

MECHANICAL STRENGTH AND REMOVAL OF A PROTECTIVE IRON CARBONATE LAYER
FORMED ON MILD STEEL IN CO₂ CORROSION

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ABSTRACT

It has been debated in the past whether, in turbulent flow, the hydrodynamic wall-shear stress can mechanically remove or damage a protective iron carbonate layer formed on mild steel in a CO₂ corrosion environment. In this study, the mechanical strength of the iron carbonate layer was measured by a tensile machine. It was shown that the adhesion strength between the iron carbonate layer and the steel substrate is in excess of 10 MPa, which is many orders of magnitude larger than the typical wall-shear stress found in turbulent flow. Experiments conducted in a small scale single-phase flow loop confirmed that the iron carbonate layer could not be removed mechanically.

KEY WORDS: adhesion strength, iron carbonate (FeCO₃) layer, mechanical layer removal, CO₂ corrosion, thin channel, hydrodynamic force, wall-shear stress

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INTRODUCTION

Considering the relatively low investment cost, carbon steel is currently the most widely used material of construction for oil and gas production facilities and pipelines. Due to the presence of water and dissolution of corrosive gases, such as carbon dioxide (CO_2), internal corrosion of mild steel equipment is a common problem encountered by the oil and gas industry. Internal corrosion of pipelines usually involves the formation of a corrosion product layer on the metal surface. As a by-product of the CO_2 corrosion process, iron carbonate (FeCO_3) layer can serve as a protective barrier in the corrosion process¹. It has also been reported that there is another very thin “passive” layer formed together with the FeCO_3 layer, which can provide further protection from corrosion². Yet, any damage to this protective FeCO_3 layer may lead to serious problems, by exposing the underlying metal to the aggressive corrosive environment. If the protective FeCO_3 layer is only partially damaged, there is apparently a possibility that a galvanic coupling can form between the FeCO_3 covered surface and the bare steel surface, which has been shown to be one of the principal mechanisms of localized attack in CO_2 corrosion³. Therefore it is important to understand under which condition the protective FeCO_3 layer could be removed.

It has been debated in the past whether, in turbulent flow, the hydrodynamic forces, commonly expressed in terms of the wall-shear stress, is powerful enough to mechanically damage/remove the protective FeCO_3 layer which forms on mild steel in CO_2 corrosion environments⁴⁻¹⁰. In the so called “upstream” pipeline applications, the typical mean wall-shear stress produced by turbulent flow is in the range of 1 to 100 Pa. This leads to a logical question: is this small force sufficient to damage/separate the FeCO_3 layer from the steel surface. It has been reported in the past^{8,11} that the mechanical properties of the FeCO_3 layer were determined, however very little information was given on the details about how the tests were conducted, making it difficult to accept the results without verification. Therefore, the current study focused on measuring the mechanical strength of the FeCO_3 layer formed on mild steel, and the results are presented below, with detailed procedural information provided.

EXPERIMENTAL PROCEDURE

Experimental setup

An FeCO_3 layer was formed in a 2 liter glass cell filled with CO_2 saturated water. A schematic of the glass cell set-up is shown in Figure 1. Square flat mild steel samples were used as the working electrode (WE). A piece of platinum served as a counter electrode (CE). A saturated Ag/AgCl reference electrode (RE) was externally connected to the cell *via* a Luggin capillary and a porous Vycor-tip. A pH probe was inserted into the solution in order to monitor and maintain the pH. After an FeCO_3 layer was formed on the mild steel substrate, a tensile machine (Instron 4500) was used for the FeCO_3 mechanical strength test, which is shown in Figure 2. The FeCO_3 covered steel sample was fixed in place on the stage by a sample holder and held tight. A “stud” that can be attached to the top of the tensile machine was glued to the FeCO_3 covered steel sample surface in advance. The stage was moved up and down at a controlled speed. The force that is needed to separate the stud and the steel sample was measured.

In separate tests, the FeCO_3 layer was formed and removed under turbulent flow conditions in a Thin Channel Flow Cell (TCFC) system. A flow chart and a schematic of the TCFC system are shown in Figure 3 and Figure 4. The test section includes a 3 mm high and 100mm wide flow channel with four testing ports for insertion of probes. The bulk of the test solution was held in the tank and was circulated by a centrifugal pump through the test section and back to the tank. A bypass in the flow loop enabled

pH monitoring and solution sampling. The temperature of the system was controlled by an electrical heater and a cooled heat exchanger. The flow rate was measured by an in-line flow meter.

Experimental method and test matrix

In order to test the mechanical strength of the FeCO_3 layer, a repeatable procedure for building the layer needed to be established first. The method that has been adopted was to apply a galvanostatic current (approximately equivalent to 1 mm/year of forced corrosion) during the layer formation process to help release sufficient Fe^{2+} near the steel surface and build a repeatable FeCO_3 layer in a short period of time. The potential of the sample was monitored during the layer formation process. The detailed test matrix is shown in Table 1. The composition of X52 steel used for this purpose is shown in Table 2.

To test the mechanical strength of the FeCO_3 layer, a tensile test method has been used, with the applied force perpendicular to the steel surface. The tests were conducted in a controlled stable environment (23°C , 50% humidity). Displacement speed was 0.5 mm/min. The various adhesives used in the tests are shown in Table 3, with A, B, C, D, E and F denoted for adhesives 3M DP8105[†], 3M DP100[†], Loctite E-120HP[†], EH401[†], Loctite E-30CL[†], and HTK UB100[†] respectively. This notation will be used throughout this paper.

Linear polarization resistance (LPR) and weight loss (WL) measurements have been used to determine the corrosion rate. A detailed test matrix is shown in Table 4. The composition of X65 used in this test is shown in Table 2.

Test procedures

The following test procedures were used and will be referred to in the results and discussion section below.

Test procedure for FeCO_3 layer formation on mild steel

- Prepare a 1wt% aqueous NaCl solution, deoxygenate the solution with CO_2 , and heat to 80°C .
- Adjust the pH to 6.6 by adding a deoxygenated NaHCO_3 aqueous solution.
- Polish steel sample with 200, 400 and 600 grit sand papers successively, rinse with isopropyl alcohol and dry with a forced air stream. Insert sample into test solution.
- Connect and make electrochemical measurements. After the corrosion potential stabilized within ± 1 mV, measure the free corrosion rate by LPR. Apply a galvanostatic current.
- Add more Fe^{2+} according to the specifications by adding a deoxygenated FeCl_2 aqueous solution.
- After 24 hours, stop the galvanostatic current and measure the free corrosion rate again by LPR.
- Take out the steel sample, rinse with isopropyl alcohol and dry the surface.
- Store sample in a desiccator.
- Analyze the surface of the sample by scanning electron microscopy (SEM).

Test procedure for the FeCO_3 mechanical strength tests

- Deposit a layer of adhesive on the steel surface (with or without the FeCO_3 layer).
- Carefully place the stud on the adhesive covered steel surface.
- Follow the curing procedure according to the type of adhesive used.

[†] Trade name.

- Fix the steel sample with the stud onto the sample holder and mount the holder on the tensile machine to determine the force required to separate the stud from the steel sample.
- When the test is finished, preserve samples for SEM and EDS analysis by storing in a desiccator.

Procedure for preparing sample cross sections for SEM analysis

- Wrap the steel sample with aluminum foil to protect the steel surface and to separate the epoxy which will be used for fixing during cross sectioning from the adhesive which was used for attaching the stud in the tests.
- Seal the wrapped sample into epoxy.
- Cut the sample at a desired position.
- Polish cross section surface with progressively finer grit sand papers.
- Observe sample cross section using the SEM.

Test procedure for FeCO_3 layer formation and removal test in the TCFC system

- Prepare a 1 wt.% NaCl aqueous solution in the tank of the TCFC system.
- Deoxygenate the system with CO_2 and heat up to 80°C .
- Adjust the pH of the solution to pH6.6 by adding a deoxygenated NaHCO_3 aqueous solution through the sampling port.
- Polish the LPR probe and the WL/SEM steel samples, rinse them with isopropyl alcohol and air dry.
- Flush mount all the test samples into the TCFC test section and adjust the flow rate to a desired low value.
- Monitor corrosion potential and corrosion rate using the LPR probe.
- Add a desired amount of Fe^{2+} into the system by injecting a deoxygenated aqueous FeCl_2 solution.
- Keep monitoring pH and Fe^{2+} concentration of solution during the test.
- After corrosion rate decreases to below 0.1 mm/year, take out one WL/SEM sample and perform the SEM analysis of the FeCO_3 layer on the mild steel surface.
- Change the flow rate to desired high value.
- Monitor the change of corrosion potential and corrosion rate of the LPR probe until the end of the test.
- Take out all samples and analyze the steel samples by using SEM.
- Drain the system and rinse with DI water.

RESULTS AND DISCUSSION

FeCO_3 mechanical strength measurements

FeCO_3 layer formation

Figure 5 shows a typical potential change curve during the FeCO_3 layer formation process which involves applying an anodic galvanostatic current to the WE. In the beginning of the test, the free corrosion rate of the sample was measured by LPR to be approximately 1 mm/year. As the anodic galvanostatic current was applied to the WE, a steady amount of Fe^{2+} was released by the steel sample into the aqueous solution close to the surface, which added to the Fe^{2+} that were injected at the beginning of the test into the bulk solution, making the solution highly supersaturated with respect to FeCO_3 . As a consequence, a layer of FeCO_3 was formed rapidly on the steel surface. This layer became

denser and more protective with time. The corrosion potential increased about 300 mV, which indicates that a passive layer had developed together with the FeCO_3 layer on the surface. At the end of the test, after 24 hours of FeCO_3 layer “building”, the measured free corrosion rate of the sample had decreased to less than 0.1 mm/year. SEM images of the top view of the FeCO_3 layer surface and a cross section of the sample after FeCO_3 layer formation is given in Figure 6, which shows an evenly covered steel substrate with an FeCO_3 layer around 10 μm in thickness.

FeCO_3 mechanical strength tests

Before conducting the FeCO_3 mechanical strength tests on mild steel samples covered with an FeCO_3 layer, the “adhesive-strength” tests were done by gluing two stainless steel studs together and pulling them apart, thereby measuring the strength of the adhesive. The results showed that the adhesive F had an especially high strength, about 53 MPa, while other adhesives had a lower strength, typically around 10 MPa. Figure 7 shows the images of the surfaces after the adhesive-strength test using adhesive F. It can be observed that the adhesive is present on both stud surfaces suggesting that the “breakage” occurred across the bulk of the adhesive rather than at the contact with the steel substrate, which means that the adhesion strength between the adhesive and the steel substrate was even higher than the measured value.

In order to demonstrate the “grip” of the adhesive on the FeCO_3 layer, Figure 8 shows a cross section image of a steel sample with an FeCO_3 layer and a cured adhesive on top of it, before the FeCO_3 mechanical strength test was conducted. It can be seen that the dense FeCO_3 layer surface was fully covered by the adhesive and in some places the adhesive penetrated deeper into the layer.

Figure 9 shows the results of mechanical strength tests in which less than 10% of the FeCO_3 failed. On most of the surface, the adhesive detached from the FeCO_3 layer, suggesting that the actual FeCO_3 strength must be larger than the measured values. With different adhesives, the values of FeCO_3 mechanical strength fluctuated, but they are all of the same order of magnitude. When compared with the measured strength of the adhesive itself, some of the results for FeCO_3 mechanical strength fall rather close, which appears to bring the validity of the results into question, however any doubt is removed when considering the tests done with adhesive F which gave a much lower value for the FeCO_3 mechanical strength compared to the strength of the adhesive itself. Therefore only the results obtained with this adhesive will be shown in the graphs below.

Figure 10 shows the SEM pictures of the steel sample surface after the FeCO_3 mechanical strength test and Figure 11 shows the corresponding stud surface. Over most of the surface area, the FeCO_3 layer was not damaged whereas the adhesive has detached from the FeCO_3 layer surface. It can be noticed in Figure 10 that there were some small areas where the steel underneath the FeCO_3 layer was exposed, which corresponds to the grey sections in Figure 11 indicating a completely detached FeCO_3 layer.

Figure 12 shows the results where almost 40% of the total area was showing FeCO_3 layer failure. Compared to the results discussed immediately above, the measured FeCO_3 mechanical strength was somewhat higher but still much lower than the strength of adhesive F. It can be seen in Figure 13 and Figure 14 that in some areas the FeCO_3 layer was detached from the steel surface, while in other areas the adhesive detached from the layer.

The results where more than 50% of the total area was showing FeCO_3 layer failure are shown in Figure 15, which agreed very well with the previous observations. As can be seen in Figure 16 and Figure 17, most of the surface of the sample and the stud were covered with FeCO_3 layer. This means that the

failure happened predominantly within the FeCO_3 layer rather than between the layer and steel substrate or the layer and the adhesive. In addition, the cross section shown in Figure 18 indicates that the adhesive didn't contact the steel substrate and has not interfered with the FeCO_3 mechanical strength measurement.

It can be concluded that the mechanical strength reported above represents a “mixed” value, which predominantly reflecting the mechanical strength of the FeCO_3 layer however there are contributions from the adhesion strength between FeCO_3 layer and mild steel substrate, and between the adhesive and the FeCO_3 layer. It was hard to distinguish how much this contribution really was, but from the analysis presented above it can be concluded that the mechanical strength of the FeCO_3 layer must have been in the excess of 10 MPa. The adhesion strength between the FeCO_3 layer and the steel substrate appears to be even higher.

FeCO_3 layer formation and removal tests in TCFC system

FeCO_3 layer formation and removal tests were conducted in a 20 liter flow loop called the Thin Channel Flow Cell (TCFC) system. Figure 19 shows the corrosion rate and corrosion potential change during the test in the TCFC. At the beginning of the test, the corrosion rate of the bare steel surface was around 1.5 mm/year. After additional Fe^{2+} was introduced, the corrosion rate decreased as time passed. This indicates that a protective layer of FeCO_3 was formed on the sample surface, which is expected due to the high super-saturation. The corrosion potential also increased about 40 mV signaling that a passive layer formed together with the FeCO_3 layer. The corrosion rate of the sample decreased to around 0.1 mm/year at the end of the layer formation process.

After a protective FeCO_3 layer was formed, the flow rate increased with a calculated wall-shear stress being around 20 Pa. The pH of the solution was monitored and the Fe^{2+} concentration was measured periodically by sampling. The super-saturation of FeCO_3 was calculated to be 300 at the beginning of the experiment and decreased to a value between 10 and 20 by the end of the experiment. A low corrosion rate and consistent corrosion potential were maintained even after the flow rate was increased, with no indication of any change related to the increased shear stress. In the SEM analysis, Figure 20, of the sample surface taken before and after the increased shear stress, there is no visible change in the layer appearance. This suggests that the FeCO_3 layer could not be mechanically removed by the turbulent flow conditions created here, which is not surprising because the shear stress created by the flow (20 Pa) was order of magnitudes lower than the measured mechanical strength of the FeCO_3 layer.

CONCLUSIONS

- Mechanical strength of the FeCO_3 layer was measured to be of the order of 10 MPa.
- The adhesion strength of the FeCO_3 layer to the steel substrate appeared to be even larger.
- A hydrodynamic wall-shear stress of 20 Pa had no effect on the mechanical integrity or protective properties of the FeCO_3 layer.

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TABLES

Table 1. Test matrix for layer formation tests

Parameter	Condition
Material	X52
Solution	1wt.% NaCl
Temperature /°C	80
CO ₂ partial pressure /bar	0.5
pH	6.6
Initial [Fe ²⁺] /ppm	50
Initial supersaturation	300
Galvanostatic current A/m ²	0.86
Test duration /hour	24

Table 2. Chemical composition of X52 and X65 steel (wt.%) (Fe is the balance)

	C	Si	Mn	P	S	Cr	Ni	Cu	Nb	Al	Mo
X52	0.094	0.22	0.97	0.012	0.005	0.028	0.03	0.02	0.03	0.04	-
X65	0.05	0.31	1.32	0.013	0.002	0.042	0.039	0.019	-	0.032	0.031

Table 3. Type of adhesives and their curing conditions

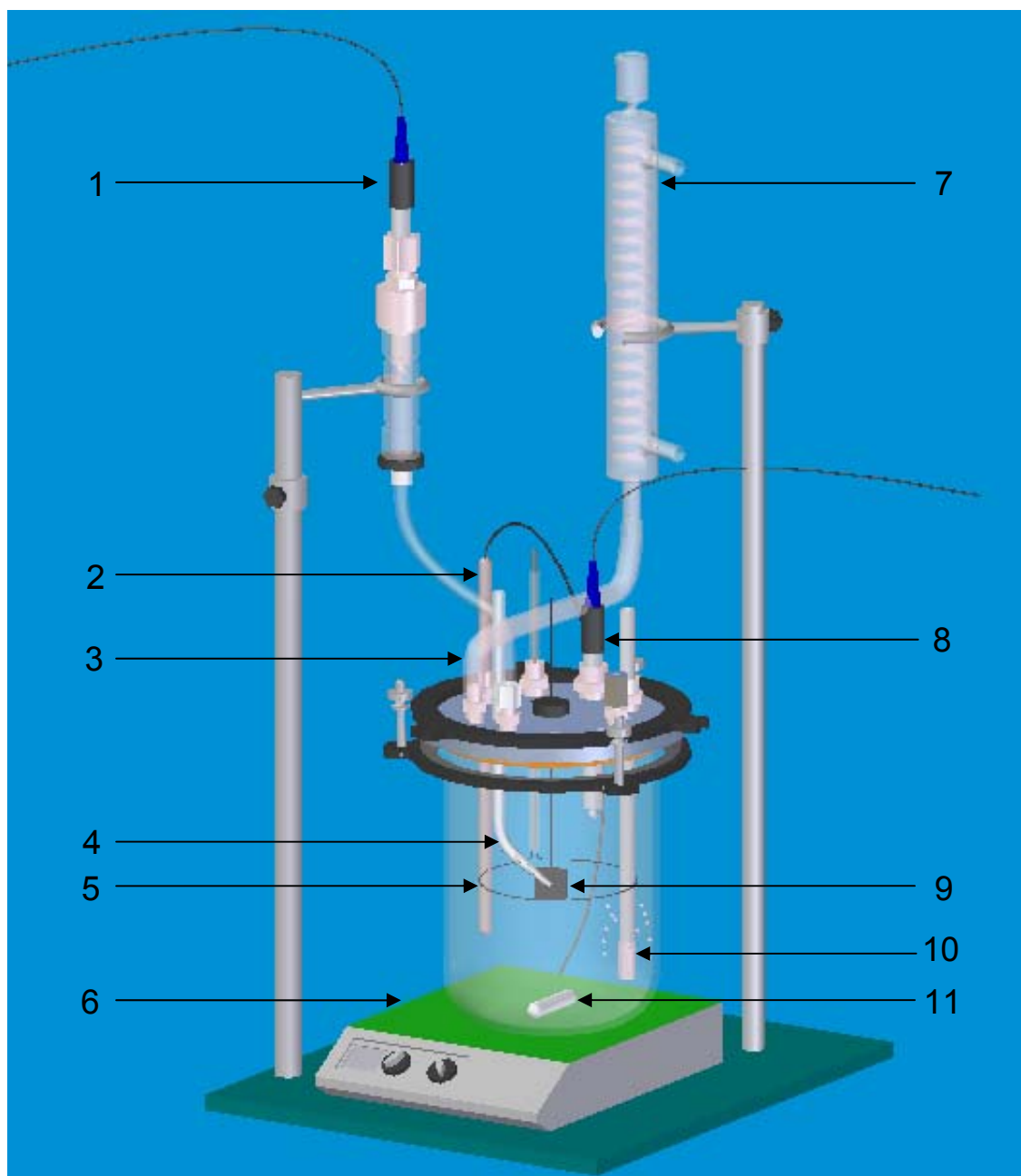
Adhesive	A	B	C
Curing condition	25°C, 1 atm	25°C, 1 atm	25°C, 1 atm

Adhesive	D	E	F
Curing condition	25°C, 1 atm	25°C, 1 atm	150°C, 70N/cm ²

Table 4. Test matrix of layer formation and removal tests in TCFC system

Parameters	Condition	
	Layer formation	Layer removal
Material	X65	
Solution	1 wt.% NaCl	
Temperature	80 °C	
CO ₂ partial Pressure	0.5 bar	
pH	6.6	
Initial [Fe ²⁺] /ppm	50	
Initial super-saturation	300	
Flow velocity	0.6 m/s	2.9 m/s
Shear stress	1.4 Pa	20 Pa

FIGURES



- | | |
|-------------------------------|---------------------------------|
| 1. Reference electrode | 2. Temperature probe |
| 3. Gas outlet | 4. Luggin capillary |
| 5. Platinum counter electrode | 6. Hot plate |
| 7. Condenser | 8. pH electrode |
| 9. Sample | 10. CO ₂ sparge tube |
| 11. Magnetic stir bar | |

Figure 1. Schematic of glass cell set-up for layer formation.

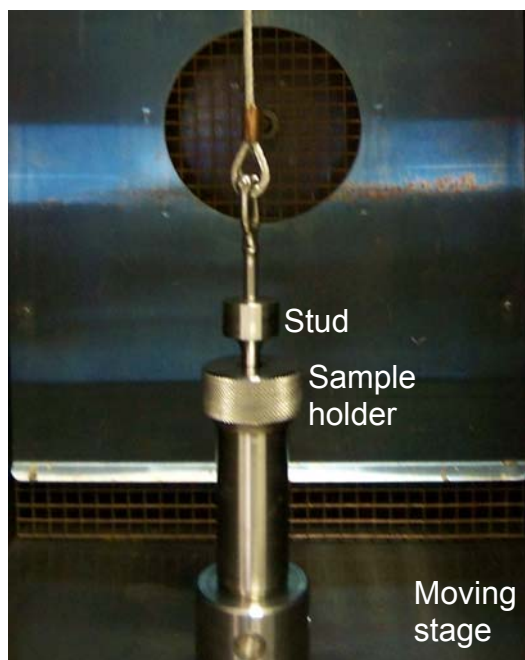


Figure 2. Mechanical strength test set-up with tensile machine.

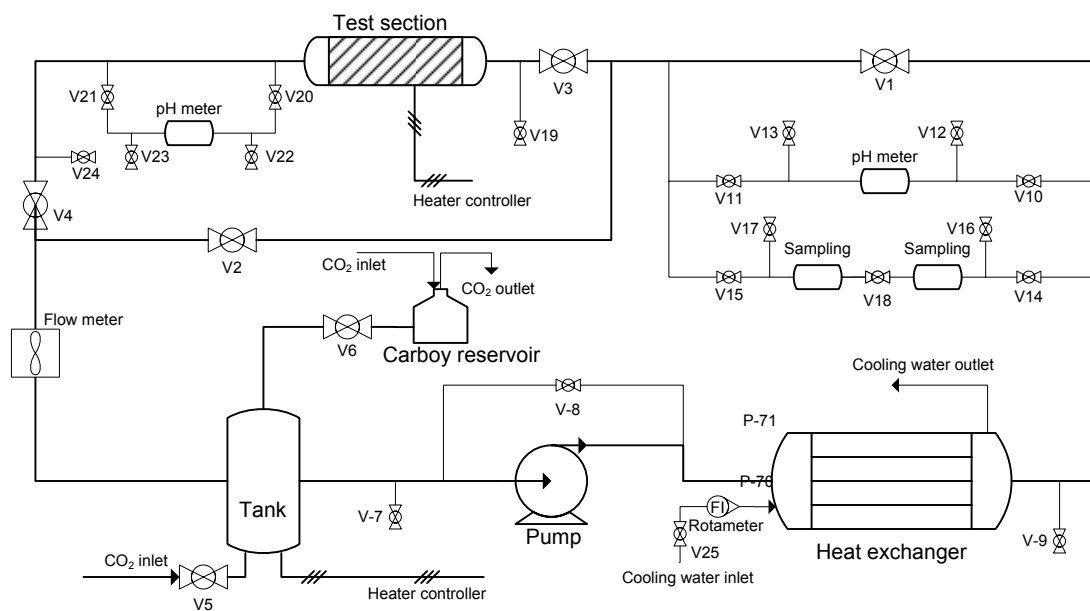
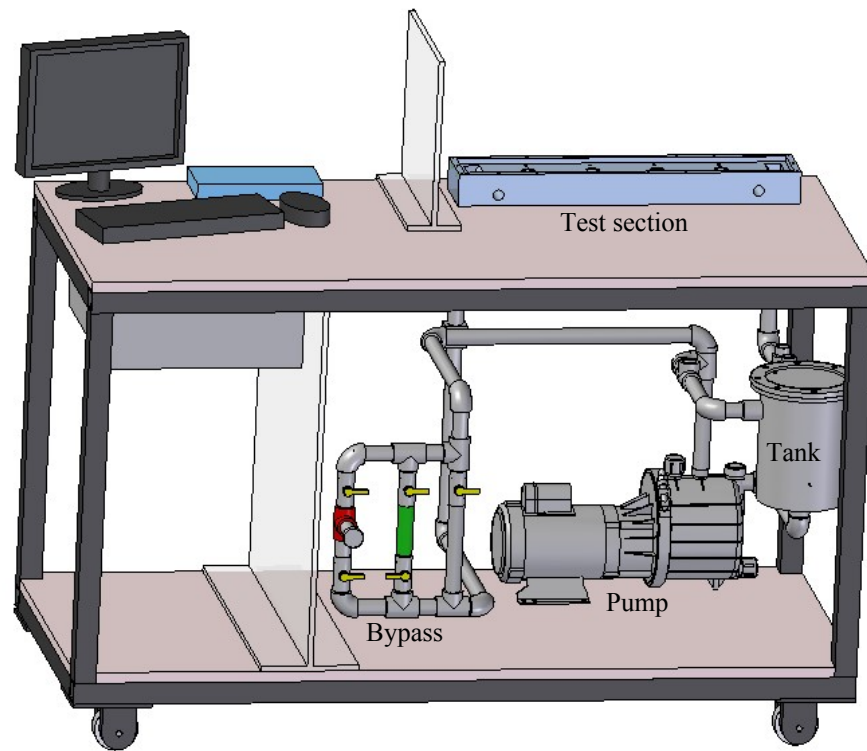
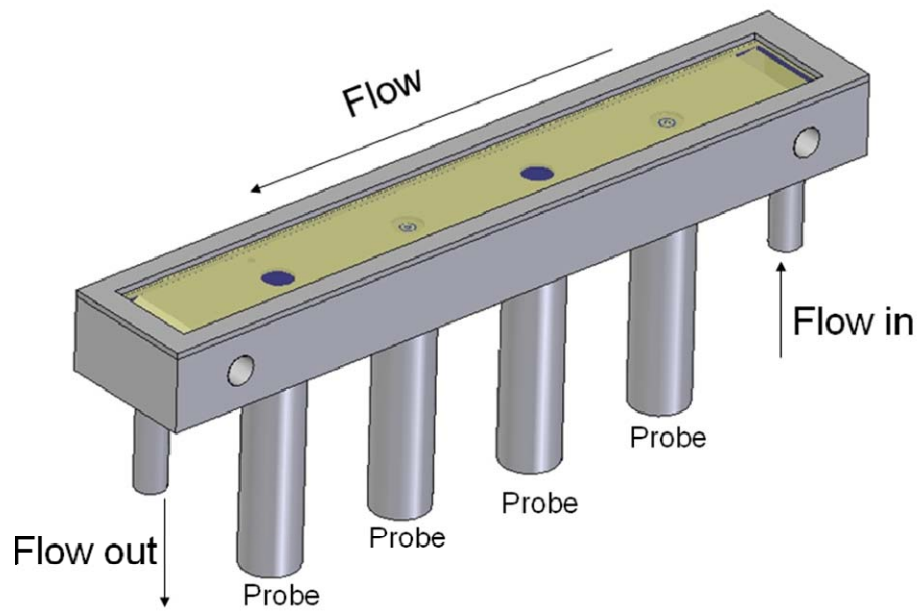


Figure 3. Flow chart of Thin Channel Flow Cell system.



(a) Thin channel flow cell system



(b) Test section

Figure 4. Schematic of Thin Channel Flow Cell system and test section.

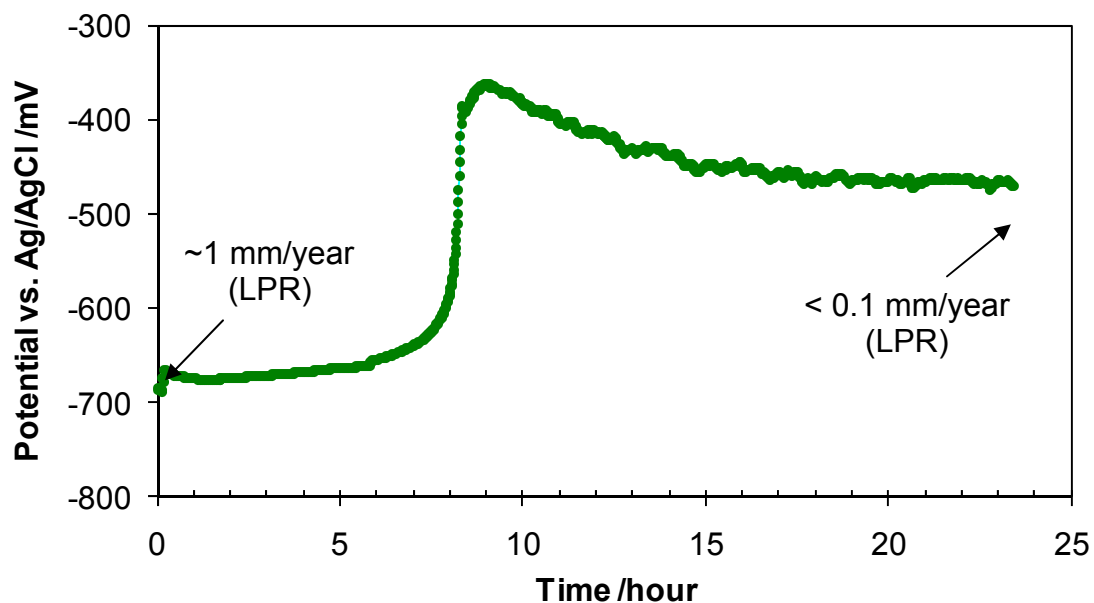


Figure 5. Potential change during layer formation process, 1 wt.% NaCl, 80°C, pH6.6, initial SS of $\text{FeCO}_3=300$.

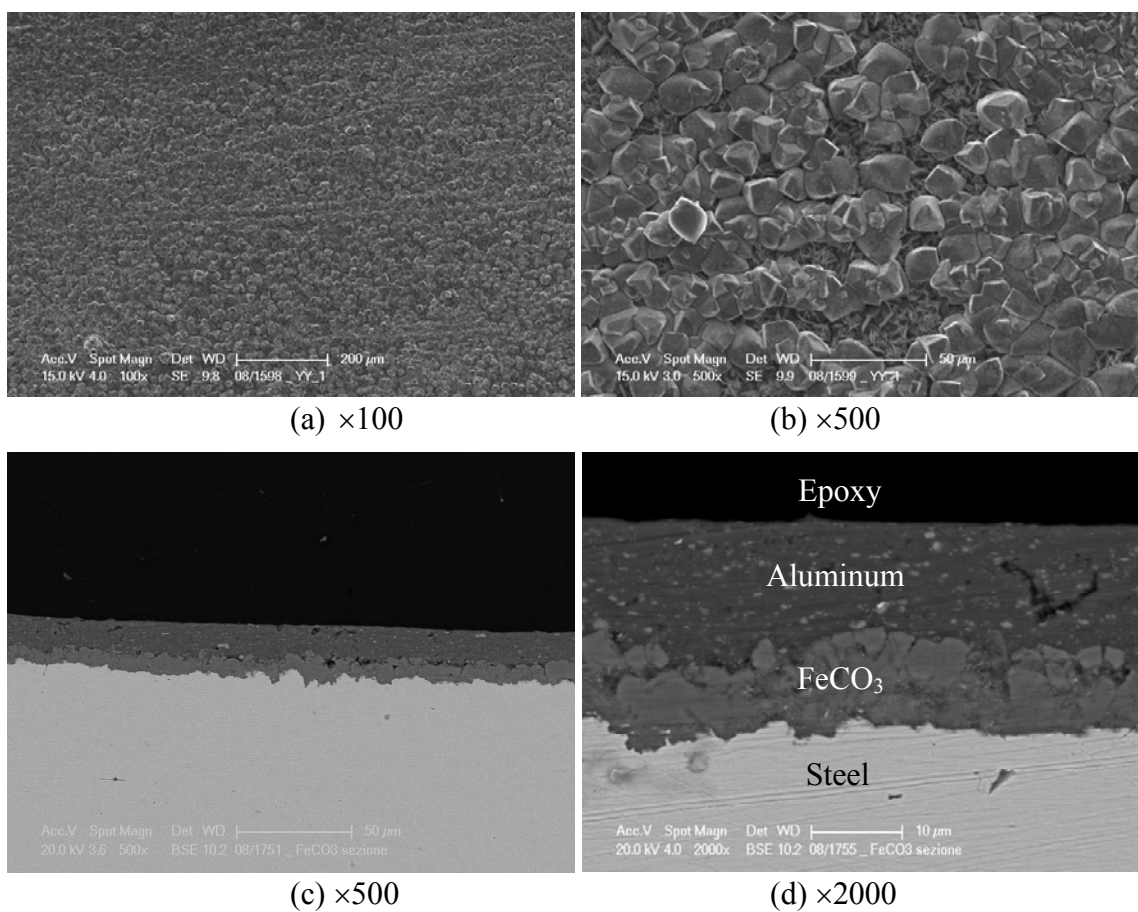


Figure 6. SEM images of surface (a, b) and cross sections (c, d) of the FeCO_3 layer.

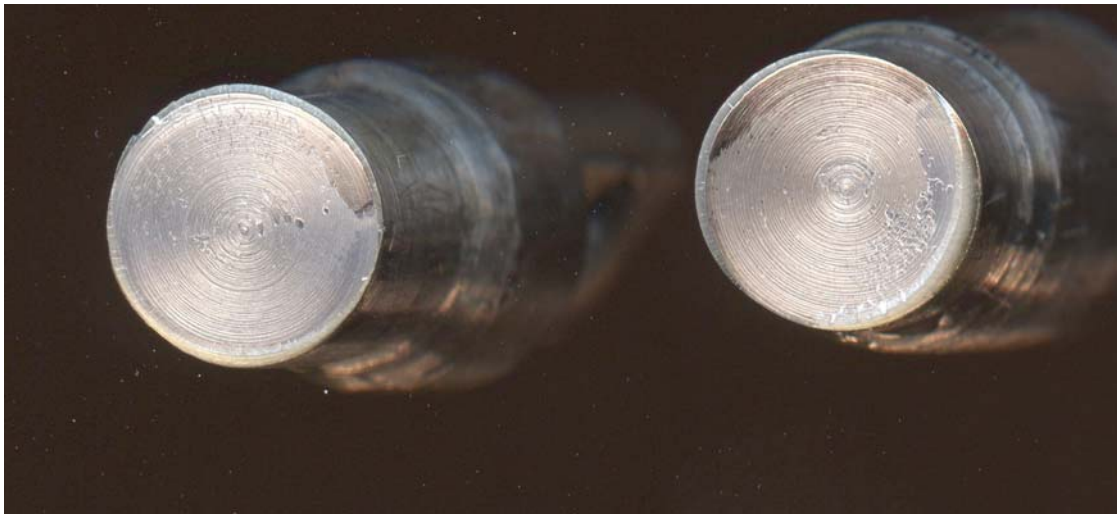


Figure 7. Surfaces of stainless steel stud after adhesive strength test of adhesive F.

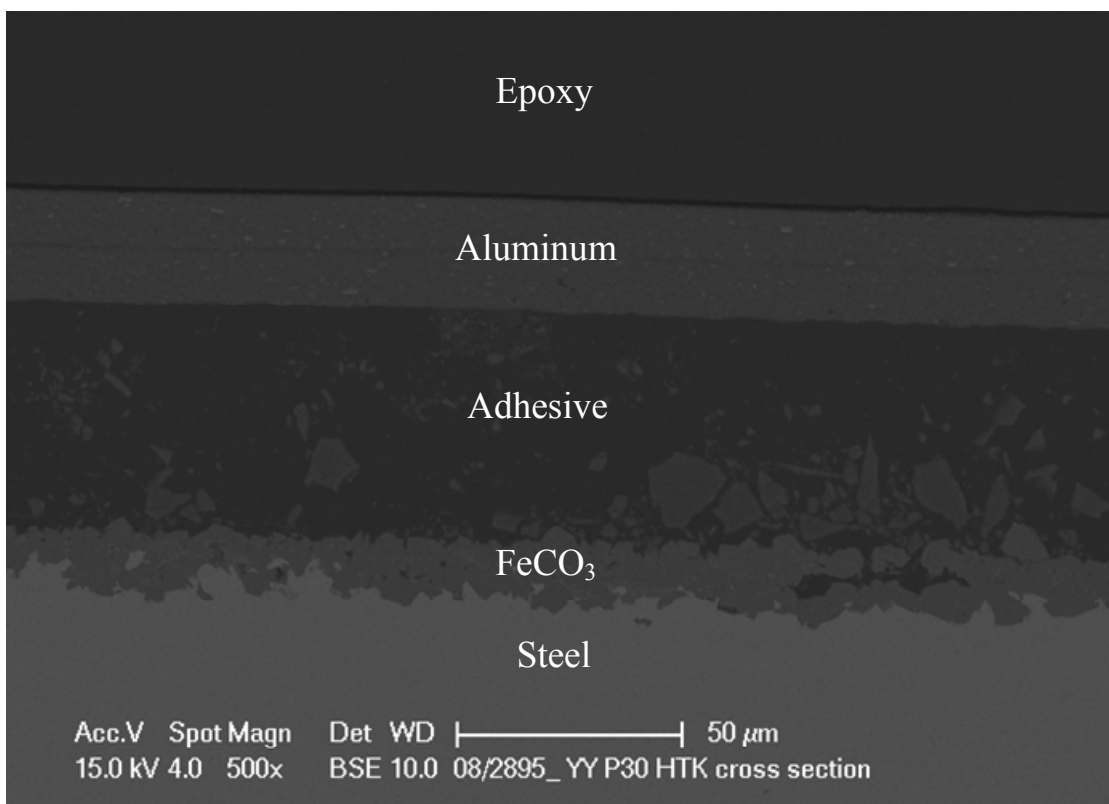


Figure 8. Cross section of FeCO₃ layer with adhesive before mechanical strength test.

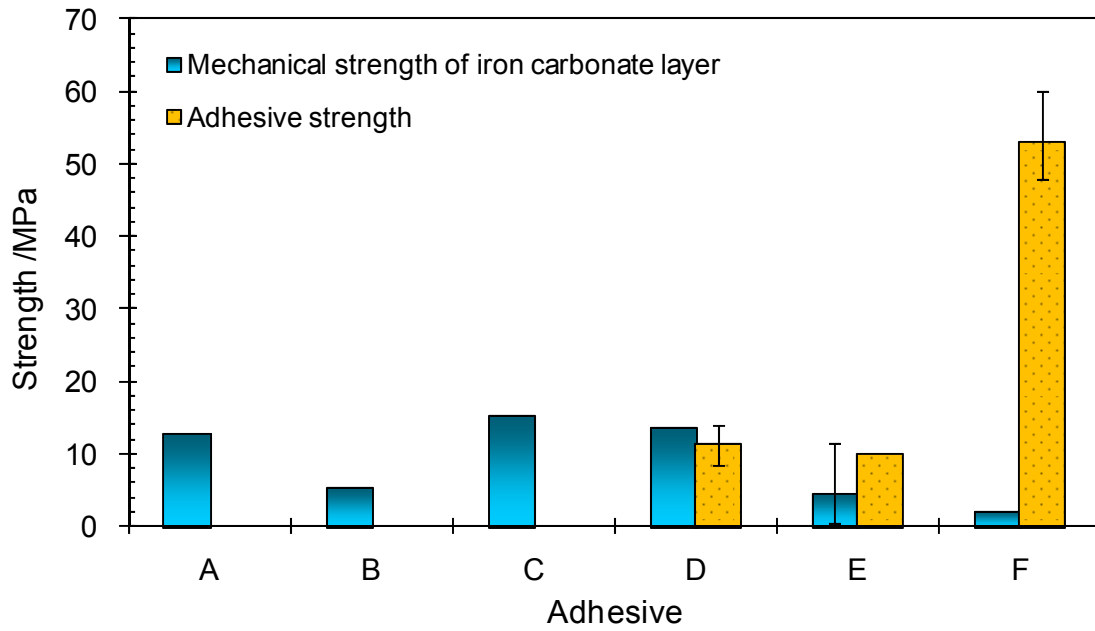


Figure 9. Mechanical strength of FeCO_3 layer on a mild steel substrate for the case in which less than 10% of the FeCO_3 failed.

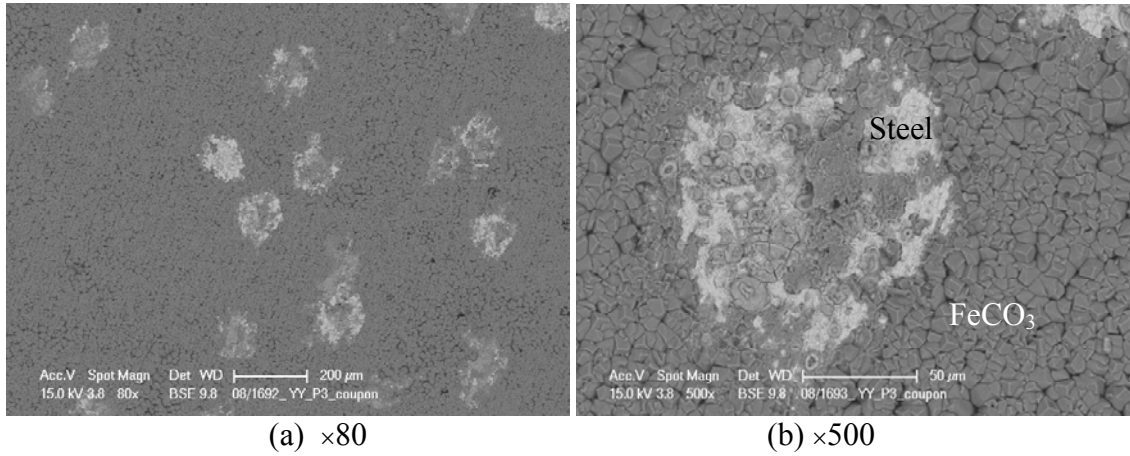


Figure 10. SEM images of the sample surface after the test in which less than 10% of the FeCO_3 failed (light grey areas).

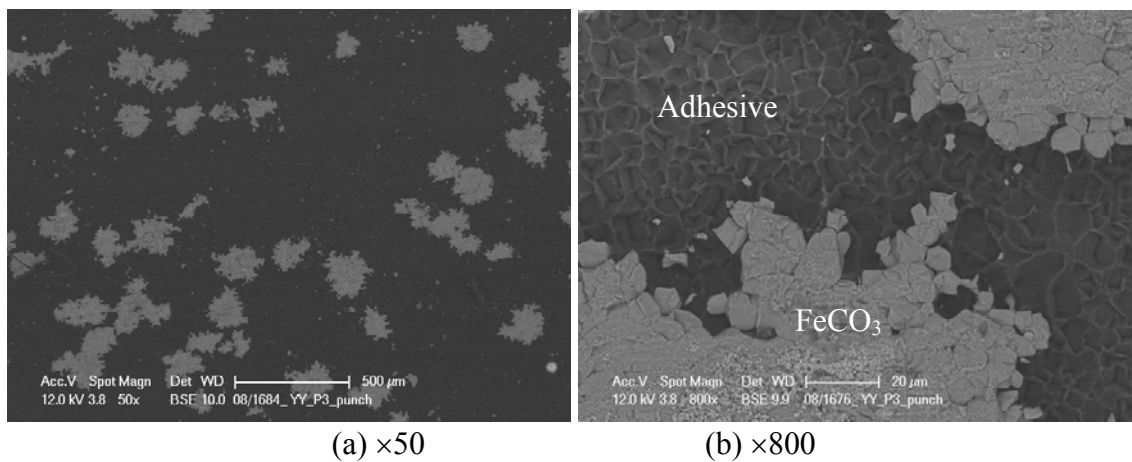


Figure 11. SEM images of the stud surface after the test in which less than 10% of the FeCO_3 failed (light grey areas).

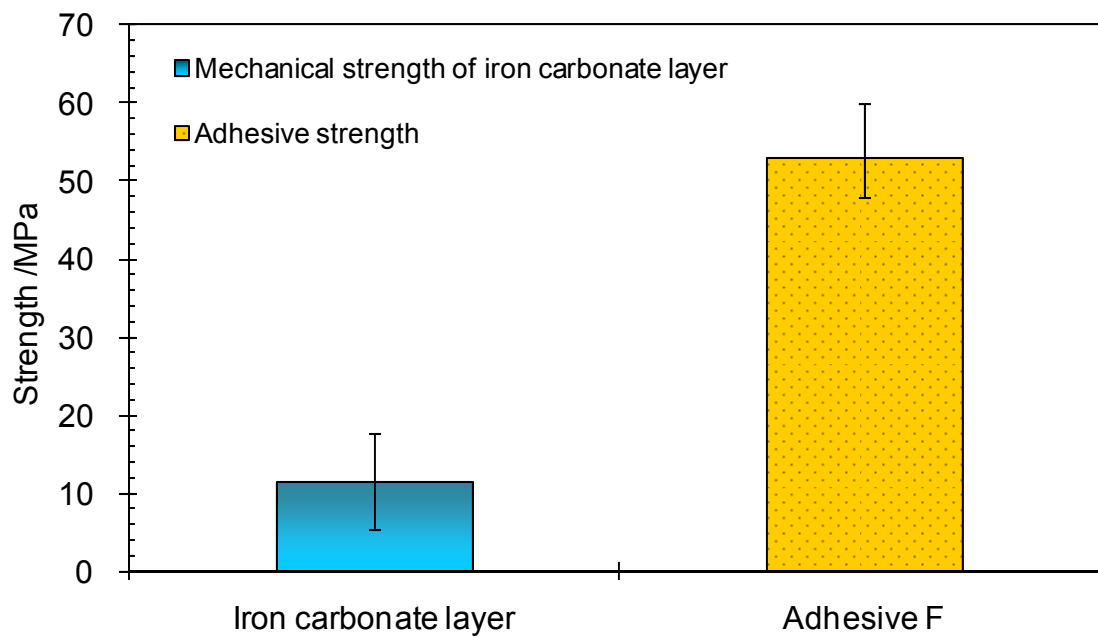


Figure 12. Mechanical strength of FeCO_3 layer on a mild steel substrate for the case in which 10% - 50% of the FeCO_3 surface failed.

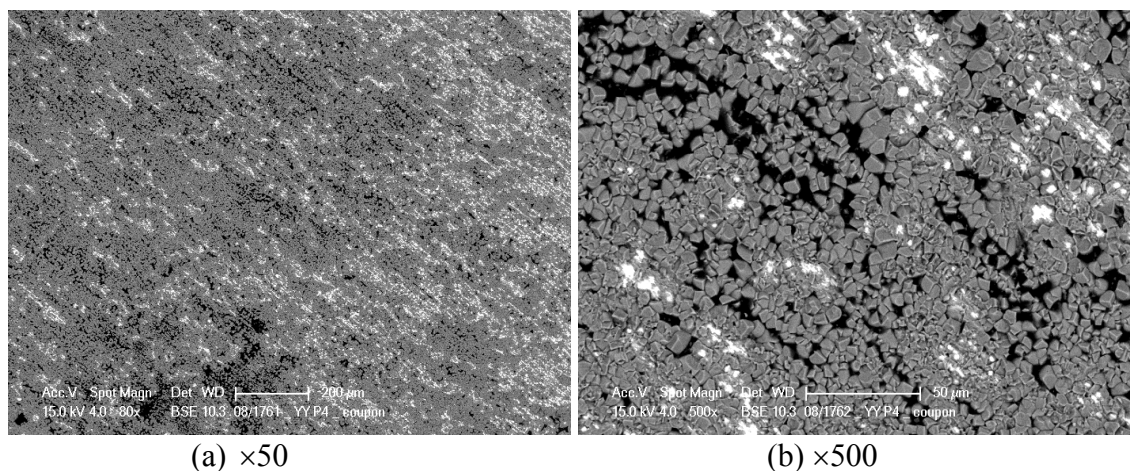


Figure 13. SEM images of the sample surface after the test in which 10% - 50% of the FeCO_3 failed (light grey areas).

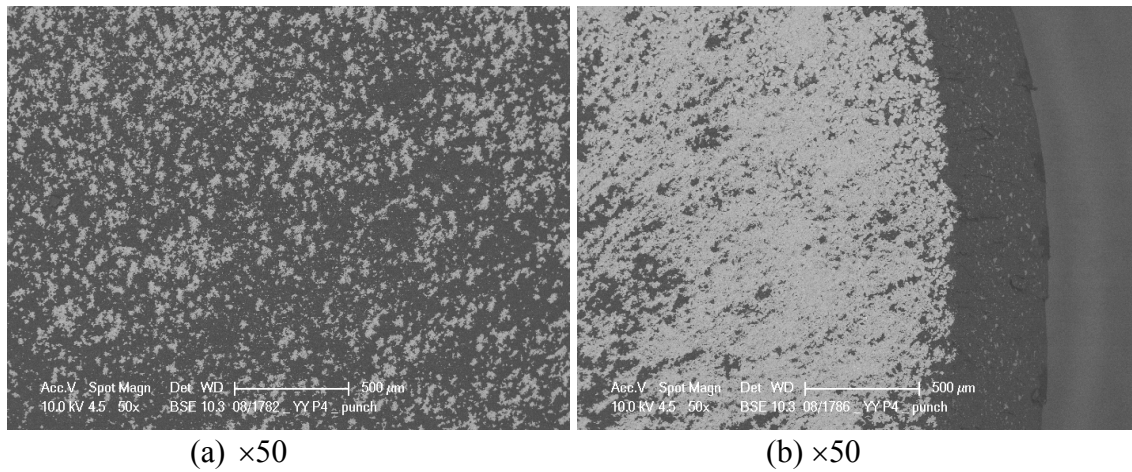


Figure 14. SEM images of the stud surface after the test in which 10% - 50% of the FeCO_3 failed (light grey areas). Images (a) and (b) are from different locations on the stud surface.

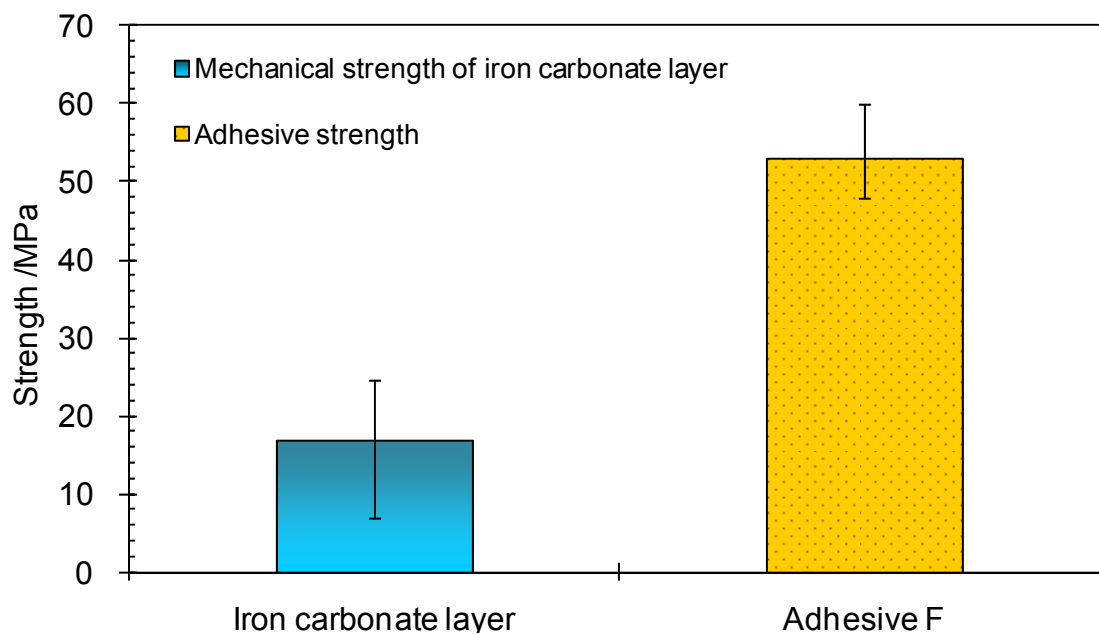
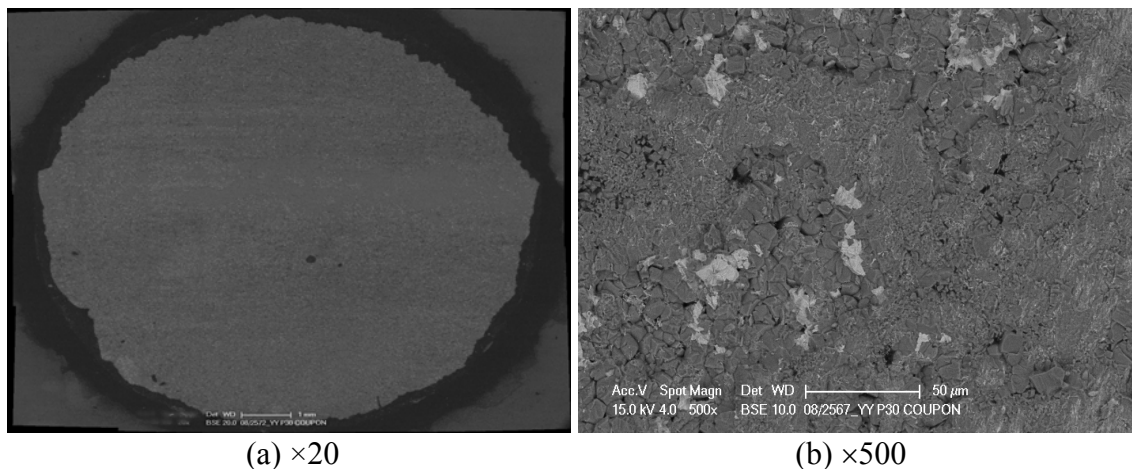


Figure 15. Mechanical strength of FeCO_3 layer on a mild steel substrate for the case in which more than 50% of the FeCO_3 surface failed.



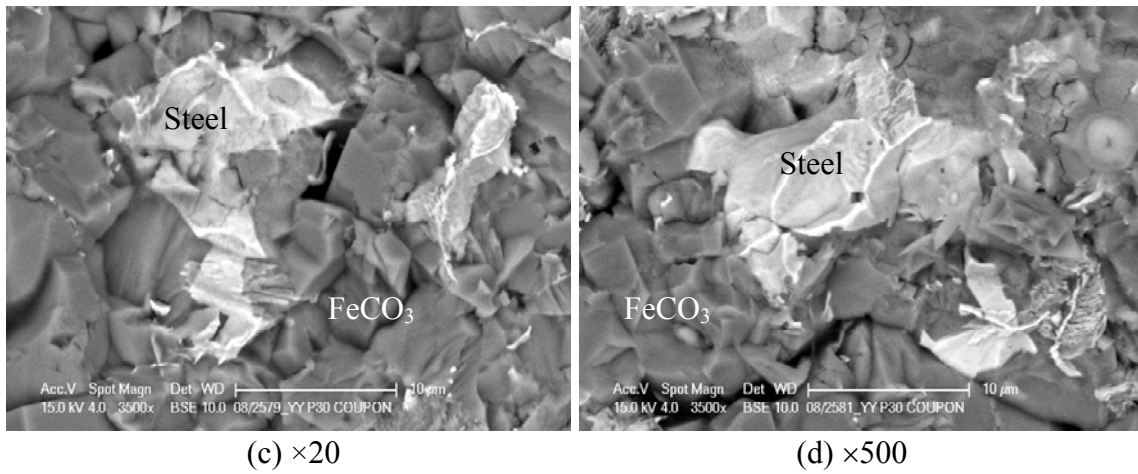


Figure 16. SEM images of the sample surface after the test in which more than 50% of the FeCO_3 failed (darker gray areas), showing small portions where the FeCO_3 detached from the steel (lighter gray areas).

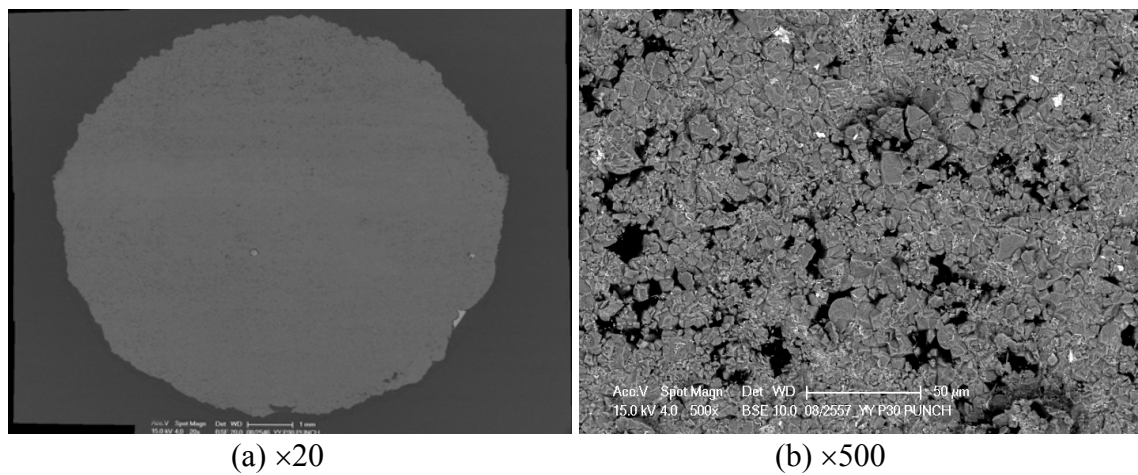
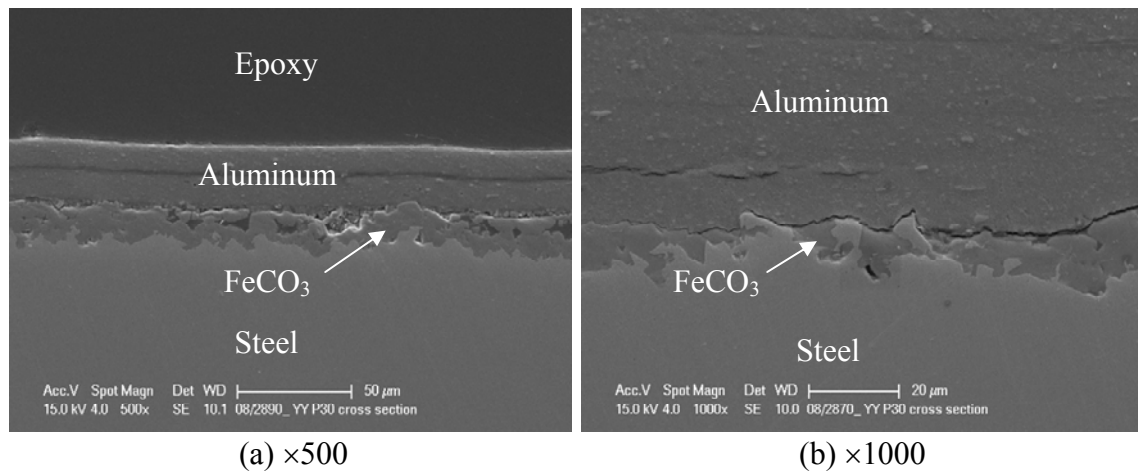


Figure 17. SEM images of the stud surface after the test in which more than 50% of the FeCO_3 failed, showing FeCO_3 detached from the sample.



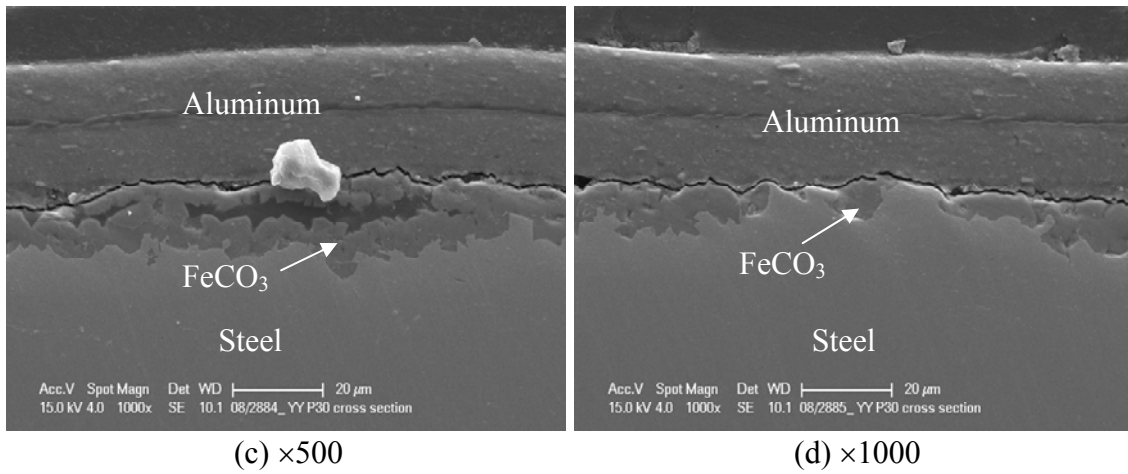


Figure 18. Cross section SEM images of the sample after the test in which more than 50% of the FeCO_3 failed, taken at a location where FeCO_3 “broke”.

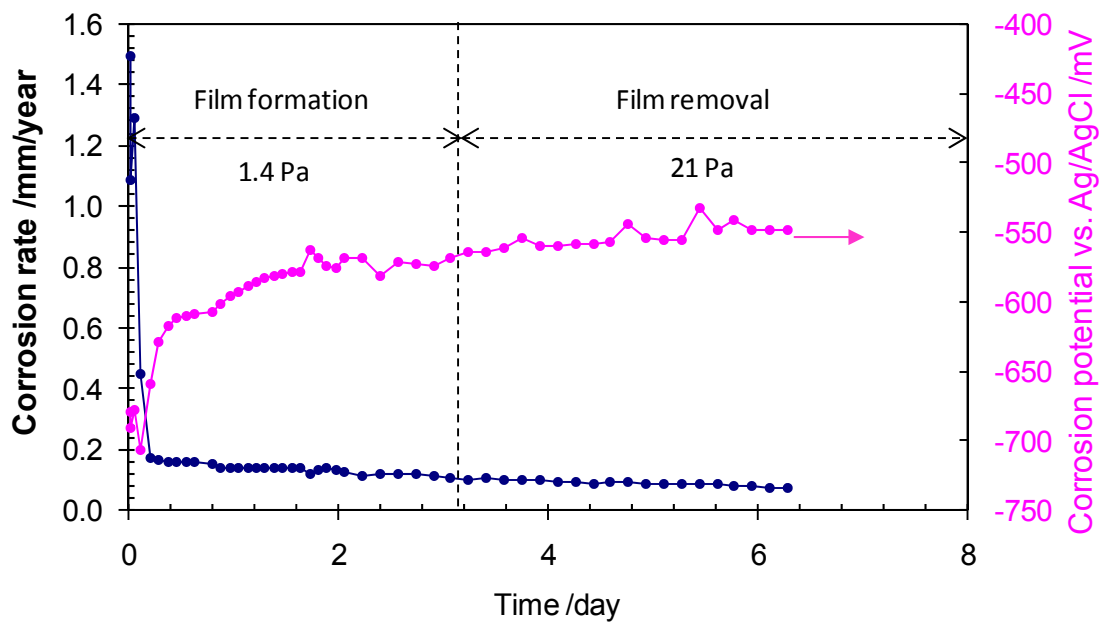
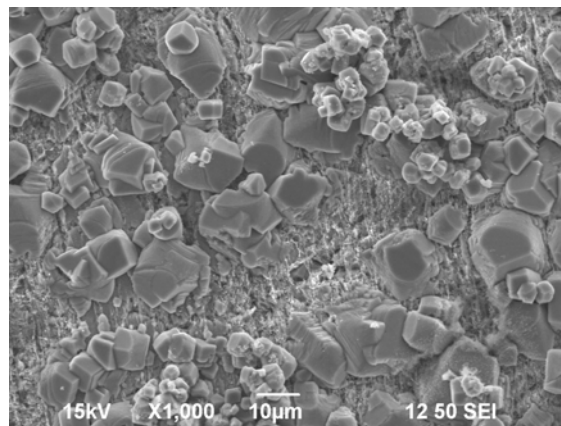
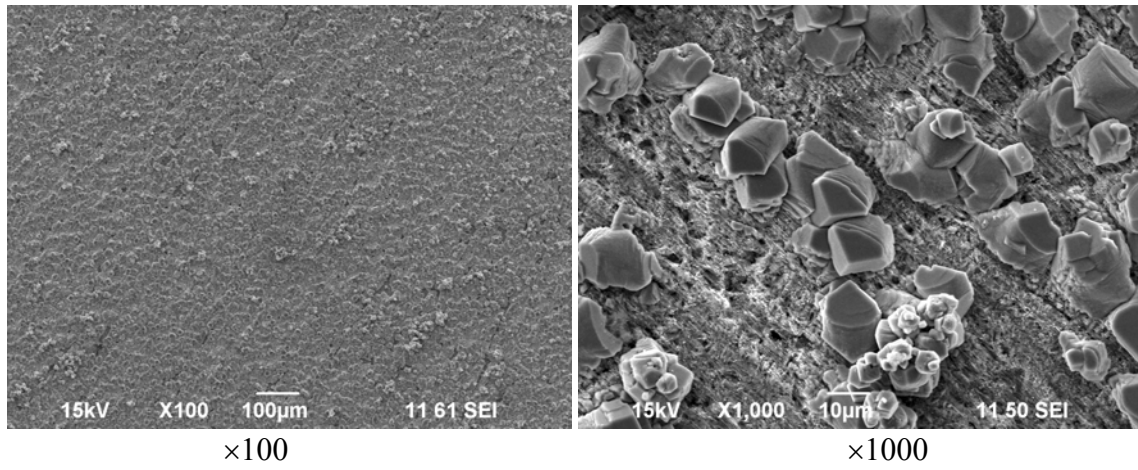


Figure 19. FeCO_3 layer formation and removal test in TCFC, 80°C , pH 6.6, 1 wt.% NaCl, initial SS of $\text{FeCO}_3=300$.



(a) Before the increase of shear stress



(b) After the increase of shear stress

Figure 20. SEM images of sample surface before (a) and after (b) the increase of shear stress in TCFC, 80°C, pH 6.6, 1 wt. % NaCl, initial SS of $\text{FeCO}_3=300$.