CAAP Quarterly Report

Date of Report: *July 10, 2016*

Contract Number: DTPH5615HCAP10

Prepared for: *USDOT Pipeline and Hazardous Materials Safety Administration (PHMSA)*

Project Title: *Chemically Bonded Porcelain Enamel Coated Pipe for Corrosion Protection and Flow Efficiency*

Prepared by: *Missouri University of Science and Technology (Missouri S&T)*

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For quarterly period ending: *June 30, 2016*

Business and Activity Section

(a) General Commitments – Dr. Genda Chen directed various project activities. Mr. Michael L. Koenigstein from Roesch Inc. oversaw the coating process of enamel on steel parts and provided feedback on research results from the material point of view.

Mr. Fan Liang, a Ph.D. candidate in civil engineering at Missouri S&T, was responsible for various material characterization and corrosion tests. Dr. Fujian Tang, a recently Ph.D. graduate under the supervision of Dr. Genda Chen participated in this project and provided input and guidance to Mr. Fan Liang for enamel coating characterization and corrosion tests. Dr. Signo Reis has been contributing to this project in enamel coating process from industrial and material point of view.

During this reporting quarter, a new corrosion instrument (1000E Potentiostat/Galvanostat/ZRA), distilled water and marine epoxy were purchased for this project using credit card. The chemical compositions of two original enamel coating (product ID 15R-972 and 15R-973) were determined by an outsourced company, The Mineral Lab, Inc.

(b) Status Update of Past Quarter Activities – Detailed updates are provided below by task.

Task 1 Optimization of enamel materials for durability, particle distribution, and thermal compatibility with steel

1a Chemical composition

The chemical compositions of two original enamel coatings (product ID 15R-972 and 15R-973) were tested in The Mineral Lab, Inc. The results are given in Table 1 and Table 2, respectively.

Table 1 Chemical composition of enamel 15R-972

Element	SiO_2	B_2O_3	Na_2O	C_aO	M_nO_2	Al_2O_3	T_iO_2	K_2O	Fe_2O_3	M_gO	P_2O_5	*Others*
Wt.%	47.73	23.17	10.6	7.58	3.58	2.16	1.92	1.25	1.12	0.41	0.39	0.09

Table 2 Chemical composition of enamel 16R-001

Element	SiO_2	B_2O_3	Na_2O	C_aO	M_nO_2	Al_2O_3	T_iO_2	K_2O	Fe_2O_3	M_gO	P_2O_5	*Others*
Wt.%	56.13	19.37	6.34	5.67	0.60	6.05	4.38	0.48	0.45	0.40	0.05	0.08

1b Thermal properties

The third type of commercially-available silicate glass slurries (with clay and borax), Tomatec, is added to prepare coatings for steel samples. This porcelain enamel is still vitreous coating that is bonded to substrate metal by fusing glass frits at a temperature of 816°C. Prior to coating steel samples, the thermal properties of glass Tomatec such as glass-transition temperature (T_g), softening temperature (T_s), and coefficient of thermal expansion (CTE) are determined by the Orton automatic recording dilatometer (model 1500).

Fig.1 shows the thermal elongation in the longitudinal direction of Tomatec coating and steel as a function of temperature. The steel has a measured CTE of 19.7 ppm/℃ while the glass Tomatec has a measured CTE of 11.35ppm/℃. The CTE of the steel remains constant over a temperature range of 100 to 600℃, while the CTE of the glass coating is constant only over a range of 200 to 500℃. The CTE difference between the steel and glass coating will generate compressive stress on the coating during cooling, which is desirable. The glass-transition temperature (T_g) is 507°C and the glass softening temperature (T_s) is 578°C.

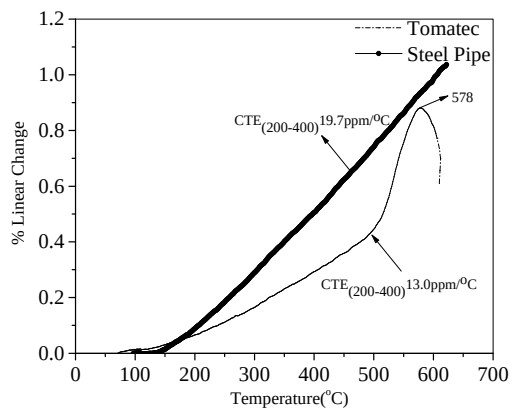


Fig. 1. Thermal properties of Tomatec coating and steel measured with Orton dilatometer

Task 2 Enameling process for coating uniformity, surface roughness, and efficiency without adverse effect on steel properties

2a Steel sample coating

The new coating Tomatec is used to coat steel samples. Prior to coating, all steel samples were steel blasted for 1 min, and cleansed with a commercially available cleansing solvent to remove oil and contamination. The glass slurry was applied manually to steel samples using a spray gun as specified in Table 3. After that, the samples were heated at 150 °C for 10 mins to drive off moisture, then fired at 816°C for 10 min, and finally cooled to room temperature.

Fig. 2 shows the coated samples in the wet process. It can be seen from Fig. 2 that the surfaces of coupons coated with enamel 16R001 have pin holes. But the surfaces of samples coated with enamel Tomatec and its mix ME4 (50 wt.% Tomatec +50 wt.% 16R001) are smooth and do not have defects.

Table 3 Coating parameters

Coating application parameters	Wet by Hand Spaying
Chain speed (m/min)	12FPM
Voltage (KV)	-
Atomisation pressure	3.5
Slip troughput per guns	0.6
Number of guns	1
Distance gun to work piece (cm)	40
Transfer efficiency (%)	40

(a) Tomatec (b) ME4 (c) 16R001

Fig. 2. Coupon steel samples (25 mm × 50 mm) coated with the wet process

2b Coating thickness and roughness

The coating thickness and roughness were measured by MiniTest 6008 and 3D Hirox microscope, respectively. Six test points were selected along the center line and borderline drawn on the surface of a sample, each having three points, as seen in **Fig.3**. The measured coating thickness average and standard deviation values at the six points are summarized in Table 4. Overall, the thicknesses of enamel coating Tomatec and the mixed coating (50 wt% Tomatec +50 wt% 16R001) is less than 200 μm. The thickness of enamel coating 16R-001 is 236$\pm$16μm, which is relatively larger than the thickness of coating Tomatec.

Table 4 Coating thickness measured by MINITEST 6008

Coating	Thickness (μm)
16R-001	236$\pm$16
Tomatec	176$\pm$15
ME4 (50 wt% Tomatec +50 wt% 16R001)	162$\pm$8

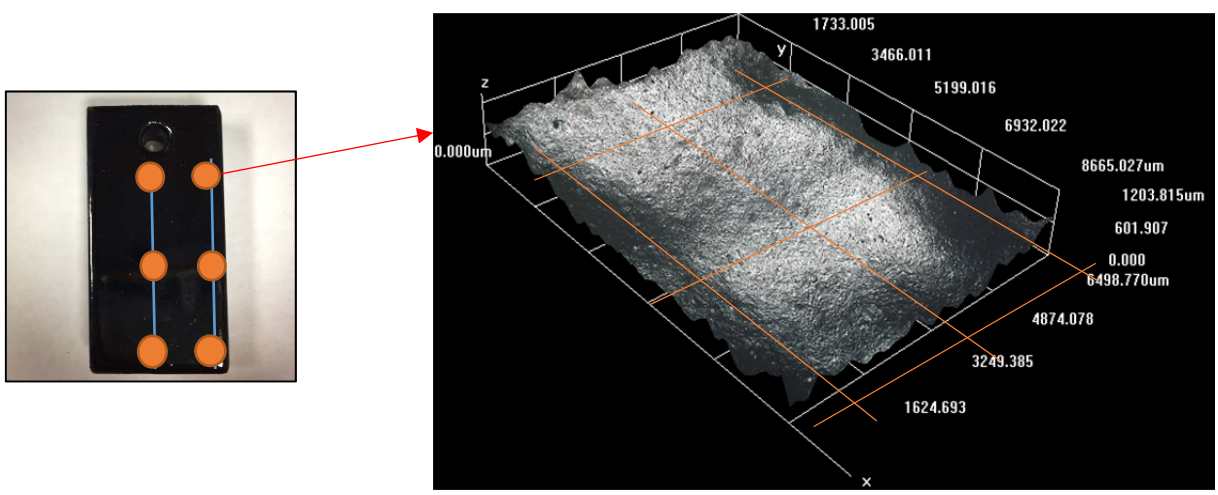


Fig. 3. 3D view of a single point using the Hirox microscope

At each of the six sample points, six topographic lines as represented in **Fig.3** could be drawn using the microscope, which amounts a total of 36 roughness values taken from each sample. The cut-off value of 0.08mm is chosen for all the tests with 3D Hirox microscope. The measured coating roughness of various samples is presented in Table 5.

Table 5 Coating roughness with enamel Tomatec and its mix

Measurement point No.	Tomatec (μm)			ME4(50 wt% Tomatec +50 wt% 16R001) (μm)		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	0.8	0.8	0.5	0.6	0.7	0.8
2	0.7	0.9	0.6	0.7	0.6	1.0
3	0.8	0.7	0.6	0.7	0.6	0.9
4	1.0	0.9	0.7	0.9	0.9	1.1
5	0.8	0.8	0.6	0.7	0.8	0.9
6	0.9	1.0	0.7	0.7	0.8	0.9
7	0.9	0.7	0.7	0.8	0.9	0.8
8	0.9	0.8	0.7	1.1	0.9	1.1
9	0.8	1.0	0.7	1.1	0.8	1.0
10	1.1	0.9	1.1	1.1	0.8	1.2
11	0.8	0.8	0.7	0.9	0.8	1.0
12	1.0	0.8	0.9	0.9	0.9	0.9
13	0.8	0.8	0.8	0.8	0.8	0.8
14	1.0	0.9	0.9	1.1	0.9	1.1
15	1.0	1.3	0.8	0.8	0.9	1.0
16	1.2	1.1	0.9	1.0	0.9	1.1
17	0.9	0.8	0.8	0.8	0.9	1.0
18	1.0	0.9	0.9	0.9	0.9	0.9
19	0.6	0.7	0.8	0.6	0.8	0.8
20	0.5	0.8	0.9	0.8	1.0	0.8
21	0.8	0.8	1.0	0.7	0.9	0.8
22	0.8	1.1	1.2	0.7	1.1	1.0
23	0.7	0.8	1.1	0.7	1.0	0.9
24	0.8	0.8	1.0	0.7	0.9	1.2
25	0.6	0.8	0.8	0.5	0.7	0.7
26	0.7	0.9	0.8	0.7	0.7	0.7
27	1.0	1.0	0.9	0.6	0.8	0.8
28	0.9	1.2	1.0	0.8	0.9	0.8
29	0.7	0.9	0.9	0.6	0.9	0.8
30	0.9	1.0	0.9	0.7	0.8	0.8
31	0.7	0.6	0.7	0.7	0.6	0.7
32	0.7	0.7	0.8	0.8	0.9	0.7
33	0.9	0.8	0.8	0.7	0.8	0.8
34	1.0	0.9	0.9	1.1	0.8	0.9
35	1.0	0.7	0.7	0.8	1.1	0.8
36	0.8	0.7	0.9	0.7	0.7	0.7
Average	0.85	0.86	0.83	0.80	0.84	0.90
STDEV	0.15	0.15	0.15	0.16	0.12	0.14

It can be seen from Table 5 that, for the mix of Tomatec and 16R-001, the roughness values are almost the same as the values for samples coated with Tomatec. Overall, the coating roughness is less than 1 μm and the standard deviation is around 0.1 μm. Table 6 shows the coating roughness summary of three coatings 16R-001, Tomatec, and ME4 (50 wt% Tomatec +50 wt% 16R001).

Table 6 Coating roughness summary

Coating	Roughness (μm)		
	Sample 1	Sample 2	Sample 3
16R-001	0.52±0.11	0.56±0.10	0.62±0.09
Tomatec	0.85±0.15	0.86±0.15	0.83±0.15
50 wt% Tomatec +50 wt% 16R001	0.79±0.16	0.84±0.12	0.90±0.14

Task 3 Characterizations of enamel-coated pipes for microstructure/porosity, chemical adhesion, and corrosion resistance

Electrochemical tests were conducted to understand the corrosion process between a metal and its surrounding electrolyte. Samples were immersed in 3.5 wt.% salt solution, which consists of distilled water and purified sodium chloride, and tested at room temperature with a setup of three electrodes: a 25.4mm×25.4mm ×0.254mm platinum sheet as a counter electrode, saturated calomel electrode (SCE) as a reference electrode, and the steel coupon as a working electrode. All three electrodes were connected to a Gamry, 1000E Potentiostat/Galvanostat/ZRA for data acquisition. The Potentiostat is used to polarize the metal sample to accelerate the corrosion process and make each measurement completed in one hour. It controls the potential between a working electrode and a reference electrode and measures the current between the working electrode and a counter electrode. The applied potential allows a redox reaction to occur and the measured current is indicative of the reaction rate.

The corrosion behavior of various coated samples was studied with open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS). The penetration of the corrosive species in electrolyte along the coating thickness towards the substrate can be evaluated by OCP. The resistance of the coating to corrosion of the substrate is studied by EIS, a non-destructive method.

A full-size pipe was cut in longitudinal and circumferential directions into small samples (25 mm × 50 mm) as shown in Fig. 4. Each sample was soldered with a copper wire to provide an electrical connection during corrosion tests. Except the front enamel coated surface (20 mm × 30 mm), all sides of the sample were covered with Marine epoxy. The tested samples are divided into two batches. The first batch contains enamel 15R-972, enamel16R-001, mixed enamel ME1 (25wt.% 15R-972 + 75wt.% 16R-001), mixed enamel ME2 (50wt.% 15R-972 + 50wt.% 16R-001), and mixed enamel ME3 (75w.% 15R-972 + 25wt.% 16R-001). The second batch contains enamel Tomatec, mixed enamel ME4 (50 wt.% Tomatec +50 wt.% 16R001), enamel GP2118-1550F, GP2118-1500F, and GP2118-1450F.

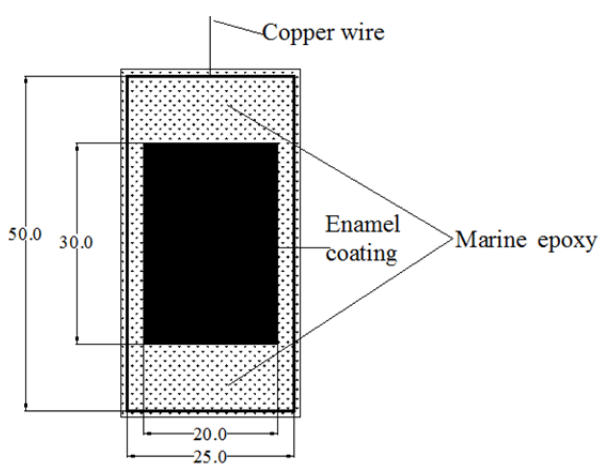


Fig.4. Test sample dimension (unit: mm)

3a-1 Open circuit potential test for the first batch

Open-circuit potentials (OCP) were recorded for one hour after the samples have been immersed in the 3.5wt.% NaCl solution for 0, 3, 6, 13, and 27 day. **Fig. 5** shows the evolution of the OCP of five representative types of enamel coated steel samples after various days of immersion.

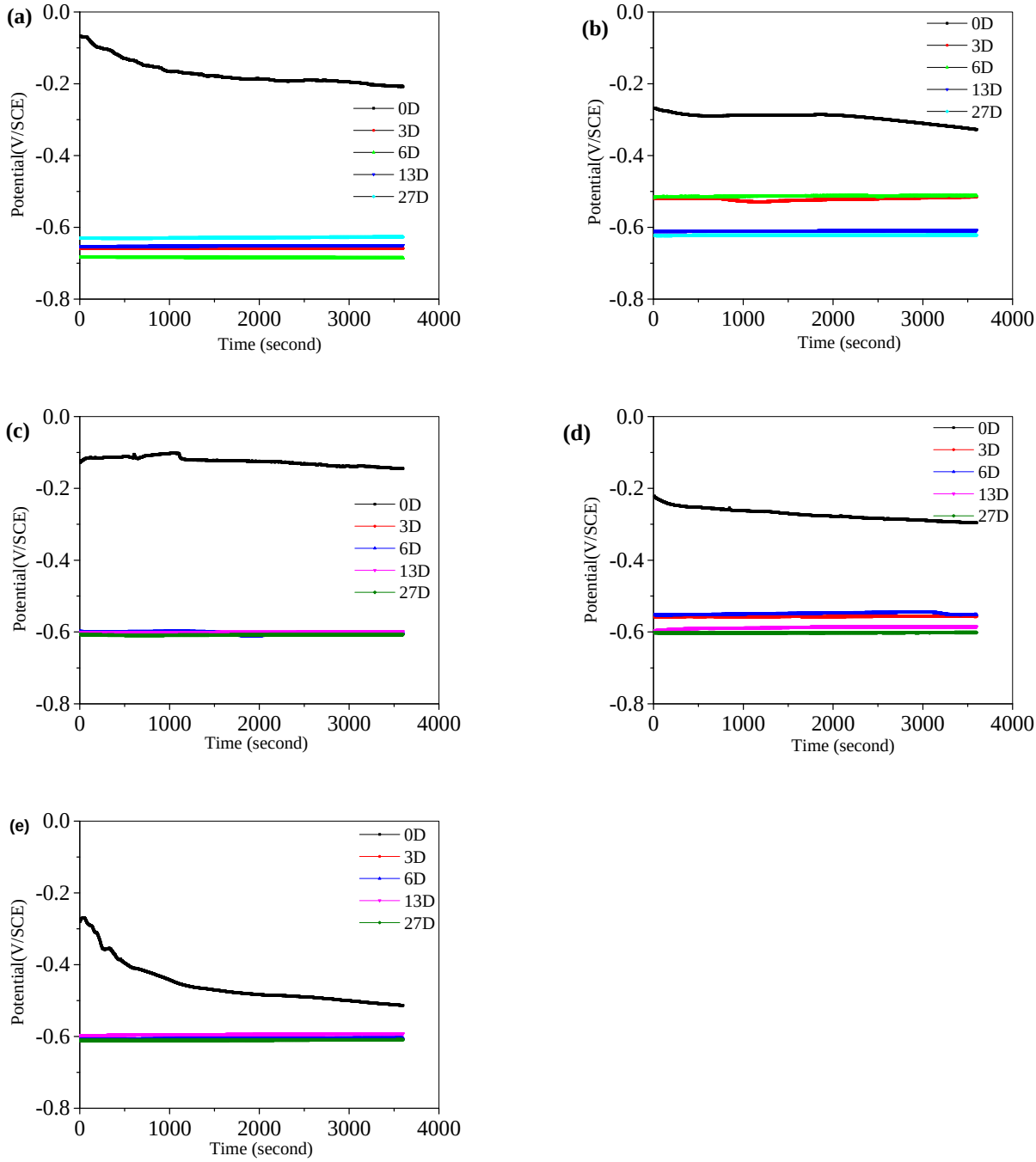


Fig. 5. Open circuit potential for: (a) 15R972-, (b) 16R001-, (c) ME1-, (d) ME2-, and (e) ME3-coated steel coupons

For samples coated with enamel 15R972, the OCP value decreased rapidly in the first 1500 seconds and slowly till -0.208 V at the end of first hour of immersion. After 3, 6, 13, and 27 days of immersion, the OCP values were stabilized at -0.659 V, -0.685 V, -0.650 V and 0.627 V, respectively. The OCP values indicate that corrosion has already taken place after 3 days. For samples coated with enamel

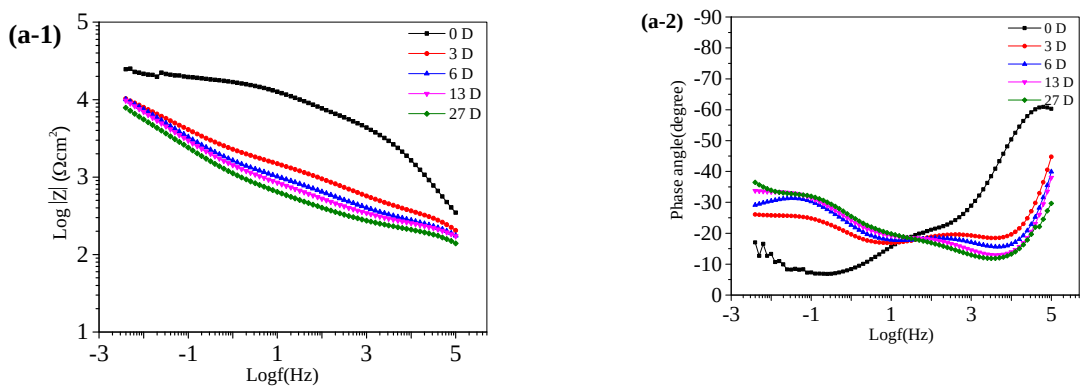
16R001, the OCP value decreased gradually from -0.268 V to -0.327 V in the first hour of immersion. After 4 and 7 days, the OCP values were stabilized around -0.51 V. In the 14 and 28 days, the OCP values were stabilized at -0.608 V and -0.622 V, respectively, an indication of corrosion. For samples coated with enamel ME1, the OCP is -0.145 V in the first hour and -0.6 V during the remaining tests. These results indicate that the sample has already corroded after 3 days. For samples coated with enamel ME2, the OCP decreased gradually from -0.223 V to -0.296 V in the first hour. After 3 and 6 days of immersion, the OCP values stabilized around -0.55 V. After 13 and 27 days, the OCP values stabilized at -0.586 V and -0.602 V, respectively, which indicate that the sample coated with enamel ME2 began to corrode. For samples coated with enamel ME3, the OCP value decreased rapidly in the first 1500 seconds and was stabilized at -0.513V in the first hour of immersion, and became -0.6V in the remaining tests, which means that the sample has corroded after 3 days. Table 7 summarizes the OCP values of various samples at the end of each one-hour test.

Table 7 Open circuit potential of different samples in different immersion day

Day	15R972 (V)	16R001 (V)	ME1 (V)	ME2 (V)	ME3 (V)
0	-0.208	-0.327	-0.145	-0.296	-0.513
3	-0.659	-0.515	-0.604	-0.557	-0.606
6	-0.685	-0.512	-0.601	-0.552	-0.605
13	-0.650	-0.608	-0.599	-0.586	-0.571
27	-0.627	-0.622	-0.607	-0.602	-0.598

3b-1 Electrochemical impedance spectroscopy (EIS) test for the first batch

The EIS tests were conducted at ten points per decade around the open circuit potential $E_{ocp}$with a sinusoidal potential wave of 10 mV in amplitude and frequency ranging from 100 kHz to 5 mHz. Each Bode plot consists of a log-log plot of impedance (log Z) versus frequency (log f) and a semi-log plot of phase angle shift (phase) versus frequency (log f). Inspection of the Bode plot readily provides useful information on coating performance. The EIS of samples coated with five different enamels are presented in the format of Bode plots in **Fig.6**.



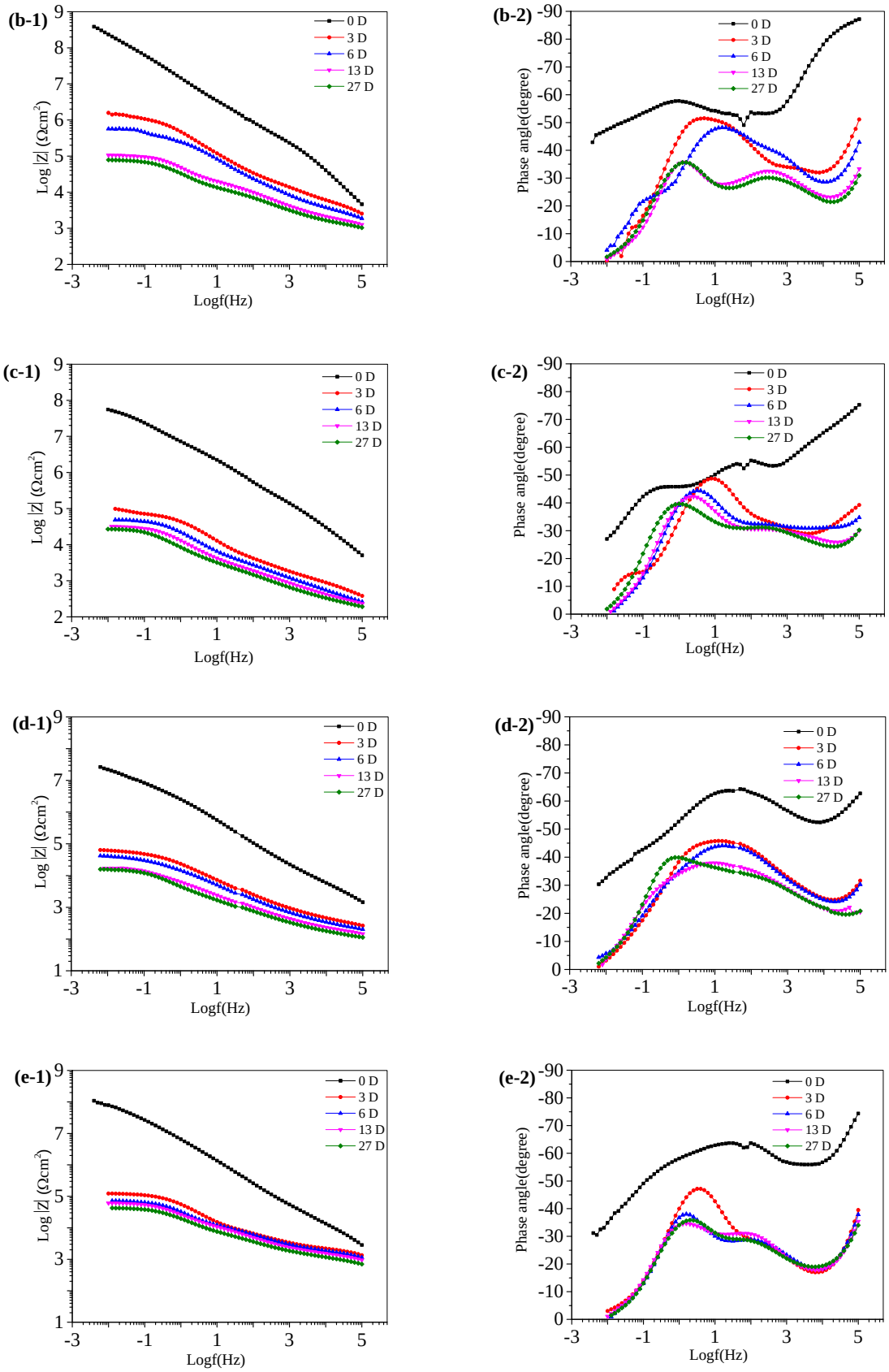


Fig. 6. EIS diagrams for: (a) 15R972-, (b) 16R001-, (c) ME1-, (d) ME2-, and (e) ME3-coated steel coupons

For enamel coating 15R-972, the coating impedance at low frequency of 0.01 Hz is 2.45×10^4 ohms in the first hour of immersion and became approximately 1.0×10^4 ohms in the following days of test. The log Z plot is not a straight line, which means that the coating does not function like a pure capacitor. Since the coating resistance is relatively small, it is less likely that the coating will prevent the sample from corrosion.

In addition, two time constants can be observed in the first hour of immersion, one at low frequency (<1 mHz), which is not obvious, and the other at high frequency (100 kHz). The second time constant appears at a phase angle of approximately -60°, which is quite different from -90°, meaning that the coating layer cannot be considered as the pure capacitor. During the following days of tests, the first time constant appears at 0.025 Hz, and the second time constant appears at over 100 kHz.

For enamel coating 16R-001, the coating impedance at low frequency of 0.01Hz is 3.76×10^8 ohms in the first hour of test and is reduced to 1.46×10^6 ohms and 5.49×10^5 ohms after 3 and 6 days, respectively. The impedance decreased to 1.07×10^5 ohms and 7.76×10^4 ohms after 13 and 27 days, respectively. Since the coating resistance is relatively small after 27 days of immersion, it is less likely that the coating will prevent the sample from corrosion.

In the first hour of immersion, two time constants can be observed at 10 Hz and 100 kHz. The second time constant appears at a phase angle of approximately -90°, which means that the coating layer can be considered as a pure capacitor. However, after the following days of immersion, three times constants can be observed, one at low frequency range, one at middle frequency range, another at high frequency range. The two time constants in the low and high frequency ranges correspond to the diffusion of porous corrosion products layer and enamel coating.

For mixed enamel ME1, ME2 and ME3, the coating impedances at low frequency of 0.01 Hz are 1.06×10^8 ohms, 2.72×10^7 ohms, and 6.60×10^7 ohms, respectively. After 3 days of immersion, the impedances drop to 1.18×10^5 ohms, 6.86×10^4 ohms, and 1.07×10^5 ohms, respectively, which are followed by small reduction during the following days of test. Since the coating resistance is relatively small after 27 days of immersion, it is less likely that the coating will prevent the sample from corrosion.

For mixed enamel ME1, three time constants appear throughout the immersion time. After 3 days of immersion, the phase angle corresponding to each time constant is shifted to higher frequency, which means that electrolyte easily penetrates into the coating and corrosion occurs at the steel substrate. For mixed enamel ME2 and ME3, two time constants appear in the first hour of immersion and the third time constant in the middle frequency range can be clearly seen after 3 days of immersion. For all the enamel coatings, the phase angle corresponding to the low frequency time constant decreases gradually over test time, and the modulus at 0.01 Hz also reduces gradually. Since the time constant in the low frequency range is clearly shown, the implied electrochemical reaction happens at the substrate metal interface. Table 8 shows the impedance at 0.01Hz of various samples over different immersion times.

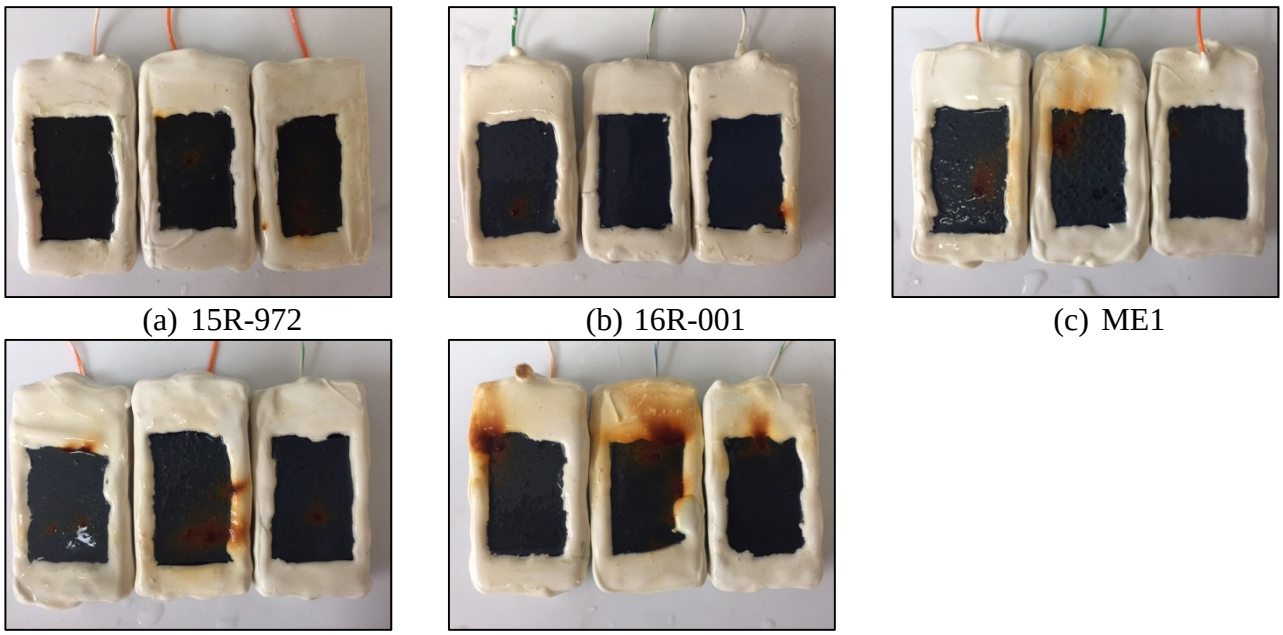
Table 8 Impedance summary of five enamel coatings at 0.01Hz

Day	15R972 (ohms)	16R001 (ohms)	ME1 (ohms)	ME2 (ohms)	ME3 (ohms)
0	2.45×10^4	3.76×10^8	1.06×10^8	2.72×10^7	6.60×10^7
3	1.03×10^4	1.46×10^6	1.18×10^5	6.86×10^4	1.07×10^5
6	1.01×10^4	5.49×10^5	7.48×10^4	4.18×10^4	7.19×10^4
13	9.74×10^3	1.07×10^5	5.69×10^4	1.77×10^4	6.12×10^4
27	7.83×10^3	7.76×10^4	2.64×10^4	1.61×10^4	4.22×10^4

According to Dr. Henry Leidheiser, corrosion underneath a coating occurs at a rate that should be concerned about when the resistance falls below 10×10^7 ohms/cm^2 of measured surface area, and that corrosion is of no concern when the resistance remains greater than 10×10^9 ohms/cm^2.

For enamel 15R-972, the impedance over a measurement surface area of 6 cm^2 is only 2.45×10^4 ohms in the first hour. Therefore, this coating cannot provide corrosion protection from the beginning. For the other coatings, the impedance is higher in the first hour of immersion, but drops to approximately 10×10^4 ohms after 27 days of immersion. They are vulnerable to electrolyte penetration and corrosion occurs on the substrate interface.

Fig.7 shows the conditions of various coating surfaces after 27 days of immersion. Brown corrosion products (mainly magnetite) can be seen from Fig. 7. Overall, these five enamel coatings cannot provide corrosion protection.



(a) 15R-972 (b) 16R-001 (c) ME1

(d) ME2 (e) ME3

Fig.7. Coating surfaces of five coatings after 27 days of immersion

3a-2 Open circuit potential test for the second batch

Thus far, the samples in the second batch have been tested for more than 9 days in the solution. **Fig. 8** shows the evolution of the OCP values of the steel samples coated with enamel Tomatec, mixed enamel ME4 (50 wt.% Tomatec + 50 wt.% 16R001), and enamel GP2118-1550F, GP2118-1500F, and GP2118-1450F.

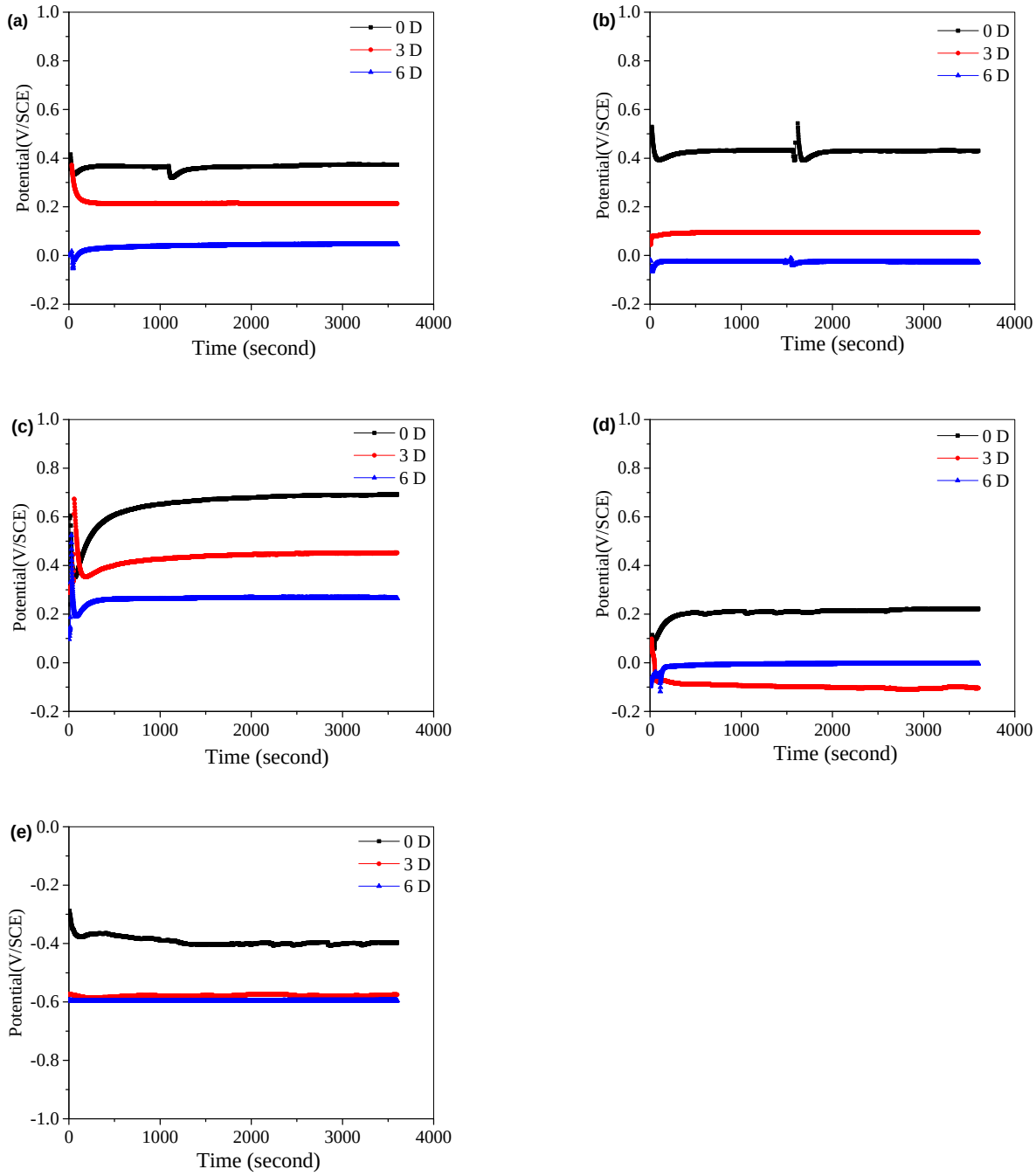
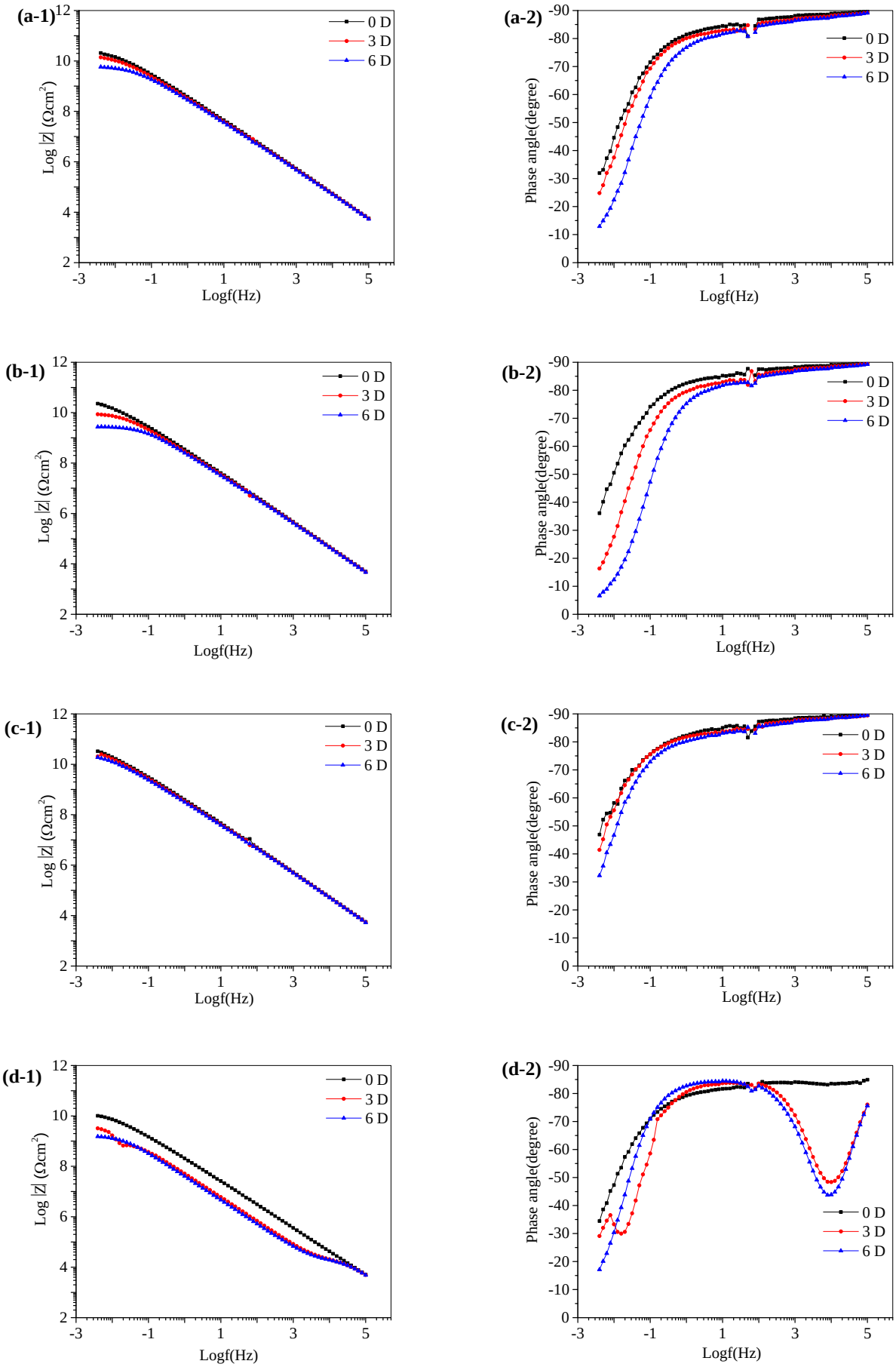


Fig.8. Open circuit potential for: (a) Tomatec-, (b) ME4-, (c) GP2118-1550F-, (d) GP2118-1500F-, and (e) GP2118-1450F-coated steel coupons

Except the enamel GP2118-1450F, the stabilized OCP values for all enamel coated samples are all much higher than the threshold value for corrosion concern after 6 days of immersion. For the sample coated with enamel GP2118-1450F, the OCP value is almost the same after 3 and 6 days of immersion, both being approximately -600mV that likely indicates the initiation of corrosion.

3b-2 Electrochemical impedance spectroscopy test for the second batch

The EIS of the samples coated with five different enamels are presented in **Fig.9** in the format of Bode plots.


(a-1)
Log |Z| (Ωcm²)
Logf(Hz)
0 D
3 D
6 D
(a-2)
Phase angle(degree)
Logf(Hz)
0 D
3 D
6 D
(b-1)
Log |Z| (Ωcm²)
Logf(Hz)
0 D
3 D
6 D
(b-2)
Phase angle(degree)
Logf(Hz)
0 D
3 D
6 D
(c-1)
Log |Z| (Ωcm²)
Logf(Hz)
0 D
3 D
6 D
(c-2)
Phase angle(degree)
Logf(Hz)
0 D
3 D
6 D
(d-1)
Log |Z| (Ωcm²)
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Phase angle(degree)
Logf(Hz)
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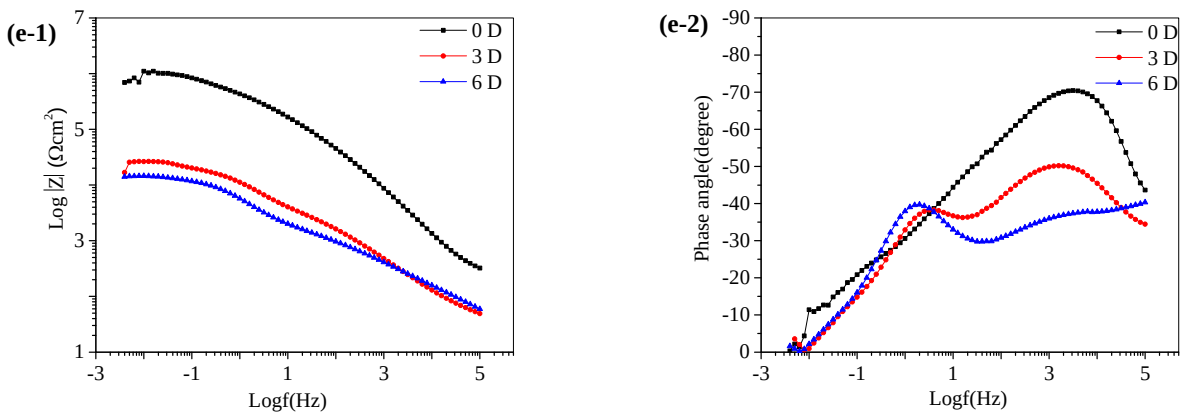
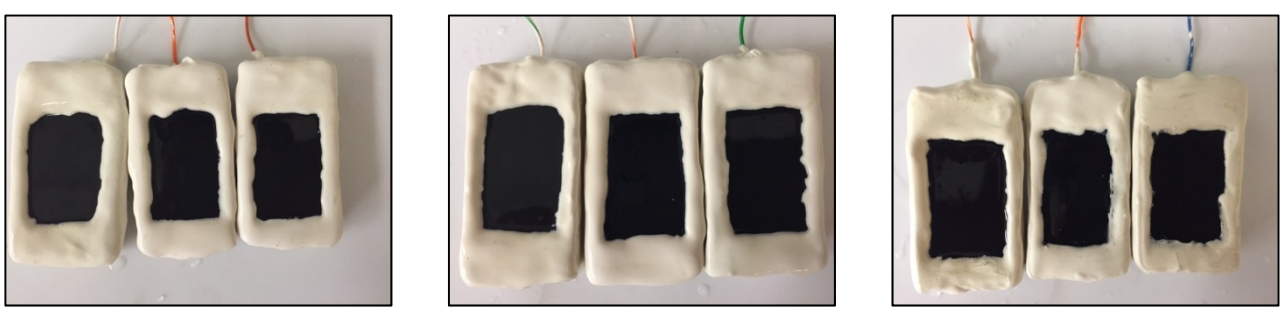


Fig. 9. EIS diagrams for: (a) Tomatec-, (b) ME4-, (c) GP2118-1550F-, (d) GP2118-1500F-, and (e) GP2118-1450F-coated steel coupons

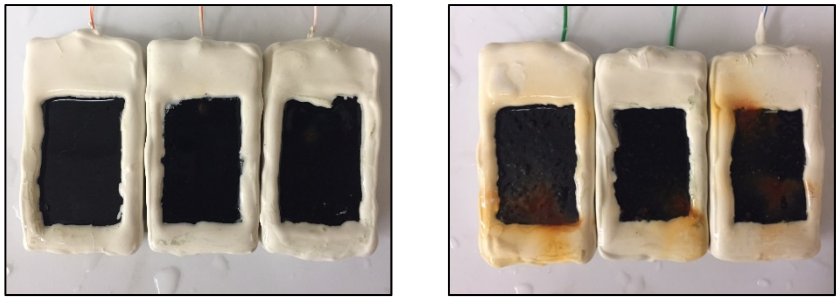
Enamel Tomatec, mixed enamel ME4 (50 wt.% Tomatec +50% wt.%16R001), enamel GP2118-1550F, and enamel GP2118-1500F have coating impedances above 10×10^9 ohms at 0.01 Hz after 6 days of immersion, which indicates a very high corrosion resistance. However, for enamel GP2118-1450F, the coating impedance is only 6.93×10^5 ohms in the first hour of immersion, and drops to 1.48×10^4 ohms. This coating cannot provide corrosion protection.

For enamel Tomatec, mixed enamel ME4 (50 wt.% Tomatec +50% wt.%16R001), and enamel GP2118-1550F, the phase angle at a high frequency of 100 kHz is close to -90°, which indicates the pure capacitor property and high resistance to electrolyte penetration. For enamel coating GP2118-1500F, the phase angle in the high frequency is close to -85° in the first hour of immersion, which means that the coating still remains in a good condition. After 3 and 6 days of immersion, two obvious time constants appear and the electrochemical reactions happen at low frequency. For enamel coating GP2118-1450F, the phase angle at over 10 kHz drops in the first hour of immersion and the peak value of phase angle decreases with the increasing immersion time. Two time constants appear after 3 and 6 days in the relatively low and middle frequency ranges.

Fig.10 shows the coating surface conditions after 9 days of immersion. It can be seen that enamel coating Tomatec, ME4, and GP2118-1550F remain intact. However, brown pitting spots can be seen on the surface of GP2118-1500F and a large corrosion area can be seen on the surface of GP2118-1450F.



(a) Tomatec (b) ME4 (c) GP2118-1550F



(d) GP2118-1500F (e) GP2118-1450F

Fig.10. Surface conditions of five coatings after 9 days of immersion

Task 4 System performance of in-situ enamel-coated pipelines-stress distribution and SCC

This task will not start till the 2nd quarter in 2017.

(c) Description of any Problems/Challenges - In this quarter, the corrosion tests were slowed down when the old corrosion test instrument broke down and the research team was waiting for the arrival of a new corrosion instrument, 1000E Potentiostat/Galvanostat/ZRA.

(d) Planned Activities for the Next Quarter - The following activities in various tasks will be executed during the next reporting quarter.

Task 1 Optimization of enamel materials for durability, particle distribution, and thermal compatibility with steel

The chemical composition of enamel powder GP-2118 and Tomatec will be tested.

Task 2 Enameling process for coating uniformity, surface roughness, and efficiency without adverse effect on steel properties

Enamel slurry and dry power application processes will be compared according to coating thickness, coating roughness, coating efficiency and corrosion resistance by using small coupon samples (25 $mm \times 50\ mm$) and large specimens ($75mm \times 150mm$).

Task 3 Characterizations of enamel-coated pipes for microstructure/porosity, chemical adhesion, and corrosion resistance

The phase composition and microstructure of the enamel coatings (15R972, 16R001, ME1, ME2, and ME3) will be investigated with X-ray diffraction and scanning electrons microscopy coupled to an energy dispersive X-ray spectroscopy.

Once confirmed with the above analysis, enamel 15R972, enamel 16R001, and mixed enamels ME1-ME3 are most likely removed from further study due to low corrosion resistance. Corrosion performance of the second batch coatings (Tomatec, ME4, GP2118-1550F, GP2118-1500F, and GP2118-1450F) will be examined in the next three months.