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APPLICATION OF EQCM TO THE STUDY OF CO_2 CORROSION

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ABSTRACT

As a by-product of the CO_2 corrosion process, iron carbonate ($FeCO_3$) film can serve as a protective barrier. Film damage, however, can lead to initiation of severe localized attack. To develop a better understanding of the initiation process for localized corrosion, an Electrochemical Quartz Crystal Microbalance (EQCM) is being employed in a $FeCO_3$ film formation and removal study. The EQCM provides *in situ* simultaneous measurement of mass change on the surface and electrochemical measurement of the corrosion process. Iron coated quartz crystals are employed to simulate the surface of carbon steel. Calibration of the EQCM was conducted by galvanostatic corrosion of an iron coated quartz crystal and has shown good accuracy. Film formation tests of the precipitation of $FeCO_3$ film has been conducted on both gold coated and iron coated quartz crystals. It has provided an *in situ* measurement of mass change and a precipitation rate has been obtained. Iron carbonate film formation was confirmed by analysis of the surface of the quartz crystal surface by SEM/EDS. EQCM is currently under evaluation for further film removal studies.

Keywords: EQCM, CO_2 corrosion, iron carbonate film, film formation and removal

INTRODUCTION

Carbon steel is the commonly used material in the oil and gas production and transportation industry. In CO_2 corrosion environment, carbon steel is attacked by the carbonic acid and releases Fe^{2+}. As the concentration of Fe^{2+} and CO_3^{2-} in the solution reaches the solubility product (Ksp) of $FeCO_3$, a layer of $FeCO_3$ film forms on the carbon steel surface by precipitation. By reducing the mass transfer of corrosive species to the steel substrate, the carbon steel surface is protected by the layer of $FeCO_3$ film.

However, if there is any damage of the protective $FeCO_3$ film, it may lead to serious localized corrosion problems by exposing the underlying metal to the aggressive corrosive environment. It can result in catastrophic failure and significant economic cost. But until now, the mechanism of the initiation of localized corrosion, in other words, the removal mechanisms of iron carbonate film is not yet well modeled or understood.

Some research of film removal has been done and corrosion rate was the only in situ measurement during the tests[1-3]. However it is not a direct reflection of iron carbonate film removal. So alternative/more direct test methods are needed. The purpose of this work is to test a new technique that can facilitate the study of CO_2 corrosion, especially for the case of $FeCO_3$ film formation and removal.

The Electrochemical Quartz Crystal Microbalance (EQCM) is a mass change sensing device which is used to measure a very small change in mass as indicated by the change of frequency of a piezoelectric quartz crystal in real time. It has a resolution in the nanogram range and enables simultaneous electrochemical measurement. Since in 1980s it has been proven that the operation of EQCM in liquid is possible[4], it has been used in different fields, such as study of corrosion, inhibition, absorption etc.[5-8] It was assumed that it could be very helpful also in the study of CO_2 corrosion due to its capability of *in situ* measurement of the mass change. However, no such research has been done yet. In the current paper, calibration of EQCM was first done to validate the measurement of the in situ mass change during CO_2 corrosion. Later, to facilitate the further study of film formation and removal, a layer of iron carbonate film was formed on the quartz crystal surface.

The correlation between mass and frequency of EQCM is described by the Sauerbrey equation:[9]

$$\Delta f = -\frac{2 f_0^2}{\sqrt{\mu_q \rho_q}} \cdot \Delta m \qquad (1)$$

Where,
Δf : frequency change, Hz,
Δm : the change in mass per unit area, g cm^{-2}
f_0 : the resonant frequency of the fundamental mode of the crystal, Hz,
μ_q : shear modulus of quartz, g $cm^{-1}s^{-2}$
ρ_q : density of quartz, g cm^{-3}

EXPERIMENTAL PROCEDURE

In Figure 1 it shows the QCM equipment[a]. It included a digital controller, crystal holder, crystal oscillator. Also it shows the AT-cut 5 MHz gold coated[a] and iron coated[b] quartz crystals used in the experiment. The gold coated quartz crystals are inert and stable, and there is no corrosion on the surface. The iron coated quartz crystals are used to simulate the condition of the real carbon steel surface. The surface area of the electrode is 1.37 cm^2. The thicknesses of the coated iron on the quartz crystals used in the tests are 0.5 and 1 microns. The QCM is used as an EQCM in the glass cell setup, which is shown in Figure 2. An Ag/AgCl reference electrode was used and a piece of platinum wire was served as a counter electrode. A pH probe was immersed into the solution to monitor the pH.

The experiments are all conducted in distilled water with 1 wt % NaCl, which was deaerated by CO_2 in advance. The pH of the solution was then adjusted by $NaHCO_3$ to the desired test condition. During the test, the CO_2 was bubbled to maintain the CO_2 saturated corrosion environment. Gold coated and iron coated quartz crystals were cleaned with N_2 gas stream before tests to remove any dust on the surface. For each test, the quartz crystals were first installed on QCM and maintained under ambient condition for a few minutes to warm up and get a stable resonance frequency (± 0.5 Hz). Then the crystal was put into the prepared solution for testing. The test matrix was shown in Table 1. After the tests, the quartz crystal surface was analyzed by SEM and EDS.

RESULTS AND DISCUSSION

EQCM calibration

Before applying EQCM in the film formation and removal study, it was necessary to prove that EQCM is able to give reasonable and accurate results. So the first step was to calibrate EQCM under the desired test conditions. As shown in Table 1, the EQCM was calibrated under room temperature and 80^oC with gold and iron coated quartz crystals.

According to Kanazawa[10], when a gold coated (5 MHz) quartz crystal exposed to 1% NaCl solution at 25^oC, a change of about 750 Hz in resonance frequency is expected, which is equal to 13.2 $\mu g/cm^2$ changes in mass. Figure 3 shows the resulted 13.6 $\mu g/cm^2$ change in mass when a gold coated quartz crystal was exposed to 1 wt% NaCl solution, purged with CO_2, 1 bar total pressure at 25^oC, and showed a reasonable agreement with the expectations. The resonance frequency of the quartz crystal also changes with temperature (around 8 $Hz/^oC$). As shown in Figure 4, when the gold coated quartz crystal was exposed to an 80^oC 1 wt% NaCl solution, the resonance frequency first increased (resulting in a decrease of mass) and then decreased (corresponding to an increase in mass) until it became constant.

When the iron coated quartz crystals was exposed into corrosive CO_2 environment, the iron began dissolving away. The mass change detected by the EQCM and the corrosion rate of iron measured by electrochemical means can be correlated by using Faraday law to confirm the validity of EQCM measurement. Figure 5 shows the signal change of an iron coated quartz crystal when exposed to 1 wt%

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[a] Stanford Research Systems Inc., CA.

[b] Inficon Inc., NY.

NaCl solution at pH4 and room temperature. There was a signal change due to the liquid effect followed by a linear mass loss due to corrosion. At the end of this test, there was no mass change detected since the complete iron coating corroded away. This was proven by EDS analysis made on the crystal after this test which shows pure Si and O element with no iron left. The total weight loss measured by EQCM was 386 $\mu g/cm^2$, which matched well with the amount of iron coated on the crystal (394 $\mu g/cm^2$). The weight loss marked in Figure 5 was measured by an analytical balance. The error of the balance is within 0.1 mg, which is of the same order of magnitude as the mass change during the test. Therefore the analytical balance could not be used for validation purposes in this case. During the initial tests, no electrochemical measurements were done. Another test series under the same condition was made, except that simultaneous electrochemical measurement was conducted, as shown in Figure 7. Compared with Figure 5, these results show good agreement and repeatability and no sign of problems due to interruption by electrochemical measurement on the QCM was detected. The corrosion rate measured by EQCM was 2 mm/year, which is similar to the corrosion rate of carbon steel under the same condition obtained previously.

Calibration tests were also made by applying a galvanostatic current to the iron coated crystal. As shown in Figure 8 (see highlighted part) a galvanostatic current which is equal to 10 mm/yr corrosion rate was applied to the crystal. As measured by the EQCM the mass change on the crystal surface indicated a 9.7 mm/yr corrosion rate. A repeated test was made as shown in Figure 9 and indicated good agreement and repeatability. Another two tests were made at 80^oC to confirm the validation of EQCM measurement at high temperature. As shown in Figure 10, the iron coated quartz crystal was exposed to 1 wt% NaCl solution at 80^oC and corroded until all the coated iron was lost. A controlled galvanostatic corrosion test was also conducted and it showed reasonable results as seen in Figure 11.

Film formation on EQCM

Since EQCM showed reasonable accuracy in the abovementioned calibration tests, further tests were made with the EQCM. The ultimate goal was to use EQCM in the iron carbonate film removal study, so first a realistic iron carbonate films needed to be formed on the quartz crystals.

Gold coated quartz crystal is very stable and has no corrosion when exposed to solution. This is a benefit when studying film removal. Therefore an attempt to form an iron carbonate film on gold coated quartz crystals was made. Since $FeCO_3$ film formation is controlled by precipitation, an initial high supersaturation (SS) with respect to $FeCO_3$ was used to achieve the film formation on a gold coated quartz crystal. Figure 12 shows the mass increase using initial SS=900 (wrt. $FeCO_3$). It was noticed that the precipitation rate changed as the Fe^{2+} was consumed as time passed. Figure 13 are the SEM pictures of the surface of the crystal after the test. It can be seen that the surface of the quartz crystal was non-uniformly covered by $FeCO_3$ crystals, which is further confirmed by EDS analysis in Figure 14. In order to build a more uniformly covered film on a gold coated quartz crystal, a polarization method was tried to simulate the lower corrosion potential seen on carbon steel in the same environment. The mass change shown in Figure 15 is due to the film precipitation on the crystal surface when being polarized at -700 mV vs. sat. Ag/AgCl electrode. The SEM and EDS analysis of the surface after the test were shown in Figure 16 and Figure 17. The $FeCO_3$ film was more uniformly distributed on the surface, but still not as dense as on the carbon steel surface. One phenomenon noticed is that the shadow shown in Figure 17 (c) was proven to be NaCl which was probably formed by dehydration after the test. In order to get a better coverage by the $FeCO_3$ film, a higher initial supersaturation was used in the subsequent test. A denser film was obtained, but it was believed that this could still be improved. Figure 18 shows the mass change curve and Figure 19 shows the SEM pictures of the film surface. Another test was done by polarizing the surface to an even much lower potential, -1000 mV vs. sat. Ag/AgCl. The results are shown in Figure 20 and SEM pictures are shown in Figure 21. From the EDS analysis shown in Figure 22, it can be seen that instead of forming $FeCO_3$, Fe^{2+} was reduced to Fe on the crystal surface due to the highly negative potential. It was concluded that forming a realistic iron carbonate film on a gold surface was difficult and that other methods needed to be explored.

Since the surface of an iron coated quartz crystals is more similar to a carbon steel surface, it was expected that a more realistic film would form on it. Figure 23 shows the mass change of an iron coated quartz crystal after being exposed to solution at 80°C and pH6.6 in two repeated tests. First the mass decreased due to corrosion and then increased when saturation point of $FeCO_3$ was reached. SEM pictures of the surface after the test is shown in Figure 24. Some $FeCO_3$ crystals are shown on the picture, but the film is not similar to the one formed on a carbon steel surface, since what was seen here represents only the initial stage of the film formation. An additional Fe^{2+} source was added to the solution in the other tests to get a higher supersaturation of $FeCO_3$ to help building a film. Figure 25 shows that the mass kept increasing after Fe^{2+} was added to the solution, which means the $FeCO_3$ precipitated on the surface due to the high supersaturation. Figure 26 and Figure 27 show the precipitation rate during the film formation. The precipitation rate calculated from the EQCM measurement was very similar to the one calculated from weight gain/loss measurement which was done by Sun[11]. This comparison validated the film formation on the iron coated quartz crystals. Figure 28 shows the SEM pictures of the surface after the test. The $FeCO_3$ crystals were rather sparse on the surface. Another iron (1 μm thick) coated quartz crystal was used instead of the 0.5 μm ones in subsequent experiments. It was expected that there would be more Fe^{2+} released from the surface to help form a better film. The mass change curve is shown in Figure 29. The SEM pictures (Figure 30) show the surface uniformly covered with corrosion product film very similar to the one formed on carbon steel (Figure 31) at similar condition. This appeared to be promising and future film removal experiments are planned based on the current results.

CONCLUSIONS

- EQCM is a powerful device which can give accurate in situ measurement of mass change and execute electrochemical measurement simultaneously.
- By using iron coated quartz crystals, more realistic iron carbonate films are obtained than on gold coated quartz crystals.
- Iron carbonate film precipitation rate has been validated compared with Sun's work, in which weight gain/loss method was used.

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Table 1. Test matrix for EQCM calibration and film formation

	Calibration	Film formation
Material	Gold and iron coated quartz crystals	
Solution	1wt% NaCl	
CO_2 partial pressure (bar)	0.96, 0.52	0.52
Temperature (°C)	25°C, 80°C	80°C
pH	4	6.6
Initial SS of $FeCO_3$	0	0, 160, 600, 900

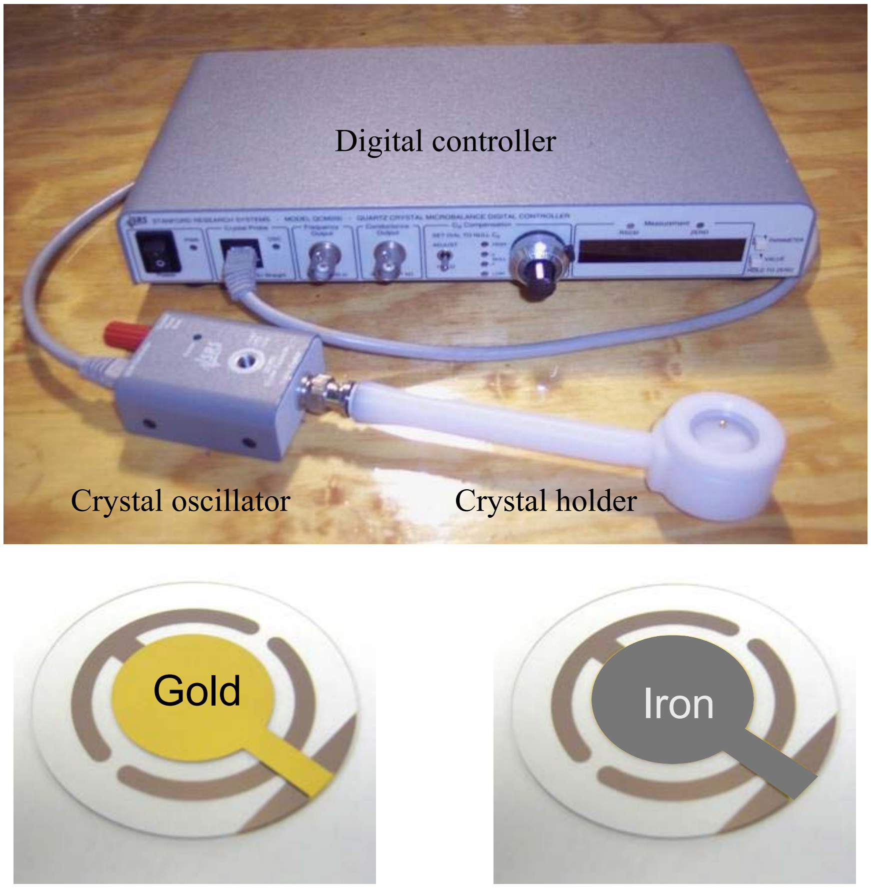


Figure 1. Quartz crystal microbalance and gold and iron coated quartz crystals

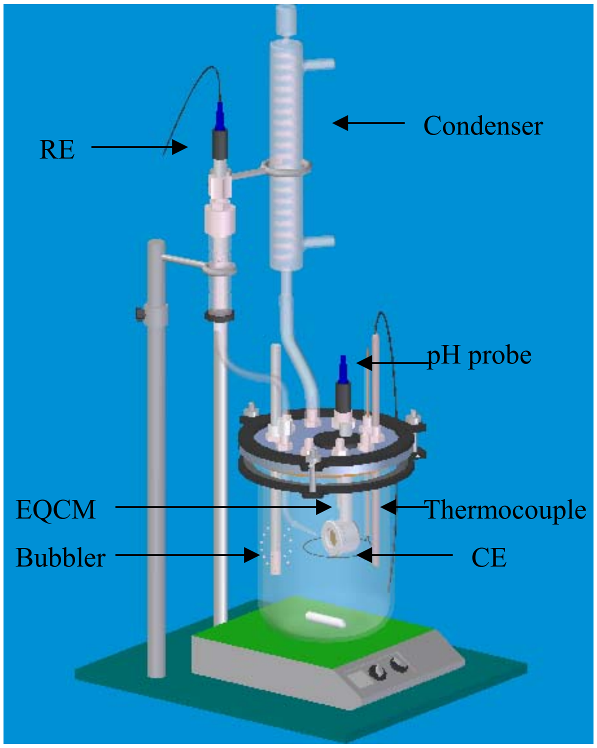


Figure 2. Glass cell setup with EQCM

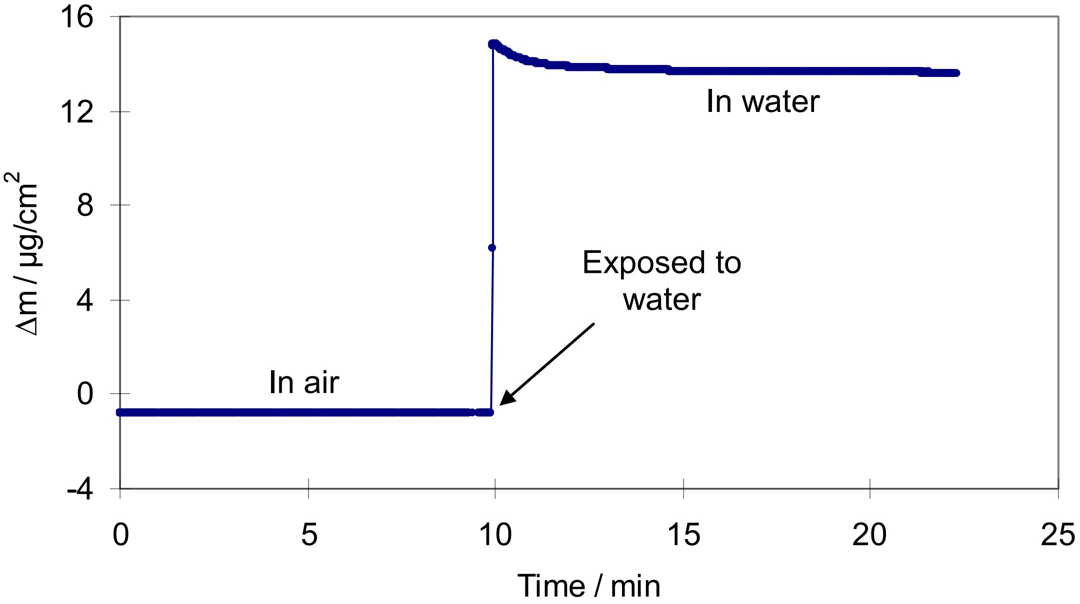


Figure 3. Signal change of QCM when exposed to 1 wt% NaCl (5 MHz, gold coated quartz crystal, 25 °C).

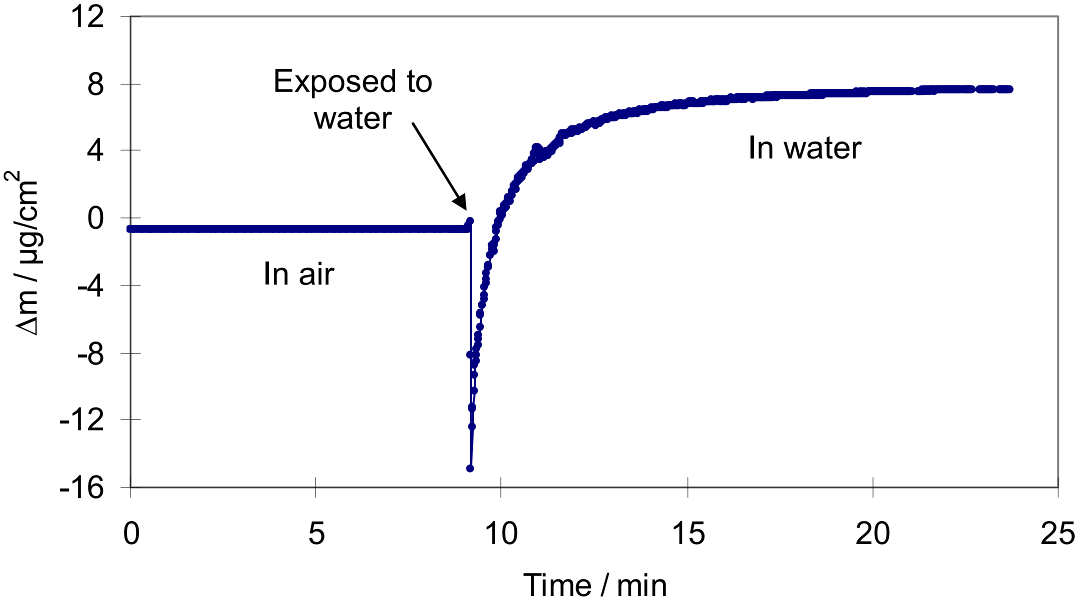


Figure 4. Signal change of QCM when exposed to 1 wt% NaCl (5 MHz, gold coated quartz crystal, 80 ^{o}C).

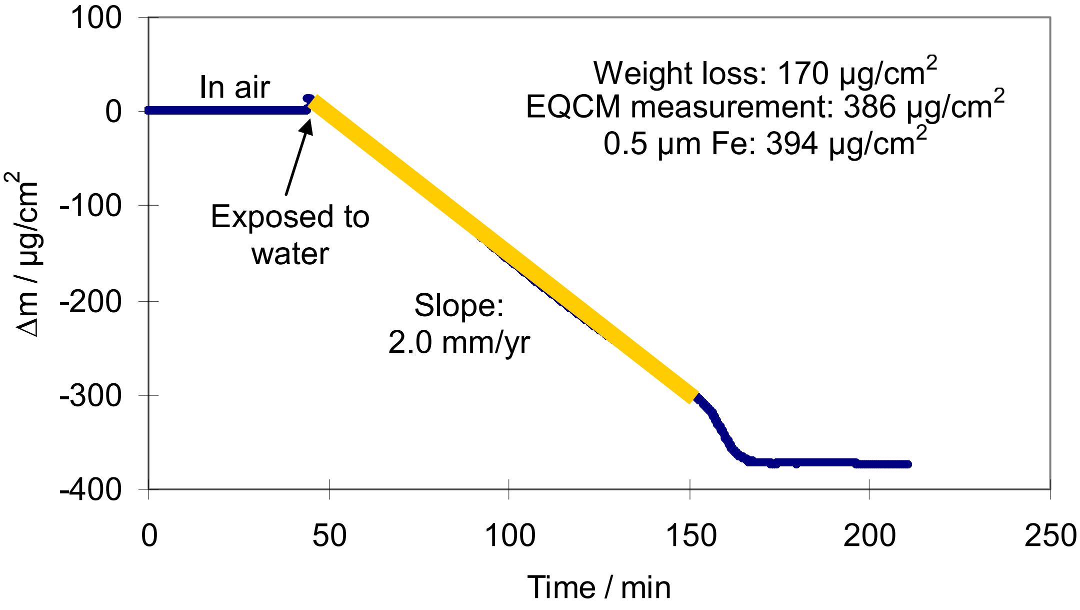
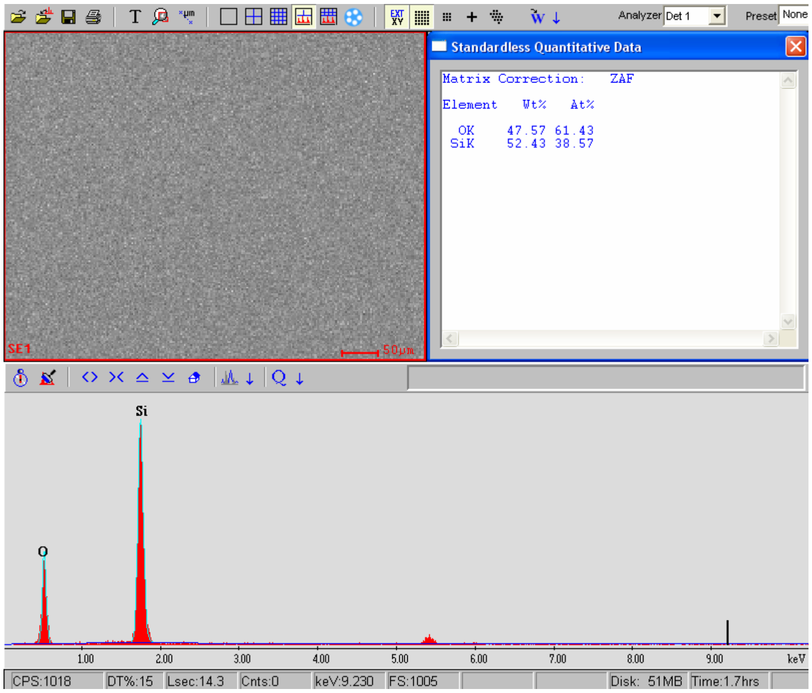


Figure 5. Signal change of QCM when exposed to 1 wt% NaCl without electrochemical measurement (5 MHz, 0.5 µm iron coated quartz crystal, 25 ^{o}C).



Standardless Quantitative Data

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Matrix Correction:   ZAF

Element    Wt%    At%

  OK     47.57 61.43
 SiK     52.43 38.57
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CPS:1018  DT%:15  Lsec:14.3  Cnts:0  keV:9.230  FS:1005  Disk: 51MB  Time:1.7hrs
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Figure 6. EDS analysis of iron (0.5 μm) coated quartz crystal after corrosion test.

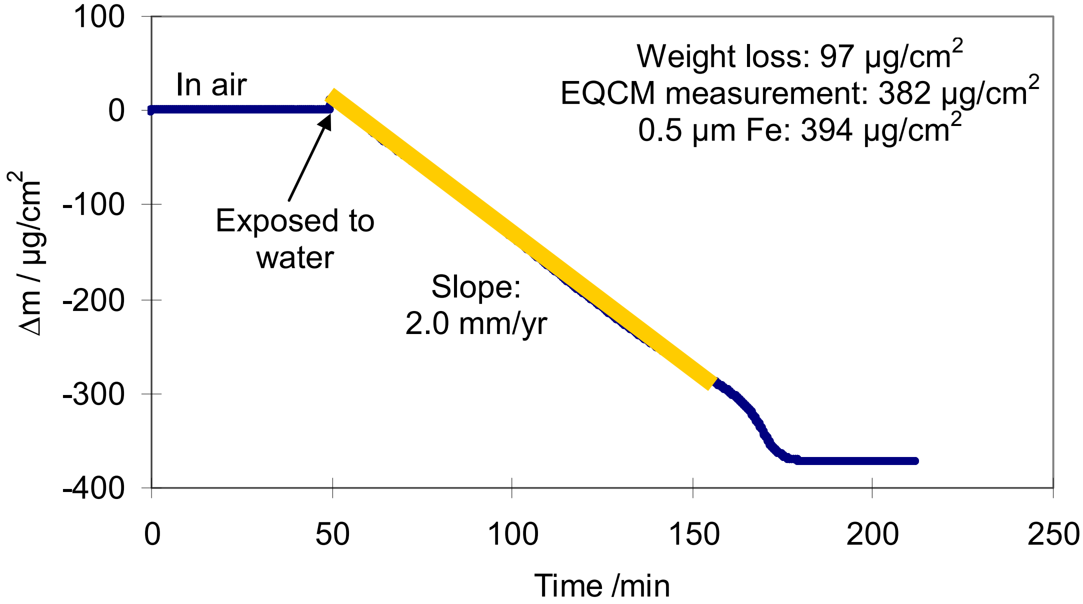


Figure 7. Signal change of QCM when exposed to water with electrochemical measurement (5 MHz, 0.5 μm iron coated quartz crystal, 25 °C).

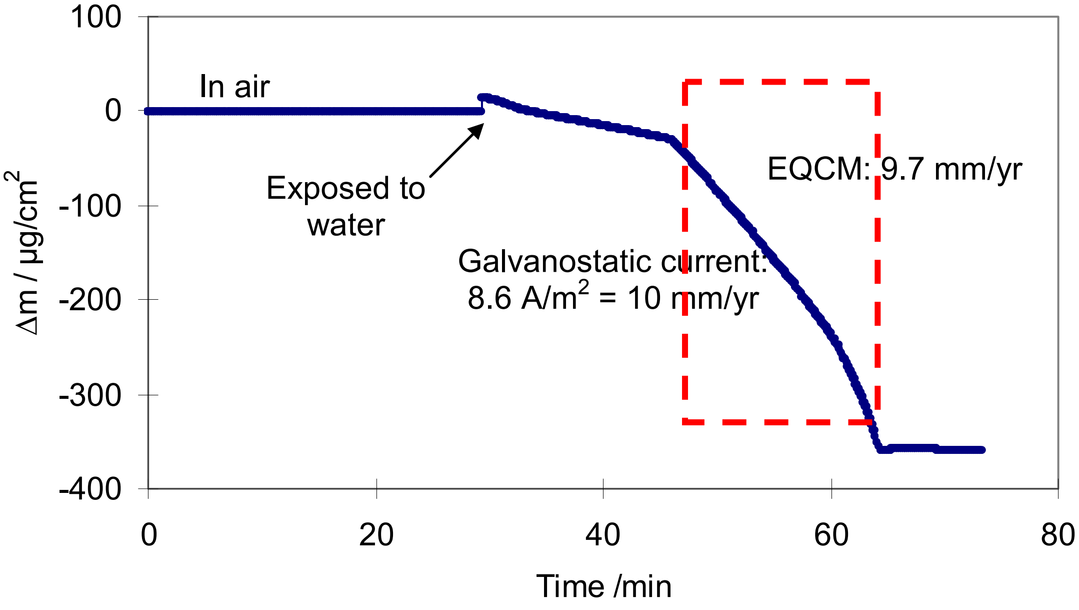


Figure 8. Mass change of iron (0.5 µm) coated quartz crystal when controlled by galvanostatic corrosion (5 MHz, 25 °C).

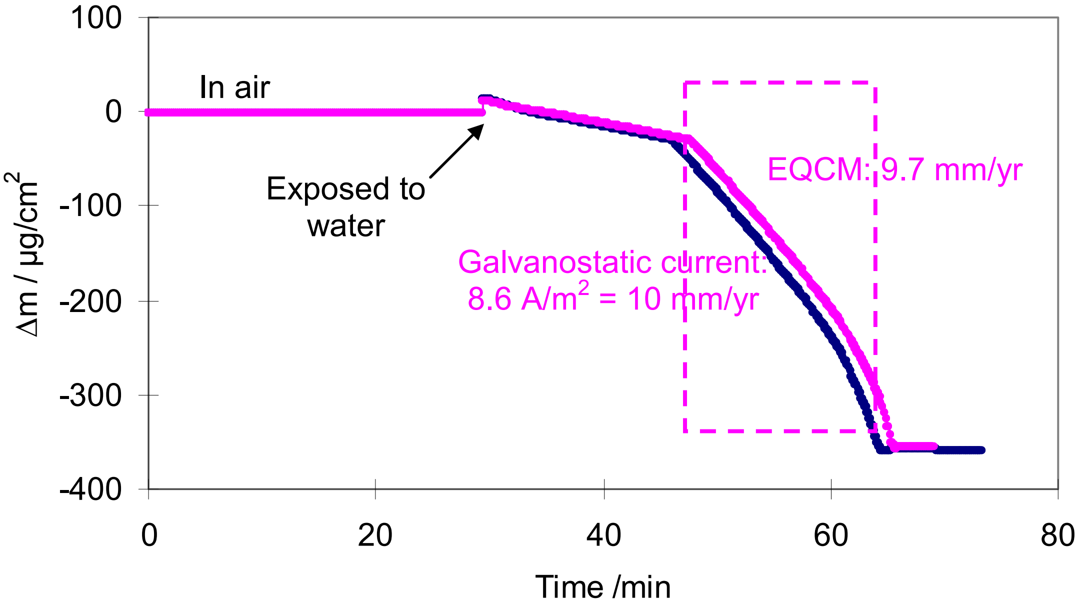


Figure 9. Mass change of iron (0.5 µm) coated quartz crystal when controlled by galvanostatic corrosion at 25 °C (repeat test).

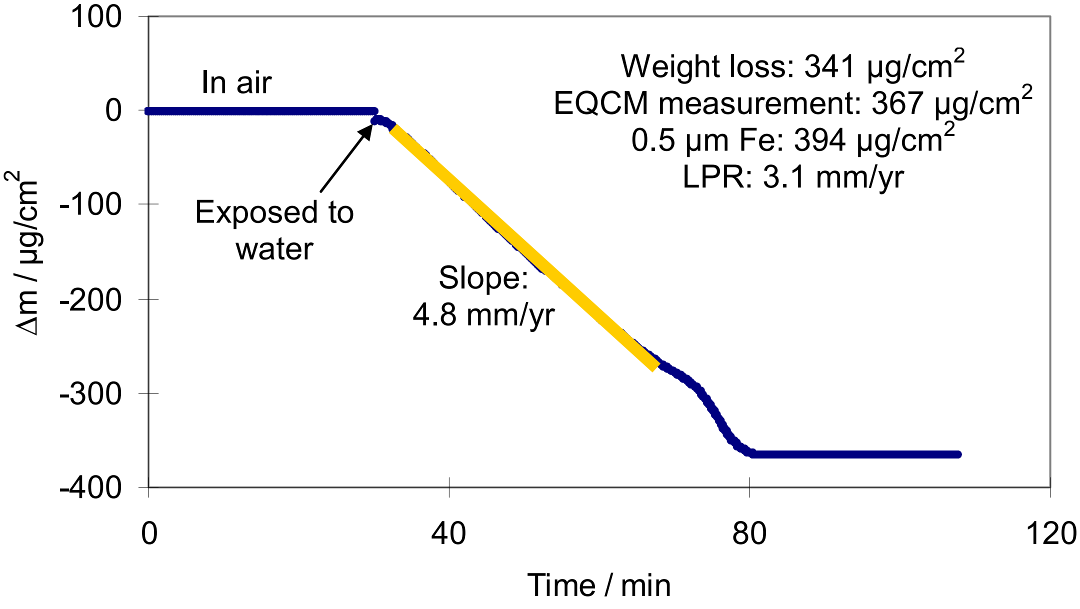


Figure 10. Mass change of iron (0.5 μm) coated quartz crystal when exposed to 1% NaCl solution at 80 °C.

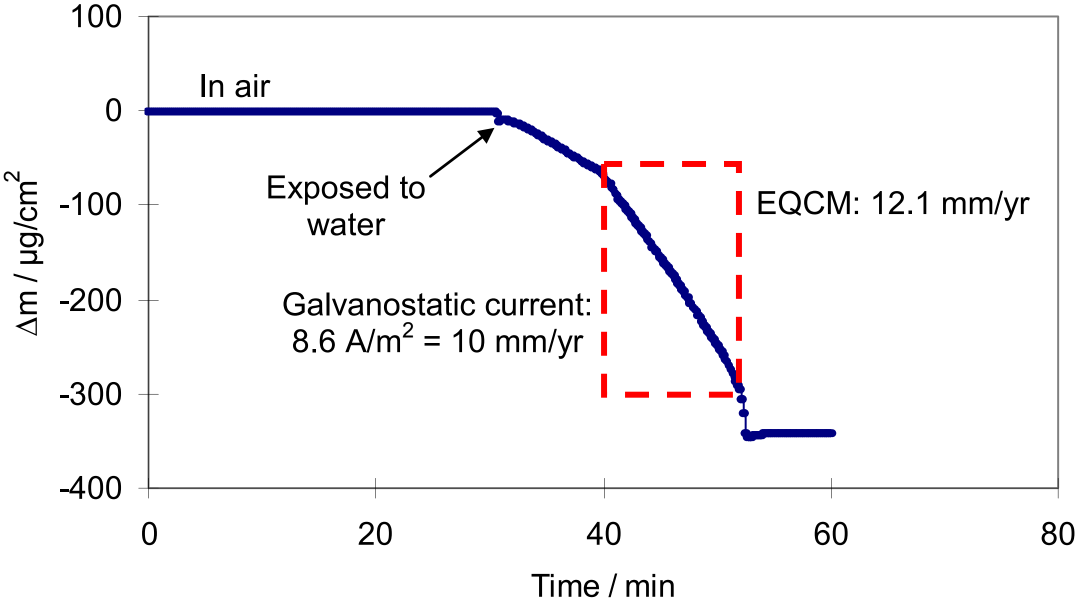


Figure 11. Mass change of iron (0.5 μm) coated quartz crystal when controlled by galvanostatic corrosion at 80 °C.

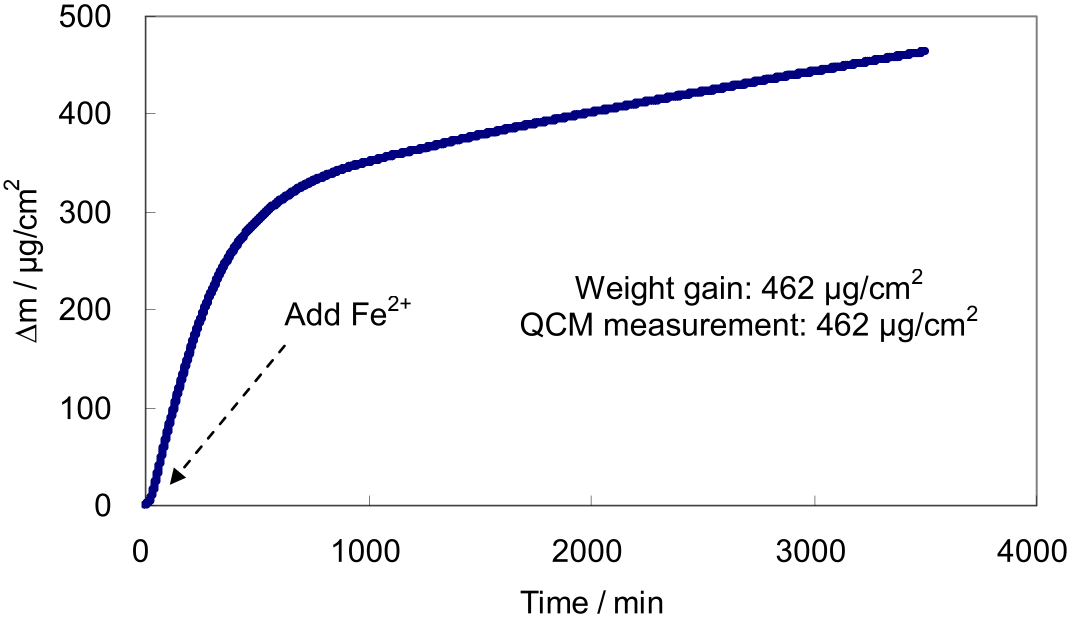


Figure 12. Iron carbonate precipitation on gold coated quartz crystal at pH6.6, initial SS=900, 80°C, 1% NaCl solution.

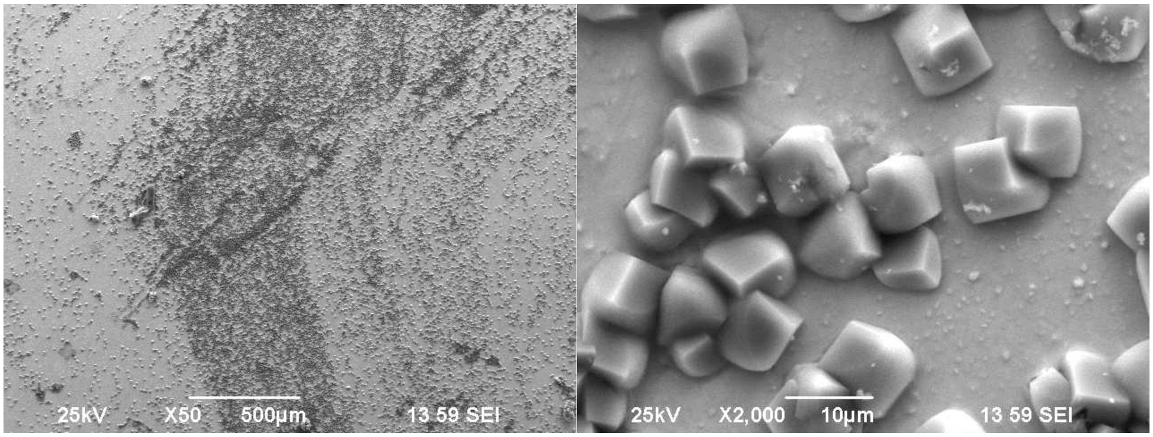
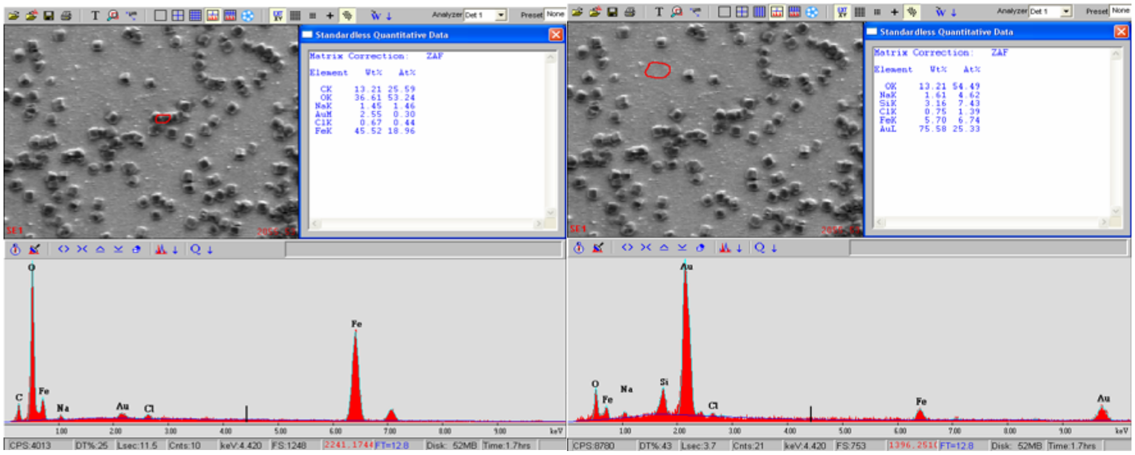


Figure 13. SEM analysis of iron carbonate film formed on gold coated quartz crystal at pH6.6, initial SS=900, 80°C, 1% NaCl solution, (a) 50X; (b) 2000X.



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Matrix Correction:    ZAF

Element    Wt%    At%

  CK     13.21  25.59
  OK     36.61  53.24
 NaK      1.45   1.46
 AuM      2.55   0.30
 ClK      0.67   0.44
 FeK     45.52  18.96
```

```
Matrix Correction:    ZAF

Element    Wt%    At%

  OK     13.21  54.49
 NaK      1.61   4.62
 SiK      3.16   7.43
 ClK      0.75   1.39
 FeK      5.70   6.74
 AuL     75.58  25.33
```

Figure 14. EDS analysis of iron carbonate film formed on gold coated quartz crystal at pH6.6, initial SS=900, 80°C, 1% NaCl solution, (a) $FeCO_3$ crystals; (b) gold.

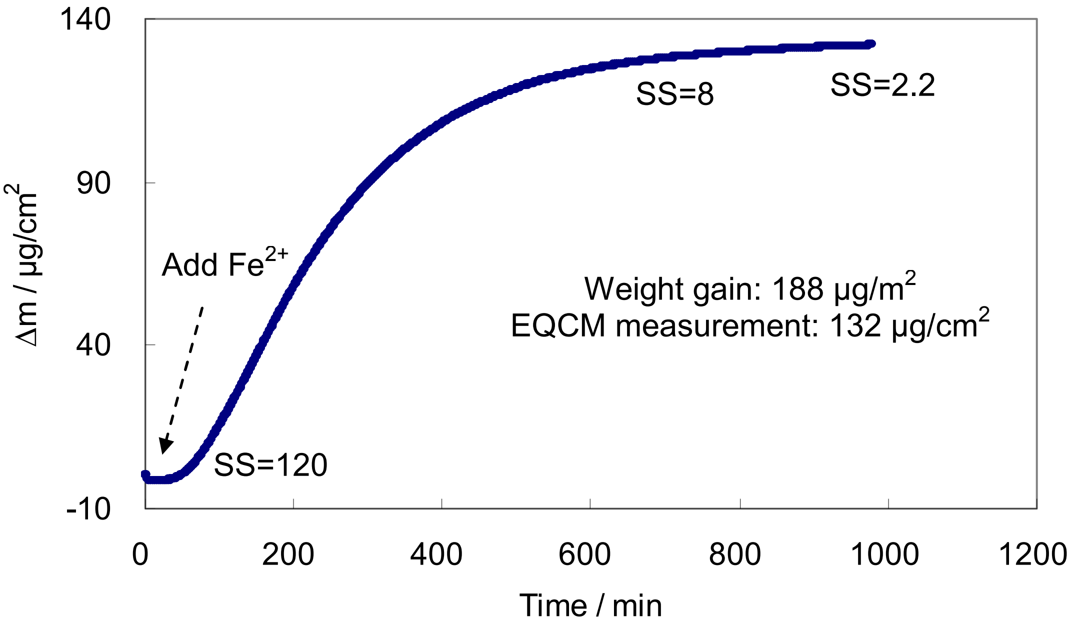
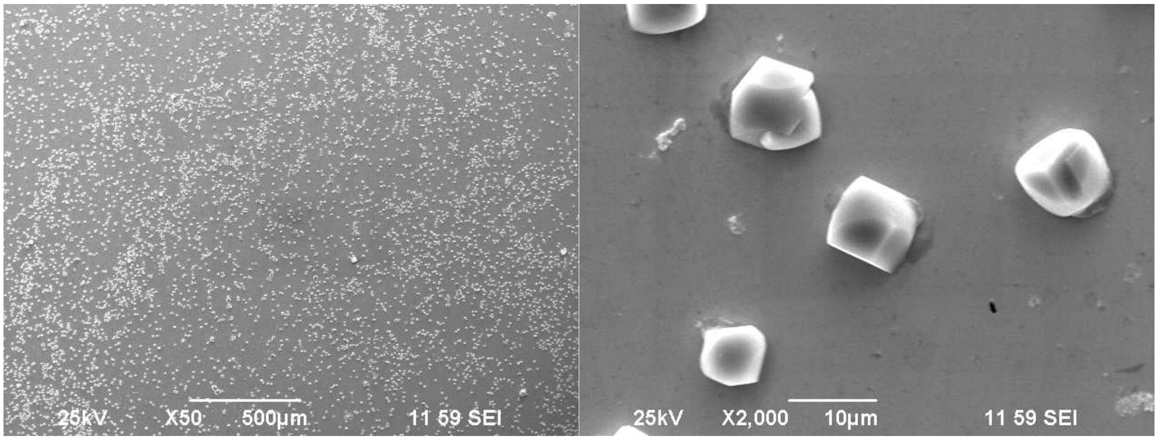
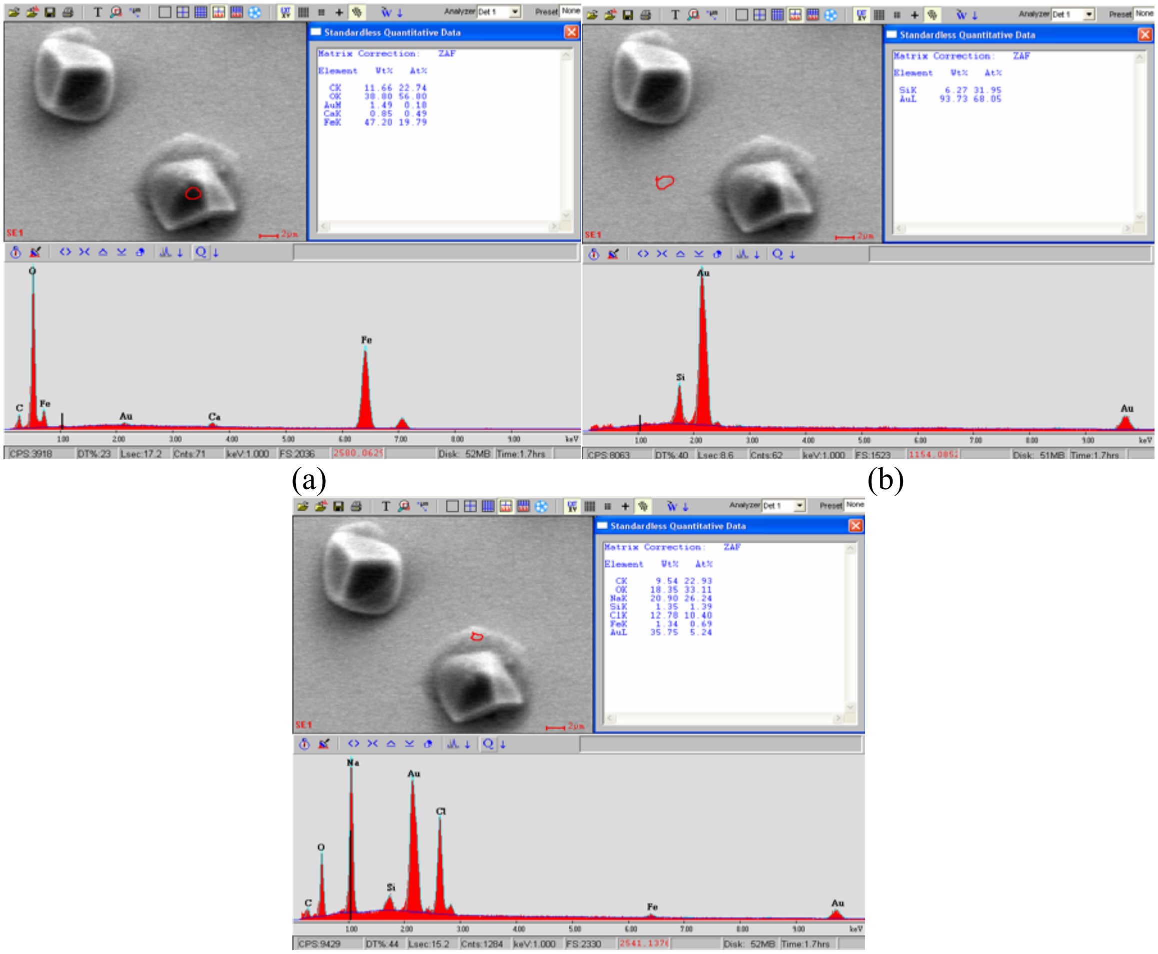


Figure 15. Iron carbonate precipitation on polarized (-700 mV) gold coated quartz crystal surface at pH6.6, initial SS=120, 80°C, 1 wt% NaCl solution.



(a) (b)

Figure 16. SEM analysis of iron carbonate film formed on polarized gold coated quartz crystal at pH6.6, initial SS=120, 80°C, 1% NaCl solution, (a) 50X; (b) 2000X.



(a)

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  OK     38.80 56.80
 AuM      1.49  0.18
 CaK      0.85  0.49
 FeK     47.20 19.79
```

(b)

```
Matrix Correction:   ZAF

Element   Wt%   At%

 SiK      6.27 31.95
 AuL     93.73 68.05
```

(c)

```
Matrix Correction:   ZAF

Element   Wt%   At%

  CK      9.54 22.93
  OK     18.35 33.11
 NaK     20.90 26.24
 SiK      1.35  1.39
 ClK     12.78 10.40
 FeK      1.34  0.69
 AuL     35.75  5.24
```

Figure 17. EDS analysis of iron carbonate film formed on polarized gold coated quartz crystal surface at pH6.6, initial SS=120, 80°C, 1% NaCl solution, (a) $FeCO_3$ crystals; (b) gold. (c) NaCl residue.

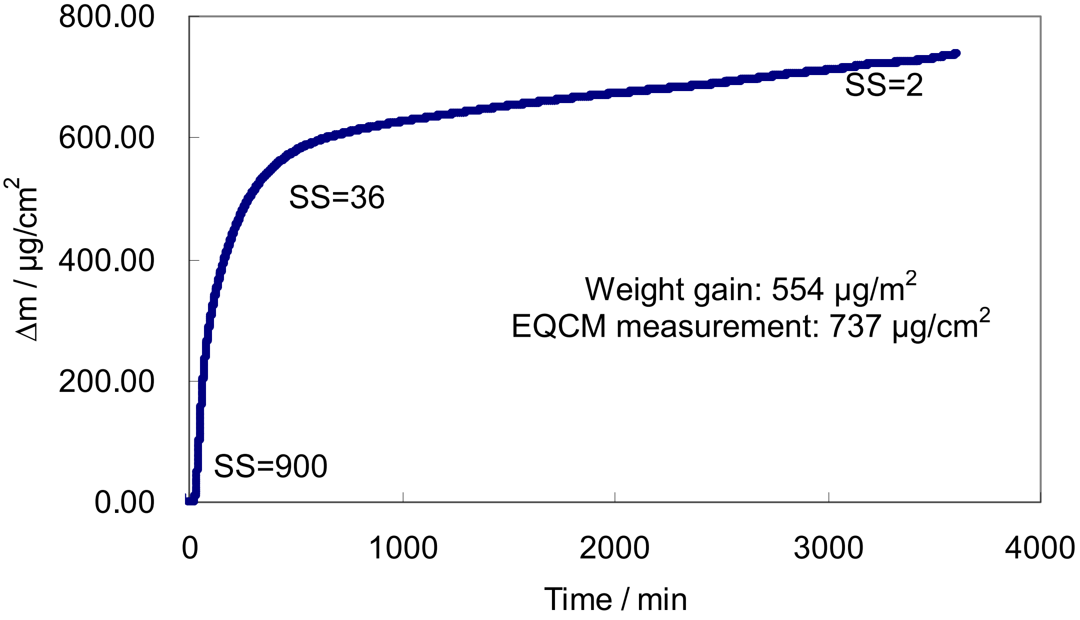
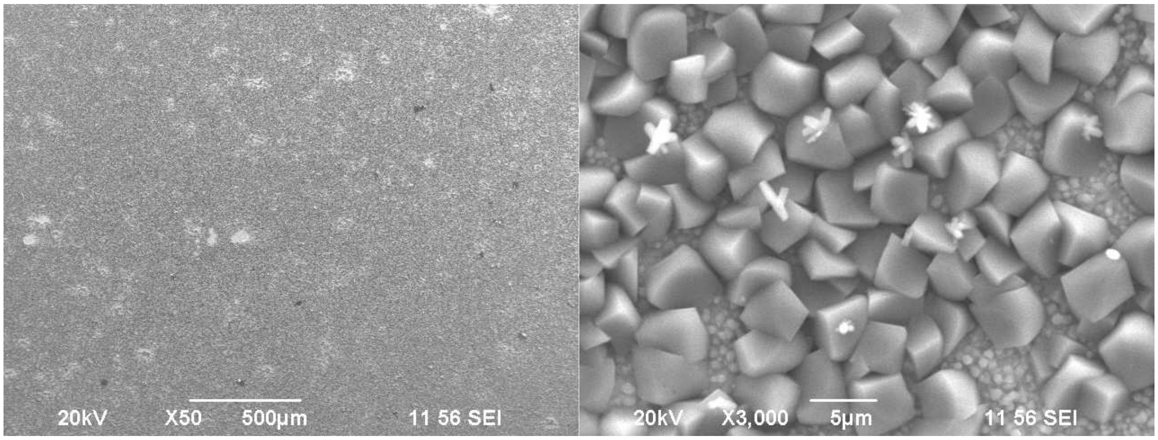


Figure 18. Iron carbonate precipitation on polarized (-700 mV) gold coated quartz crystal surface at pH6.6, initial SS=900, 80°C, 1% NaCl solution.



(a) (b)

Figure 19. SEM analysis of iron carbonate film formed on polarized gold coated quartz crystal at pH6.6, initial SS=900, 80°C, 1% NaCl solution, (a) 50X; (b) 3000X.

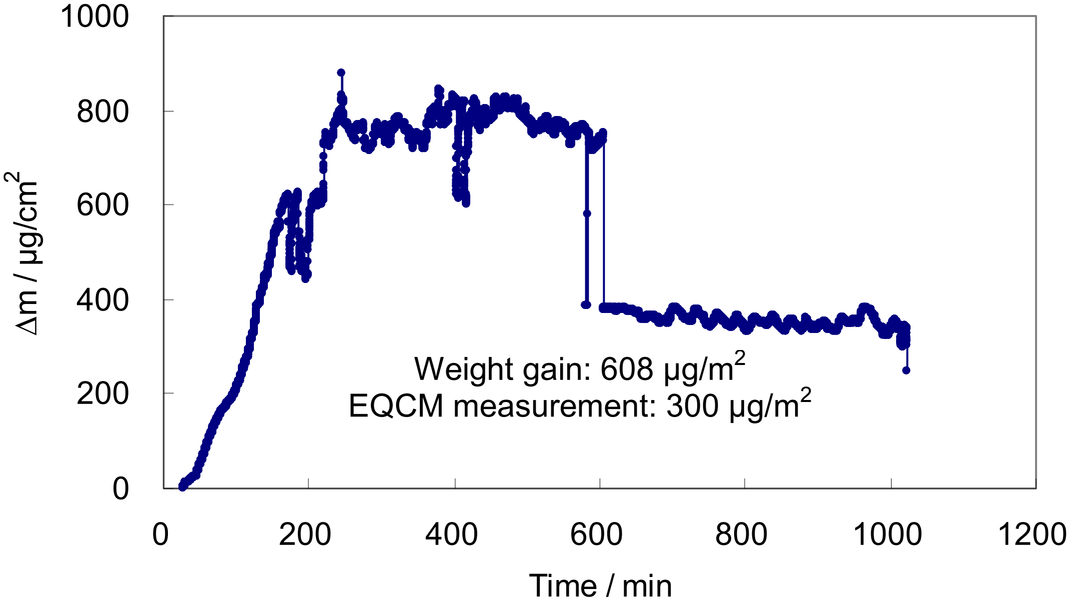
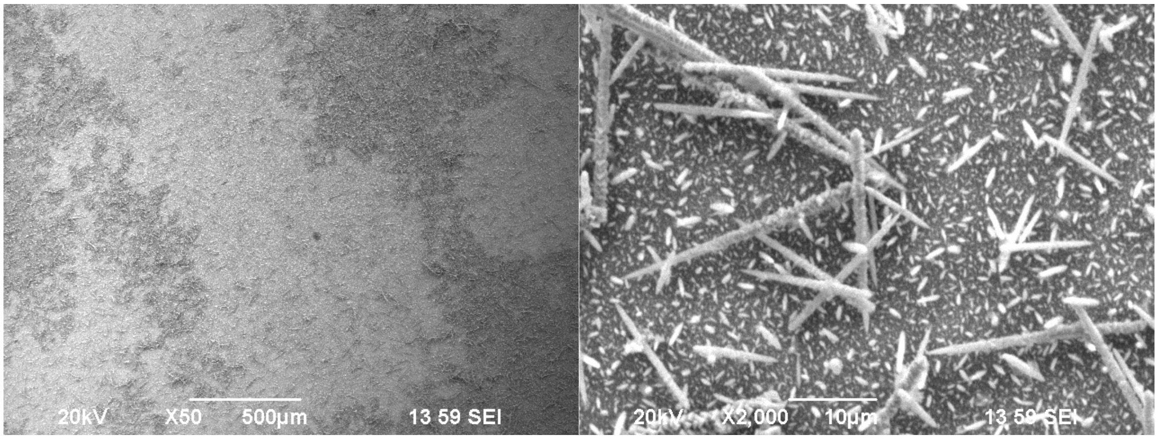
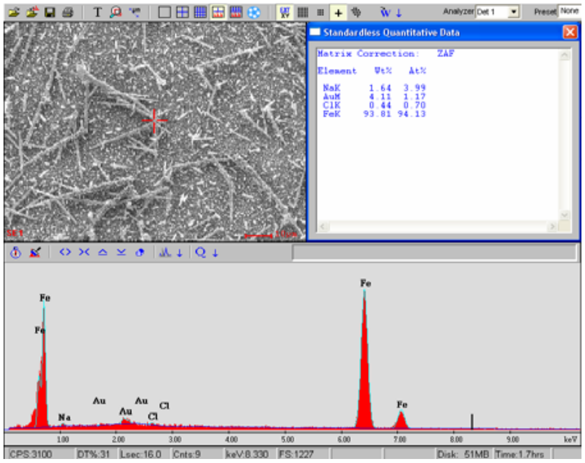


Figure 20. Iron carbonate precipitation on polarized (-1000 mV) gold coated quartz crystal surface at pH6.6, initial SS=900, 80°C, 1% NaCl solution



(a) (b)

Figure 21. SEM analysis of iron carbonate film formed on polarized (-1000 mV) gold coated quartz crystal at pH6.6, initial SS=900, 80°C, 1 wt% NaCl solution, (a) 50X; (b) 2000X.



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Matrix Correction:   ZAF

Element    Wt%    At%

 NaK      1.64   3.99
 AuM      4.11   1.17
 ClK      0.44   0.70
 FeK     93.81  94.13
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Figure 22. EDS analysis of the film formed on polarized (-1000 mV) gold coated quartz crystal surface at pH6.6, initial SS=900, 80^oC, 1 wt% NaCl solution.

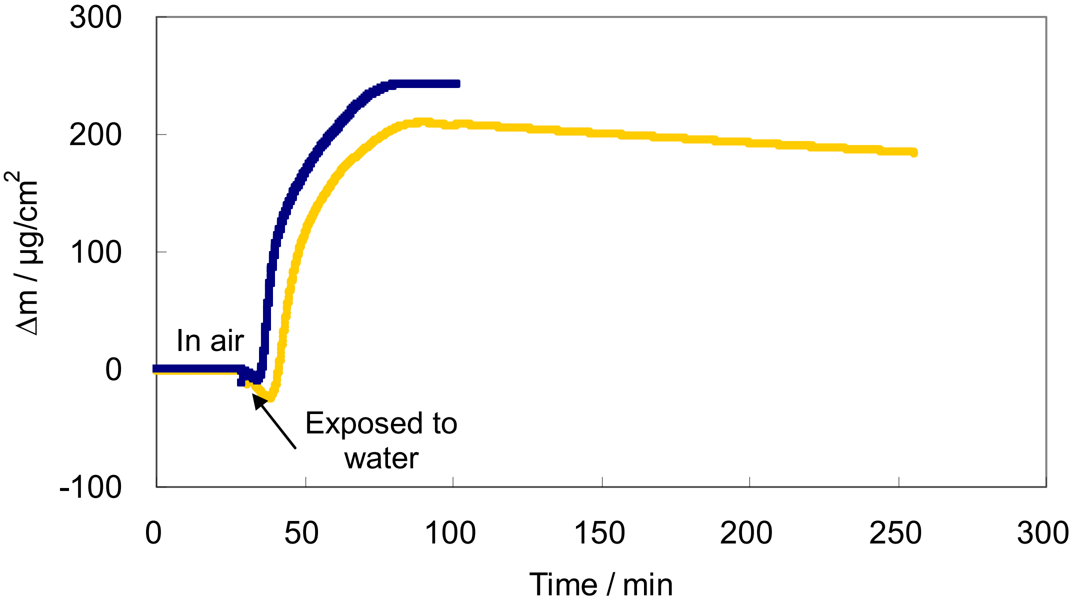
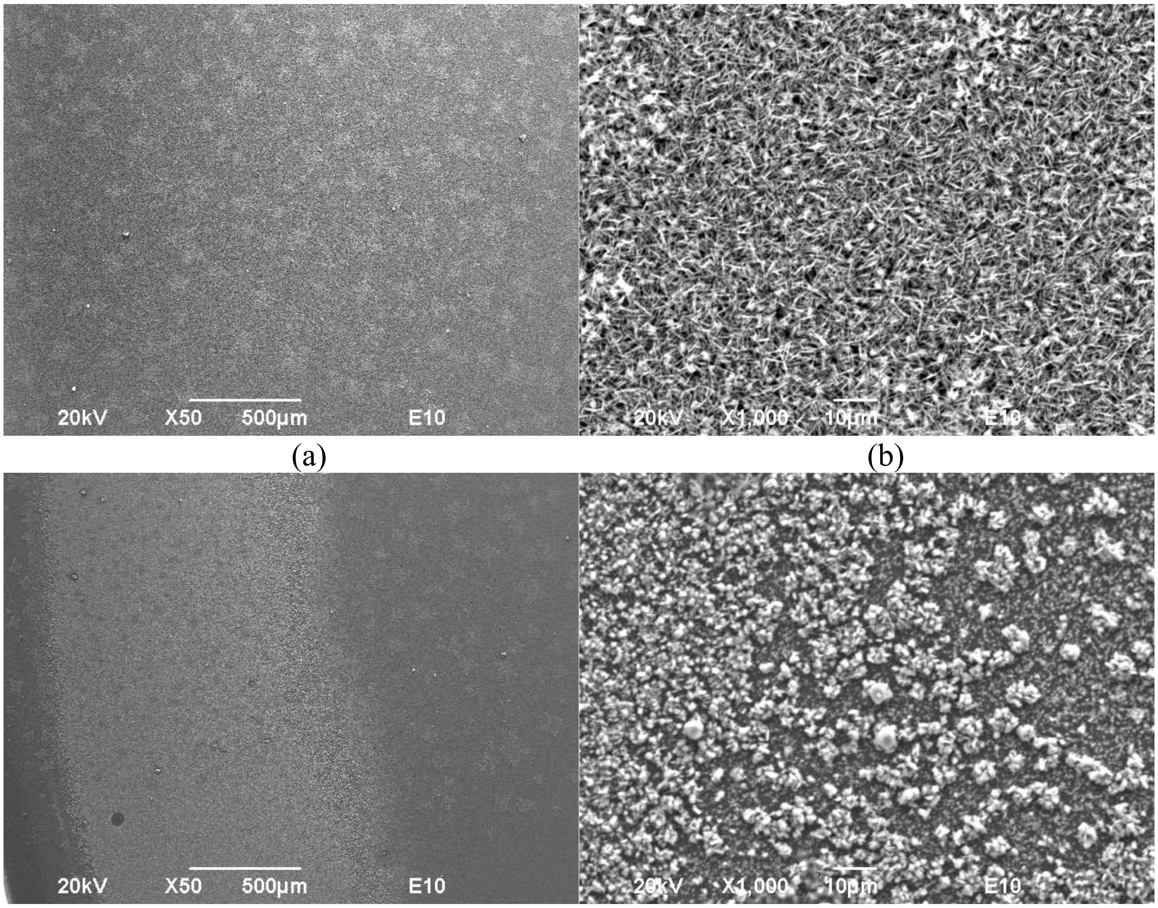


Figure 23. Iron carbonate precipitation on iron (0.5 µm) coated quartz crystal surface at pH6.6, initial SS=0, 80^oC, 1 wt% NaCl solution (repeat).



(a) (b)

(c) (d)

Figure 24. SEM analysis of iron carbonate film formed on iron (0.5 µm) coated quartz crystal at pH6.6, initial SS=0, 80^{o}C, 1 wt% NaCl solution, (a) location 1: 50X; (b) location 1: 1000X; (c) location 2: 50X; (d) location 2: 1000X.

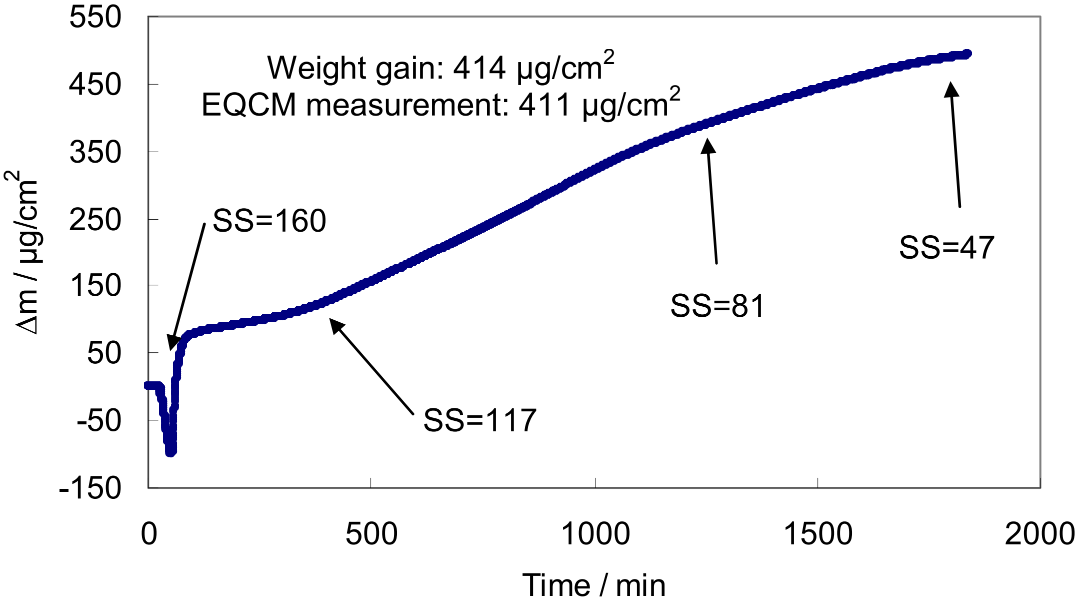


Figure 25. Iron carbonate precipitation on iron (0.5 µm) coated quartz crystal surface at pH6.6, initial SS=160, 80°C, 1 wt% NaCl solution.

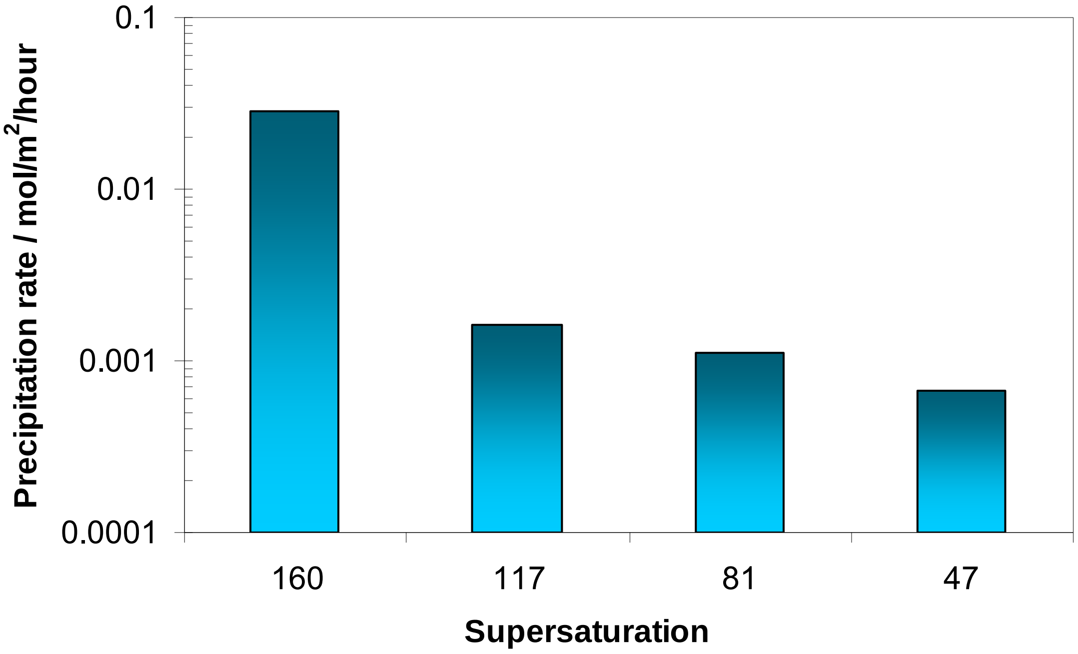


Figure 26. Iron carbonate precipitation rate change on iron (0.5 µm) coated quartz crystal surface at pH6.6, initial SS=160, 80°C, 1 wt% NaCl solution.

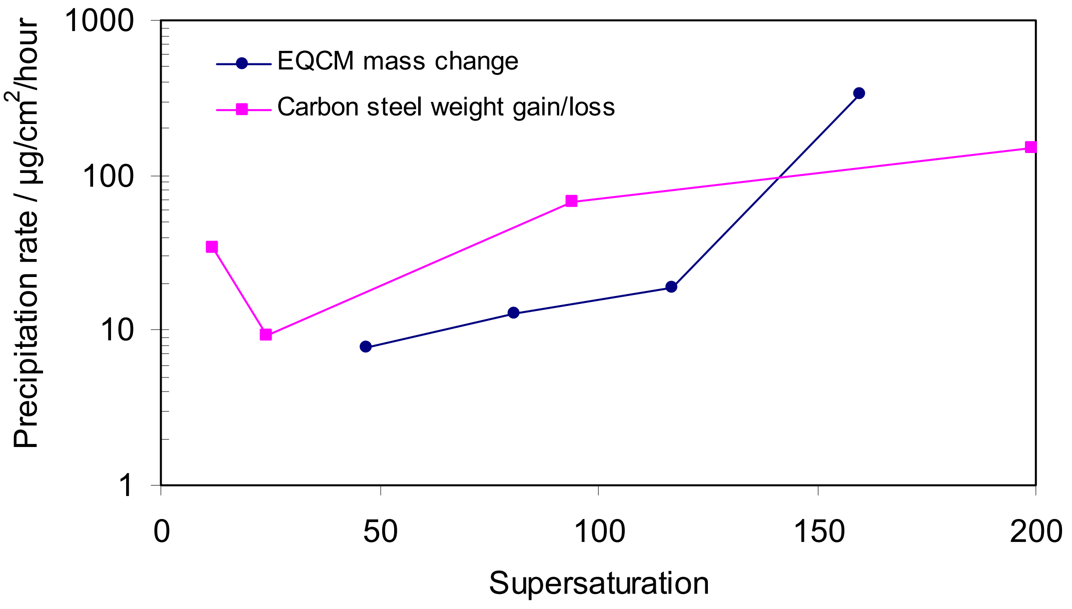
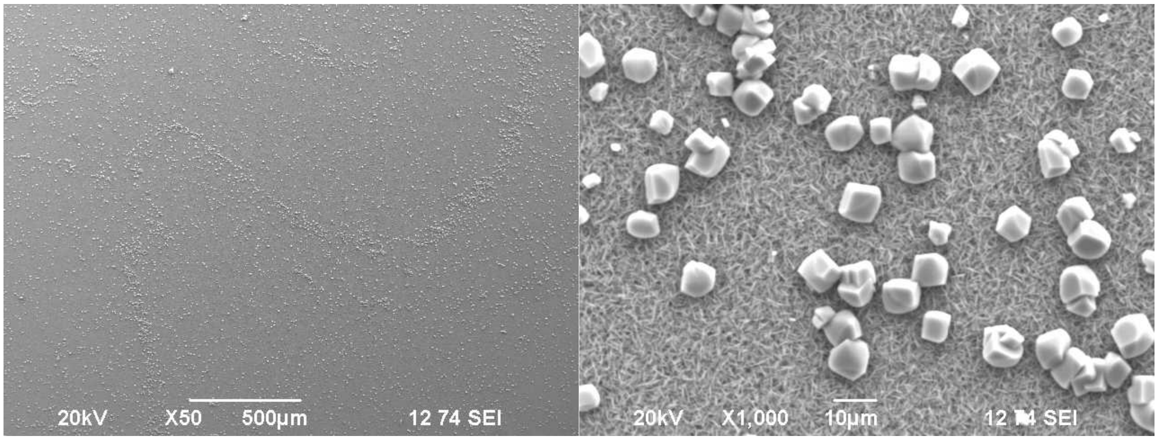


Figure 27. Iron carbonate precipitation rate comparison.



(a) (b)

Figure 28. SEM analysis of iron carbonate film formed on iron (0.5 µm) coated quartz crystal at pH6.6, initial SS=160, 80°C, 1 wt% NaCl solution, (a) 50X; (b) 1000X.

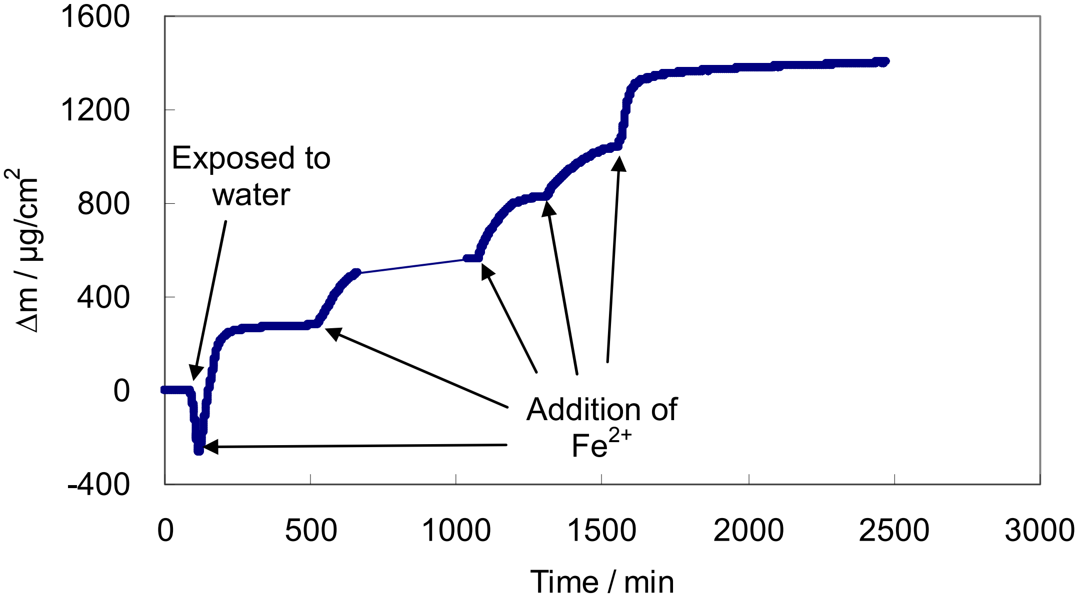
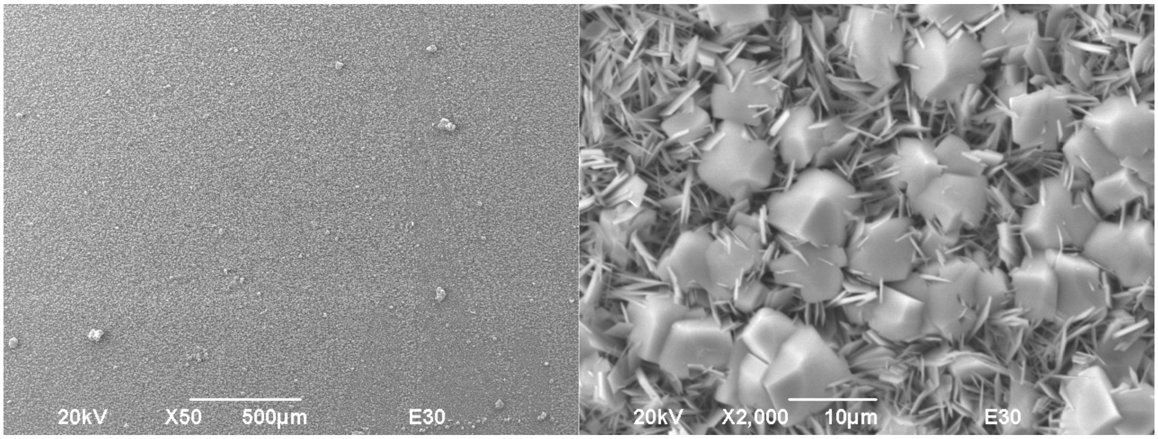


Figure 29. Iron carbonate precipitation on iron (1 μm) coated quartz crystal surface at pH6.6, initial SS=600, 80°C, 1 wt% NaCl solution.



(a) (b)

Figure 30. SEM analysis of iron carbonate film formed on iron (1 μm) coated quartz crystal at pH6.6, initial SS=120, 80°C, 1 wt% NaCl solution, (a) 50X; (b) 2000X.

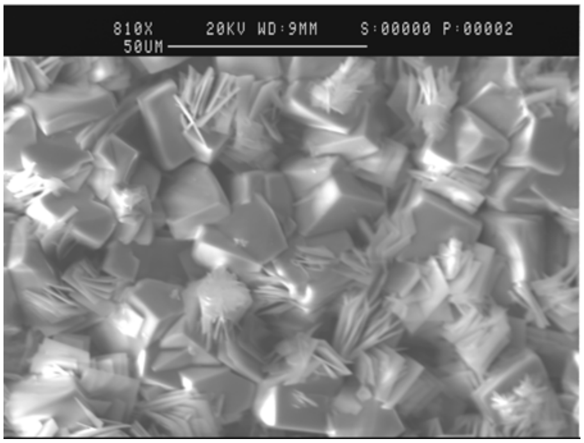


Figure 31. SEM analysis of iron carbonate film formed on carbon steel at pH6.3, initial SS=300, 80^{o}C, 1 wt% NaCl solution, 800X.