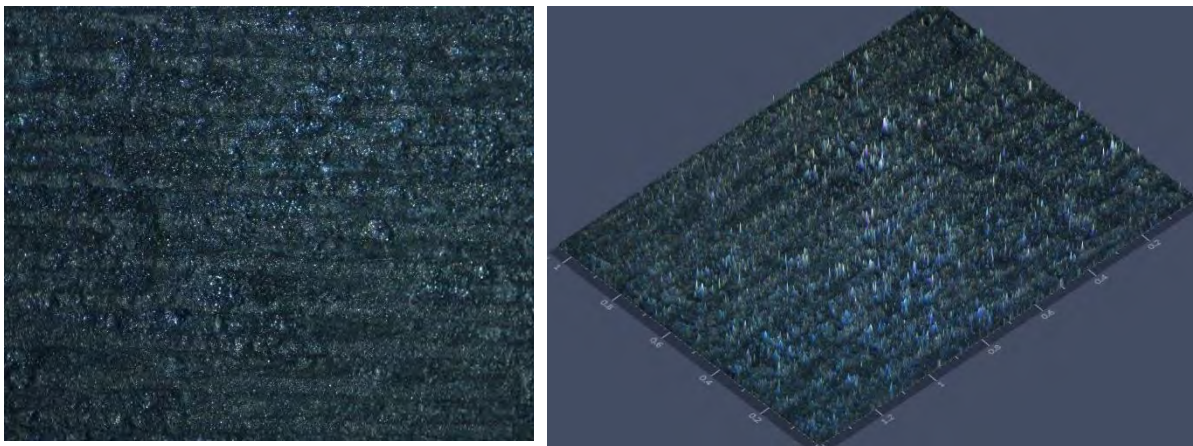


Figure 25 & 26: Specimen F4 after treatment @16x magnification, 2D and 2.5D Solution F, an aqueous solution, was able to break down and remove the oxide layer on the metal surface just as well as solution E. However, the 2.5D image shows the surface features to be less defined compared to the specimen treated by E, where ridges of clean metal can still be seen. This could be an indication that a different form of reaction had taken place in solution F as compared to the chelation mechanism in solution E, whereby the iron in Fe_2O_3 could have been redeposited onto the surface of the metal upon the breakdown of the oxide layer.

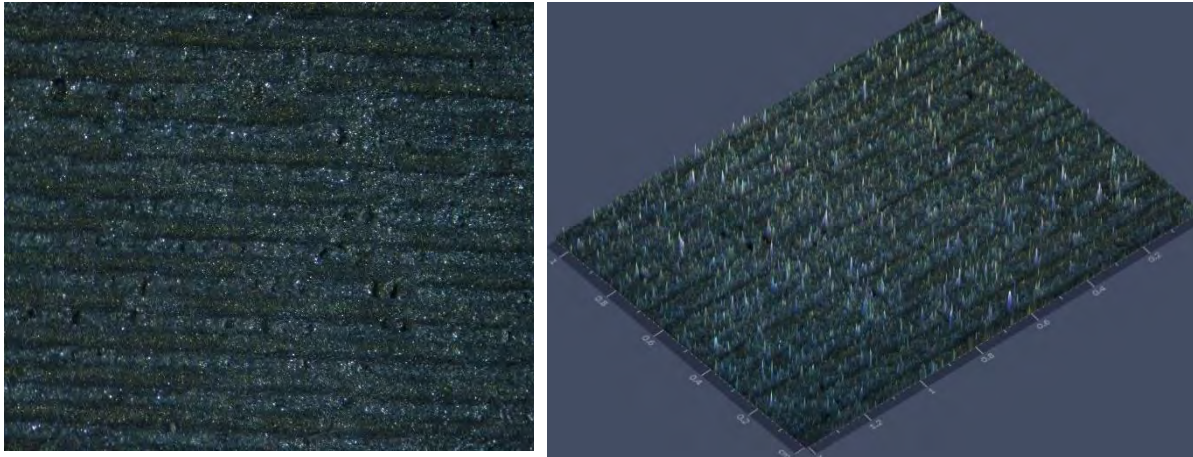


Figure 27 & 28: Specimen G3 after treatment @16x magnification, 2D and 2.5D. Solution G removed the oxide layer by reaction with it, leaving a clean steel metal surface. Although acid reacts with both iron in its pure form and in the oxide layer, the loss of pure iron from the surface does not seem significant. This could be because the specimens were removed immediately after all the oxide layer had reacted with the acid, which prevented the acid from reacting too much with the pure iron present on the surface beneath the oxide layer. It should be noted that acid at lower concentrations such as 10% HCl have a lesser tendency to attack the metal, which could be another reason why there was no significant loss in pure iron. As seen in specimen E and F, specimen G also appears slightly greenish, which is indication that corrosion treatment with an acid also provides little to no passivity against corrosion to the metal surface, and that corrosion will occur instantaneously upon the specimen's removal from the acid solution.

Observation after Treatment:

Solution	Time before corrosion observed (days)
C	Not Observable
D	2
E	3
F	3
G	Almost immediate

As the surface of specimens C were coated with a black oxide layer, it was difficult to observe any visible corrosion on the surface. It can also be seen that solutions E and F could provide slightly more protection to the metal as compared to the other solutions D and G.

Other key observations:



Figure 29 & 30: Solution E before and after treatment

Solution E displayed a change in colour from colourless to dark brown-black when used to treat a corroded specimen. This is an indication that the Fe^{3+} ions have been chelated from the oxide layer into the solution, resulting in the darkening of the solution. It also supports the claim that solution E has effectively removed the oxide layer from the surface of the metal and has held the Fe^{3+} ions in suspension without any further reaction with pure iron on the metal surface.

However, the chelate within the solution was unable to settle and turbidity remained high as seen in Figure 30 even after undergoing filtration twice. Further studies are advised as failure of the chelate particles to settle and be filtered out might pose an environmental issue when disposed into water bodies.



Figure 31: Solution F after treatment

Similar to solution E, solution F presented a colour change from yellow to gray. The solids produced from the reaction between the solution and the oxide layer were able to settle at the bottom of the bottle. The type of solid formed and the difference in turbidity of the solution are further suggestion that although solution E and F are both aqueous methods of corrosion removal, they undergo different reactions with the oxide layer in order to break down and remove rust present on the metal surface.



Figure 32: Change in solution C during treatment process

The figures from left to right illustrate the addition of rust converter and the transition from a milky white emulsion liquid into a glossy black coating of Fe_3O_4 .

5. Conclusion

Due to the limited amount of time for research and experimentation, the present report is unable to present a clear comparison between the rust converters, solution C and D. However, it can be distinguished that solution C utilising MRST was able to provide a more even and presentable finish to the metal. After the layer of rust is converted into a stable ferrosferric oxide, coating can be done to give the metal part a new and clean look, as well as to further protect the surface of the metal from future corrosion.

Acid treatments such as the use of HCl are less recommended compared to aqueous methods such as solution E and F due to the dangers and health hazards that accompany the preparation of diluted acid solution. Furthermore, aqueous methods of corrosion treatment are

easily disposed as opposed to acid treatments, where neutralisation of the acid is required before the solution can be disposed of.

The use of EIS in this research was intended to discover if the aqueous methods had any ability to passivate the metal surface from corrosion. However, since the results could only be used comparatively within this report, solid evidence that MRST is able to provide corrosion protection after removing the oxide layer from the metal surface could not be obtained. It can however ascertain that MRST is highly effective in treating and removing surface corrosion and is more efficient compared to a commercial aqueous product.

6. Recommendations

From this research and all experiments and observations conducted within the time frame of this research, the team has come up with the following recommendations on the direction as to which this study should head towards.

There were multiple possible areas where human error could have affected the results, hence it is recommended to conduct EIS with stricter procedures and proper calibration and to have a consistent method of analysis. Furthermore, EIS Tafel plot alone cannot clearly prove the effectiveness of corrosion treatment. Hence, further experimentation must be done along with more observations over a longer period, since corrosion is a long process and must be studied closely over a much longer period.

References

- [1] Van Loon Chemical Innovations. (2019). *Corrosion Testing via Electrochemical Impedance Spectroscopy (EIS) - Van Loon Chemical Innovations*. [online] Available at: <https://vlci.biz/corrosion-testing-via-electrochemical-impedance-eis/>
- [2] Abdel Salam Hamdy, E. El-Shenawy, T. El-Bitar, 2006. Electrochemical Impedance Spectroscopy Study of the Corrosion Behavior of Some Niobium Bearing Stainless Steels in 3.5% NaCl. *International Journal of Electrochemical Science* [online], August 2006, 1, 171-180. Available at: <http://www.electrochemsci.org/papers/1040171.pdf>
- [3] NCH Europe. *What is Rust?* [online] Available from: <https://www.ncheurope.com/en/what-is-rust>

- [4] Anne Marie Helmenstine, 2018. *How Rust and Corrosion Work* [online] Available from: <https://www.thoughtco.com/how-rust-works-608461>
- [5] Corrosion Doctors. *Rust Chemistry* [online] Available from: <https://corrosion-doctors.org/Experiments/rust-chemistry.htm>
- [6] Tdwhs.nwasco.k12.or.us. (2019). *Corrosion of Iron*. [online] Available at: <http://tdwhs.nwasco.k12.or.us/staff/bfroemming/Corrosioniron.html>
- [7] C. R. Tomachuk, C. I. Elsner, A. R. Di Sarli, 2013. Electrochemical Characterization of Chromate Free Conversion Coatings on Electrogalvanized Steel. *Materials Research – Ibero-American Journal of Materials* [online], Jan/Feb 2014, 17. Available at: http://www.scielo.br/scielo.php?pid=S1516-14392013005000179&script=sci_arttext
- [8] The Balance. (2019). *Here Are the Different Methods of Corrosion Prevention for Metals*. [online] Available at: <https://www.thebalance.com/corrosion-prevention-2340000>
- [9] Pooja Patel (2019). *Pros and Cons of Different Rust Removal Methods*. [online] Available at: <https://prezi.com/ijqinrcuxzw/pros-and-cons-of-different-rust-removal-methods/>
- [10] Gamry Instruments. *Basics of Electrical Impedance Spectroscopy* [online] Available at: <https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/>
- [11] V. Lavaert, M. Moors, E. Wettinck. (2002). An EIS Study of the Influence of Imperfections on the Corrosion Behaviour of an Organic Coated Steel System. *Journal of Applied Electrochemistry* [online], February 2002, 32, 853-857. Available at: <https://link.springer.com.ezp1.lib.sp.edu.sg/content/pdf/10.1023%2FA%3A1020543407413.pdf>