CAAP Quarterly Report

Date of Report: *October10, 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: *September 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, allied epoxy mount, distilled water, marine epoxy and PosiTest AT-M instrument were purchased for this project using credit card. The chemical compositions of two types of alkali borosilicate enamel powder (product ID Tomatec and GP-2118) 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 types of alkali borosilicate enamel powder (product ID Tomatec and GP2118) were given in Table 1.

Table 1. Chemical composition of enamel powder Tomatec and GP-2118

Glass	Composition (wt.%)											
	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	BaO	*Others*
Tomatec	60.3	12.84	7.20	2.37	5.37	4.49	0.14	2.12	3.48	0.17	1.47	0.12
GP-2218	57.5	16.95	9.60	3.31	4.70	1.02	1.41	3.63	1.49	0.21	0.04	0.21

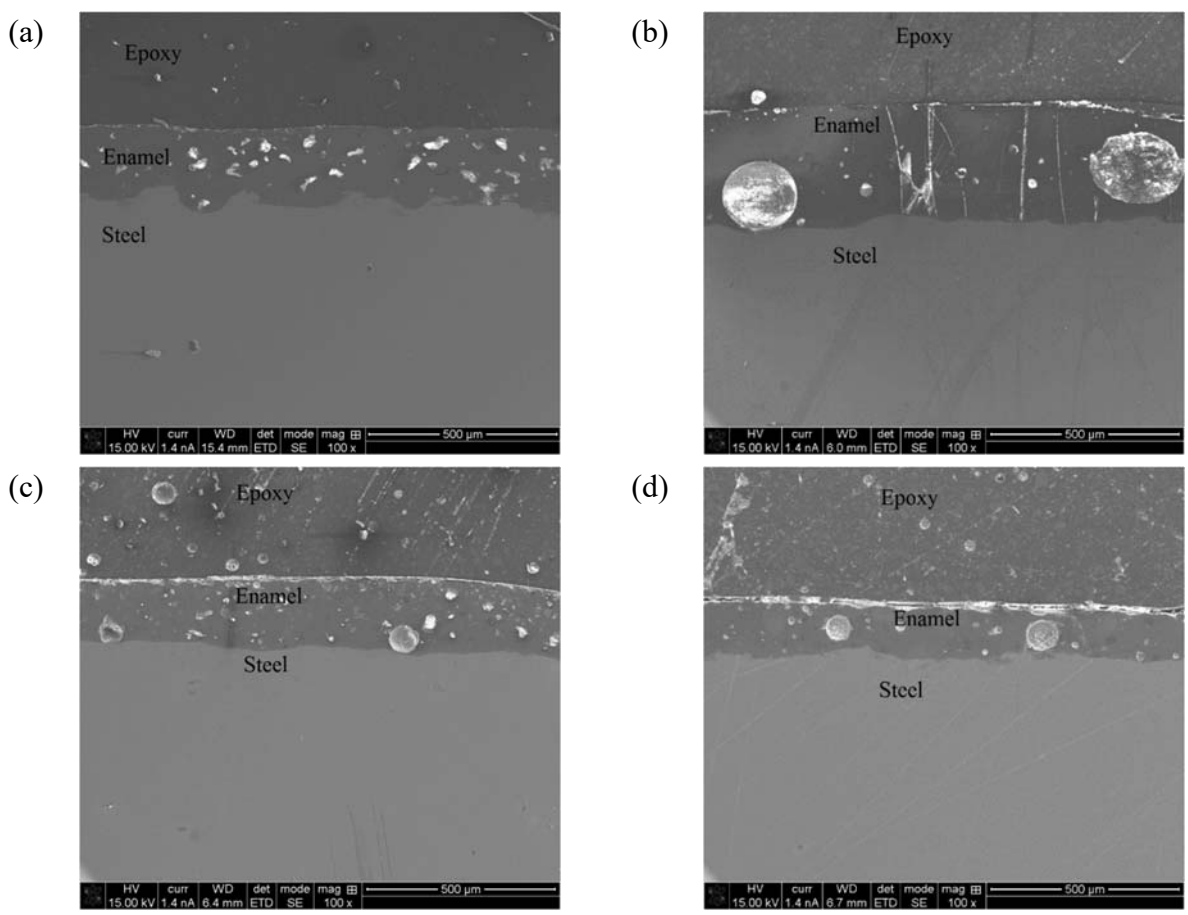
Task 3 Characterizations of enamel-coated pipes for microstructure/porosity, chemical adhesion, and corrosion resistance

3a SEM images of enamel coating PE1, PE2, ME1, ME2, and ME3

Enamel 15R-972, enamel16R-001, enamel 15R-972 (25 wt.%) + 16R-001 (75 wt.%), enamel 15R-972 (50 wt.%) + 16R-001 (50 wt.%), and enamel 15R-972 (75 wt.%) + 16R-001 (25 wt.%) are designated by PE1, PE2, ME1, ME2, and ME3, respectively.

Cross sections of the coating systems were prepared for microstructure analysis with a scanning electron microscopy (SEM, Helios 600). Each enamel-coated sample was first cold mounted in epoxy resin (EpoxyMount, Allied High Tech Products, Inc.) and cut into a 10.0 mm-thick cross-section using a diamond saw. The cross sections were then abraded with carbide papers to 1200 grit, rinsed with deionized water, and finally dried in air at room temperature prior to examination.

Cross-sectional SEM images of five enamel-coated steel samples are presented in Fig. 1. The thicknesses of enamel coating PE1, PE2, ME1, ME2, and ME3 are approximately 250 μm, 363 μm, 227 μm, 159 μm, and 409 μm, respectively. The air bubbles observed in the enamel coatings were released from the high-temperature chemical reaction of the enamel with the steel substrate (particularly carbon element) during enameling process. All the enamel coatings have many isolated small pores. All the coatings except PE1 have a few large pores. PE2 has the fewest number of small air bubbles but has a few air bubbles as large as 220 μm in diameter, which is almost the same as the thickness of the coating ME2. ME1, ME2, and ME3 have some large air bubbles of approximately 90 μm in diameter.



(e)

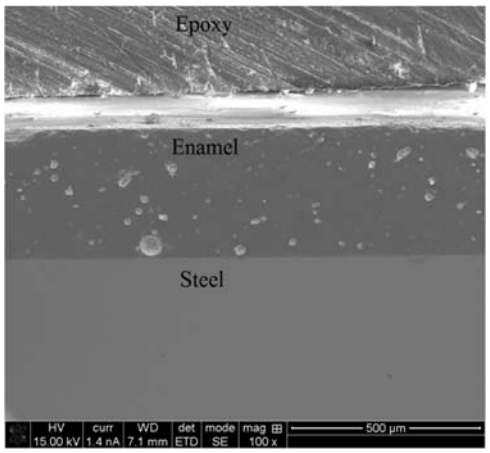


Fig.1. SEM images of: (a) PE1-, (b) PE2-, (c) ME1-, (d) ME2-, and (e) ME3-coated steel samples.

3b Electrochemical tests

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 the working electrode and the reference electrode and measures the current between the working electrode and the 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. 2. 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 Tomatec and mixed enamel ME4 (50 wt.% Tomatec +50 wt.% 16R001). Here, enamel Tomatec and enamel ME4 were coated on steel samples at 1500 °F. The second batch contains enamel GP2118-1550F, GP2118-1500F, and GP2118-1450F that were coated on steel samples at 1550 °F, 1500 °F, and 1450 °F, respectively.

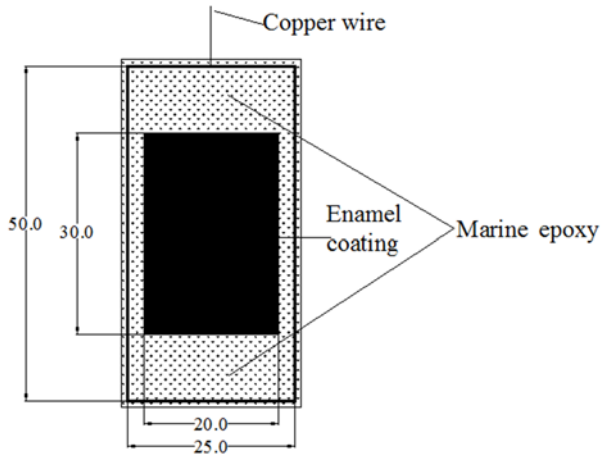


Fig.2. Test sample dimension (unit: mm).

3b-1 Open circuit potential test for the first batch of test samples

OCP values were recorded for one hour after 0, 3, 6, 13, 27, 41, 55, and 69 days, respectively. Fig. 3 shows the evolution of the OCP values of two representative types of enamel-coated steel samples after various days of immersion.

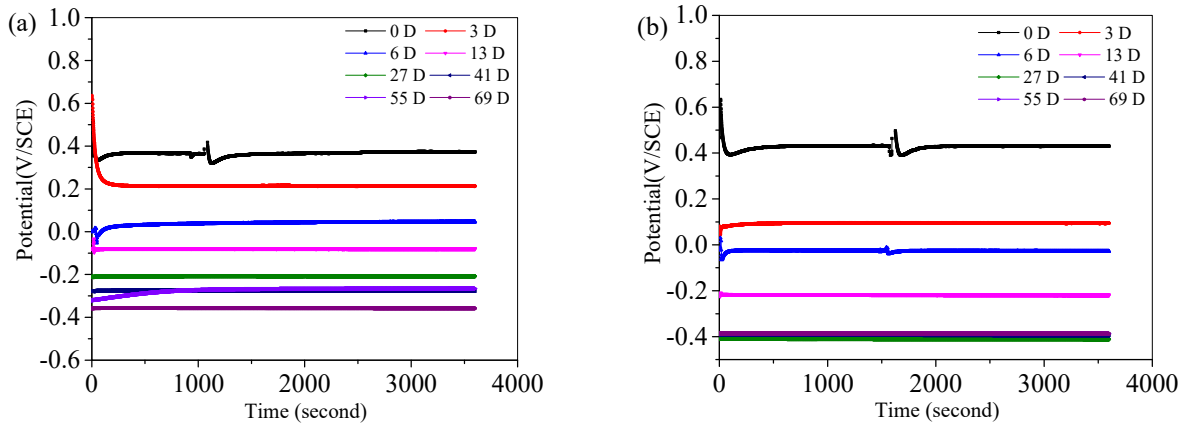


Fig. 3. Open circuit potential for: (a) Tomatec-, and (b) ME4-coated steel samples.

For samples coated with enamel Tomatec, the OCP values were rapidly stabilized during each test and decreased gradually over a period of 69 immersion days. The OCP values remained at 0.373 V, 0.213 V, 0.046 V, -0.080 V, -0.208 V, -0.277 V, -0.266 V and -0.358 V after 0, 3, 6, 13, 27, 41, 55, 69 days, respectively. They are all larger than -0.6 V. Therefore, little water and chloride ions are expected to have penetrated through the coating.

For samples coated with enamel ME4, the OCP values were also stabilized immediately after each test and decreased gradually throughout the test period of 69 days. The OCP values remained at 0.430 V, 0.094 V, -0.028 V, -0.219 V, -0.411 V, -0.394 V, -0.387 V and -0.387 V after 0, 3, 6, 13, 27, 41, 55, and 69 days, respectively. Since they all exceed -0.6V, little water and chloride ions may penetrate through the coating.

3b-2 Electrochemical impedance spectroscopy (EIS) test for the first batch of test samples

After the OCP measurement for each sample, EIS tests were conducted with a sinusoidal potential wave of 10 mV in amplitude around the open circuit potential E_{ocp} and frequency ranging from 100

kHz to 5 mHz. The EIS of two representative samples coated with enamel Tomatec and ME4 are presented in the format of Bode plots in Fig.4. Each plot consists of a log-log plot of impedance (Log $|Z|$) versus frequency (Log f) and a semi-log plot of phase angle versus frequency (Log f).

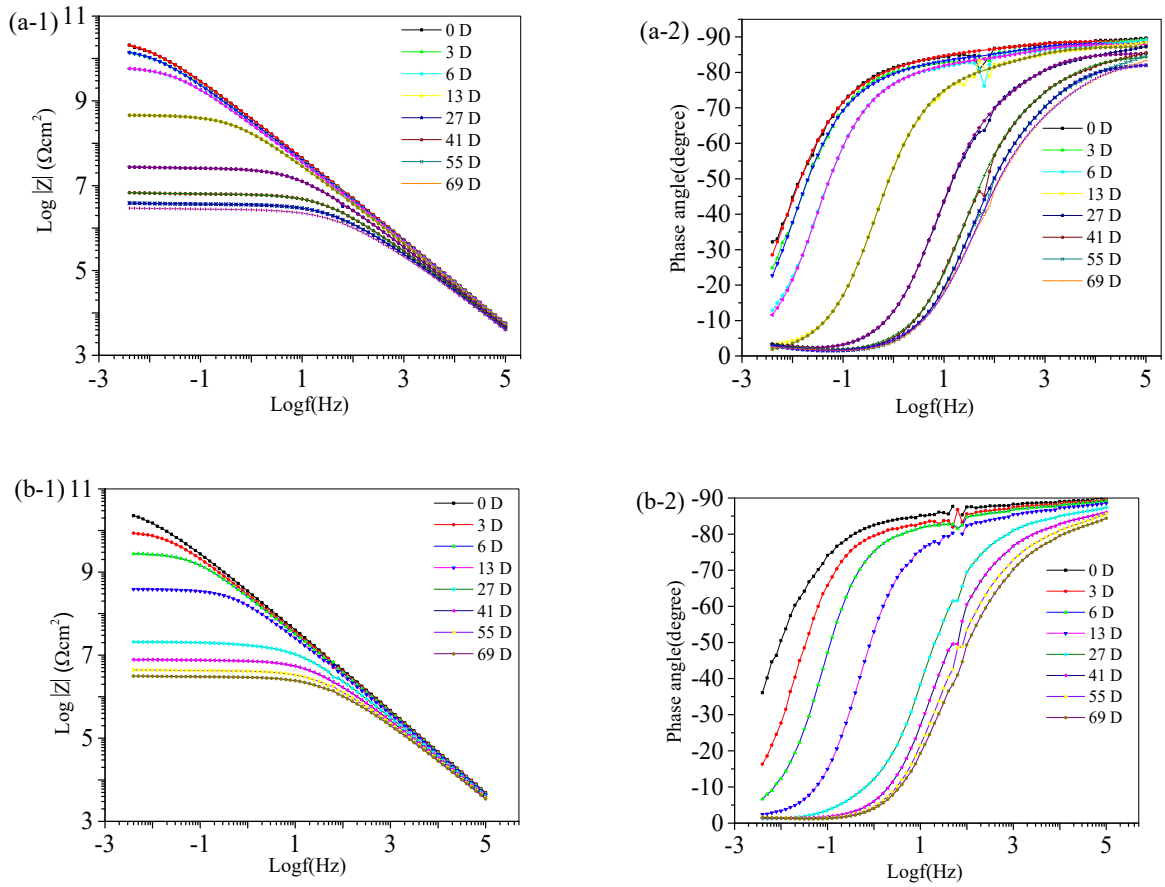


Fig. 4. EIS diagrams for: (a) Tomatec-, (b) ME4-coated samples.

As shown in Fig.4, the two enamel-coated samples showed similar trends. The impedances of enamel-coated samples at low frequency range dropped slightly in the first six days of immersion, significantly in the following five weeks, and slowly again in the final four weeks. The impedance diagram started with a horizontal line in the very low frequency range, and the plateau was gradually widened and extended to the middle frequency range over the immersion time. Therefore, the impedance spectra gradually deviated from the pure capacitive behavior, indicating that the coating resistance decreased and the coating capacitance increased as a result of NaCl solution penetration into the coatings. The phase angles in the high frequency range were close to 90° throughout the tests up to 69 days. However, the phase angles in the low and middle frequency ranges decreased quickly with the increasing immersion time due to the rapidly reduction of coating resistance. Table 2 shows the impedance of various samples at 0.005 Hz over different immersion durations.

Table 2 Impedance summary of two enamel coatings at 0.005Hz

Day	Tomatec ($\Omega\ cm^2$)	0.5 16R & 0.5 Tomatec ($\Omega\ cm^2$)
0	2.069×10^{10}	2.276×10^{10}
3	1.393×10^{10}	8.622×10^{9}
6	5.776×10^{9}	2.739×10^{9}
13	4.564×10^{8}	3.869×10^{8}
27	2.763×10^{7}	2.082×10^{7}
41	6.867×10^{6}	7.786×10^{6}
55	3.927×10^{6}	4.426×10^{6}
69	3.116×10^{6}	3.145×10^{6}

The impedances of enamel Tomatec- and ME4-coated samples over a measurement surface area of 6 cm^2 are $2.069\times 10^{10}\ \Omega$ and $2.276\times 10^{10}\ \Omega$, respectively, on the first immersion day and gradually decreased to $3.116\times 10^{6}\ \Omega$ and $3.145\times 10^{6}\ \Omega$ after 69 days of immersion. The coating can remain protection against chloride penetration as long as the electrical resistance of the coating is above its threshold (10^6 to $10^7\ \Omega\ cm^2$). Therefore, after 69 days of immersion, the two types of enamel coatings can still protect the coated samples from chloride penetration. This conclusion was supported by the surface conditions of the tested samples at the end of tests, as illustrated in Fig.5. It can be seen from Fig. 5 that both Tomatec and ME4 samples remain intact without any corrosion sign.

(a) Tomatec (b) ME4

Fig.5. Surface conditions of two coatings after 69 days of immersion.

3c-1 Open circuit potential test for the second batch of test samples

Fig. 6 shows the OCP values of the steel samples coated with enamel GP2118-1450F, GP2118-1500F, and GP2118-1550F up to 69 days of immersion. The OCP value of enamel GP2118-1450F-coated sample decreased rapidly in the first 800 seconds and was then stabilized at -0.465 V at the end of the first hour immersion. The OCP values dropped to -0.572 V and -0.617 V after 3 and 6 days of immersion. After that, the values remained around -0.650 V until the end of all tests. Since the OCP values were smaller than -0.6 V, corrosion likely initiated after 13 days of immersion.

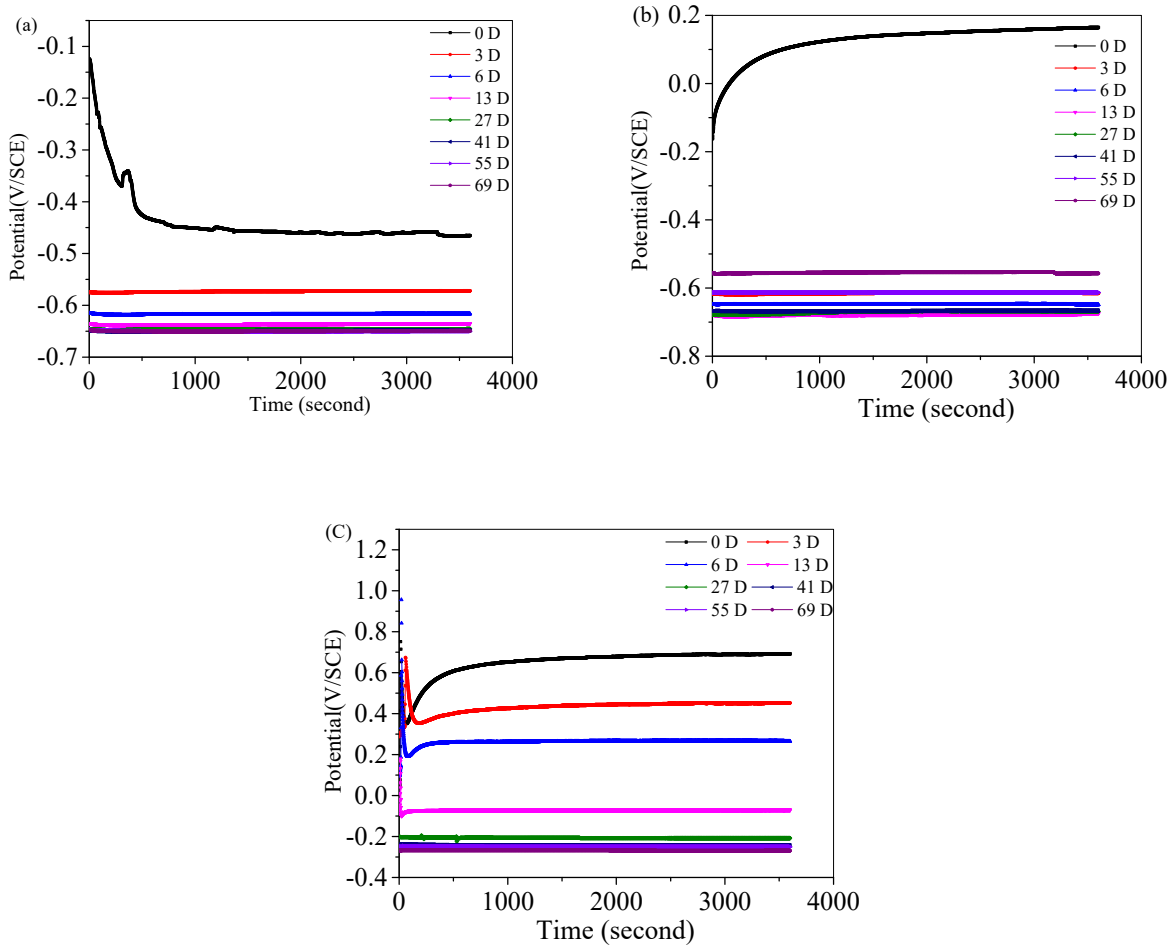


Fig.6. OCP for: (a) GP2118-1450F-, (b) GP2118-1500F-, and (c) GP2118-1550F-coated steel samples.

The OCP value of enamel GP2118-1500F-coated sample increased gradually from -0.162 V to 0.120 V in the first 1000 seconds and was then stabilized at 0.164 V at the end of the first hour immersion. The OCP value dropped dramatically to -0.616 V after 3 days of immersion, an indication of corrosion activities. The value remained around -0.60 V to -0.70 V in the following immersion days until the end.

For the sample coated with enamel GP2118-1550F, the OCP value was quickly stabilized in each hourly measurement. The stable value decreased gradually up to 41 days of immersion and then remained nearly unchanged to the end of tests after 69 days of immersion. Specifically, the stable value is 0.692 V, 0.452 V, 0.265 V, -0.071 V, -0.208 V, -0.243 V, -0.250 V and -0.269 V after 0, 3, 6, 13, 27, 41, 55, and 69 days, respectively. These values are all higher than -0.6 V, indicating that little water and chloride ions that may have penetrated through the coating.

3c-2 Electrochemical impedance spectroscopy test for the second batch of test samples

The EIS test results of enamel GP2118-1450F-, GP2118-1500F-, and GP2118-1550F-coated steel samples are presented in the format of Bode plots in Fig.7. For the enamel GP2118-1450F-coated steel sample, the impedance over a measurement surface area of 6 cm^2 is 9.199× $\mathbf{10^6}$ **Ω** at 5 mHz after the first hour of immersion, drops to 8.858× $\mathbf{10^4}$ **Ω** after 3 days and one hour of immersion, and finally is stabilized around $\mathbf{10^4}$ **Ω** after 27 days of immersion. Therefore, this coating cannot prevent chloride penetration.

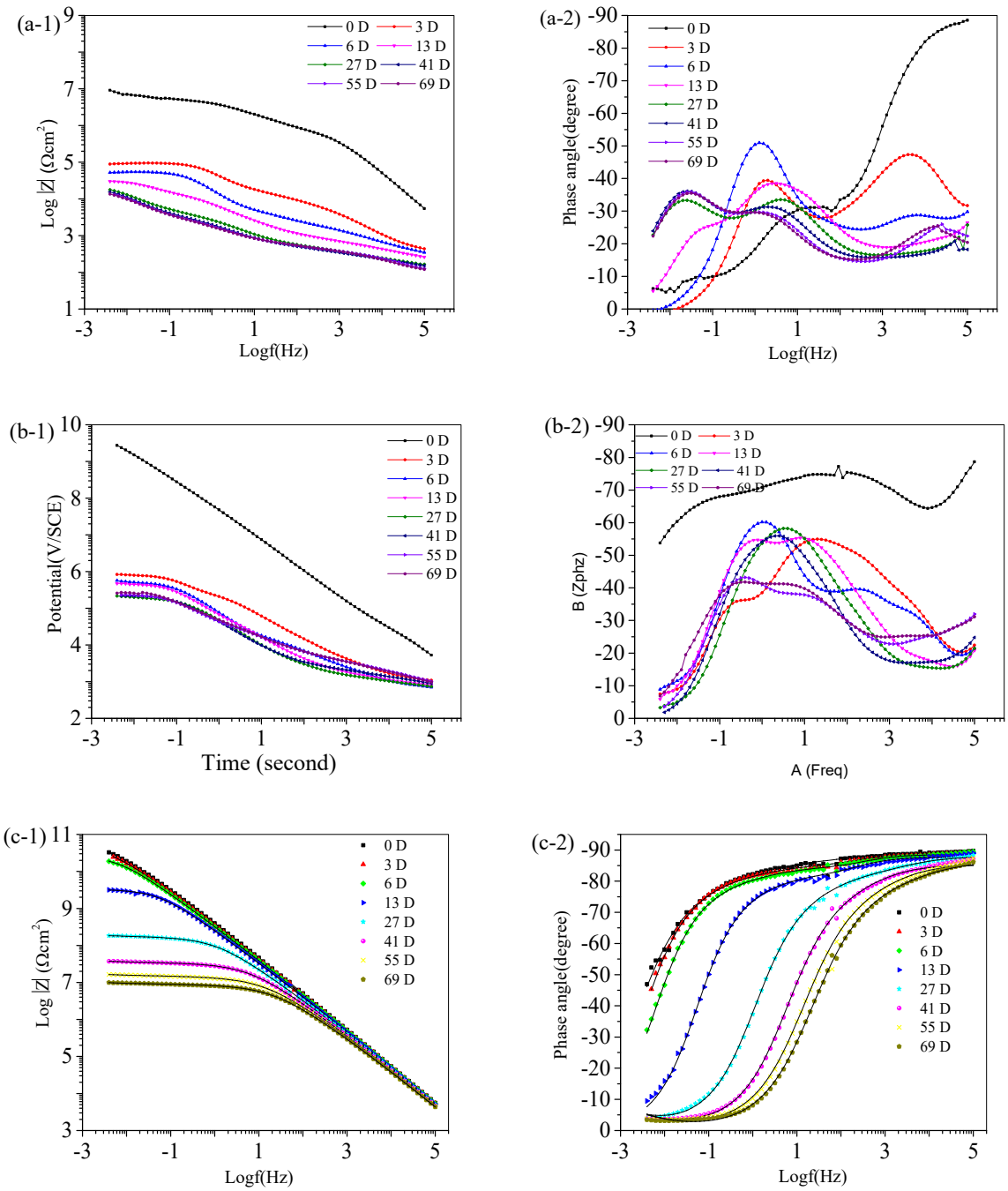


Fig. 7. EIS diagrams for: (a) GP2118-1450F-, (b) GP2118-1500F-, and (c) GP2118-1550F-coated steel samples.

For the enamel GP2118-1500F-coated steel sample, the impedance over a measurement surface area of 6 cm^2 is 2.739×10^9 Ω at 5 mHz in the first hour of immersion and the impedance diagram over the entire test frequency range is a straight line, indicating that the coating functions like a pure capacitor. However, the impedance drops dramatically to 8.342×10^5 Ω after 3 days and one hour of immersion and further to approximately 10^5 Ω after 27 days of immersion. In the first hour of immersion, two maximum peaks of approximately 80° can be observed in the middle and high frequency ranges of the phase-angle diagram. After 3 days and one hour of immersion, the phase angle drops significantly as the coating resistance decreases and the coating capacitance increases. Since the impedance at low frequency, 5mHz, and the phase angle at high frequency, 100 kHz, are both small, the enamel GP2118-

1500F-coated steel sample is vulnerable to electrolyte penetration and thus corrosion at the electrolyte-substrate interface.

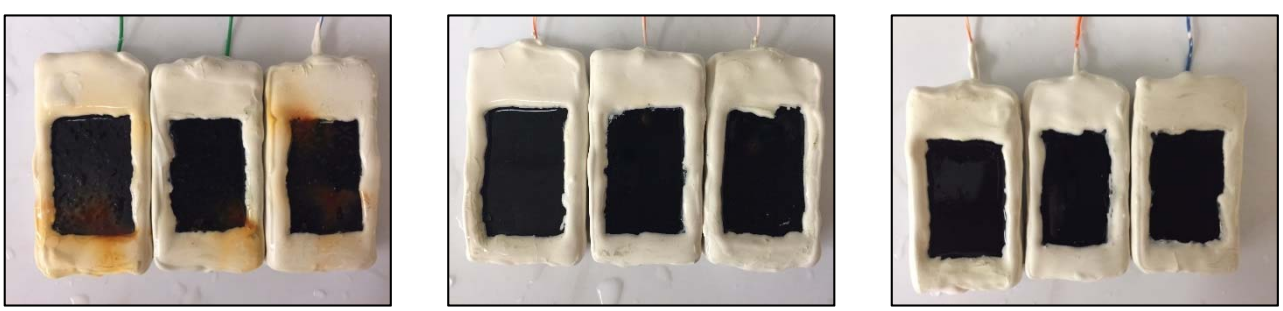
The bode diagrams of the enamel GP2118-1550F coated sample are similar to those of enamel Tomatec-coated sample as shown in Fig. 4a. In the first hour of immersion, the impedance diagram is nearly an inclined straight line. As the immersion time increases, the impedance diagram starts with a horizontal line at very low frequency and is gradually transitioned to the inclined straight line at high frequency. Over the immersion time, the impedance at 5 mHz decreases and the horizontal plateau extends gradually from the very low frequency range to the middle frequency range. The phase angles in the high frequency range are close to 90° throughout the test period up to 69 days. However, the angles in the low and middle frequency ranges decrease quickly with the increasing immersion time due to the rapid reduction of coating resistance. Table 3 summarizes the impedances of various samples at 5 mHz over different immersion durations.

Table 3 Impedances of five enamel coatings at 5 mHz

Day	GP2118-1450F ($\Omega\ cm^2$)	GP2118-1500F ($\Omega\ cm^2$)	GP2118-1550F ($\Omega\ cm^2$)
0	9.199×10^6	2.739×10^9	3.280×10^{10}
3	8.858×10^4	8.342×10^5	2.041×10^{10}
6	5.206×10^4	5.712×10^5	1.887×10^9
13	3.019×10^4	4.751×10^5	3.174×10^8
27	1.778×10^4	2.161×10^5	1.841×10^8
41	1.549×10^4	2.170×10^5	3.736×10^7
55	1.308×10^4	2.337×10^5	1.641×10^7
69	1.355×10^4	2.578×10^5	9.036×10^6

The impedances of GP2118-1450F and GP2118-1500F coated steel samples over a measurement surface area of 6 cm^2 are respectively $9.199\times 10^6\ \Omega$ and $2.739\times 10^9\ \Omega$ in the first hour of immersion and gradually decrease to $1.355\times 10^4\ \Omega$ and $2.578\times 10^5\ \Omega$ after 69 days and one hour of immersion. Therefore, after 69 days of immersion, these two coatings cannot prevent chloride penetration. The impedance of GP2118-1550F coated steel sample over a measurement surface area of 6 cm^2 is $3.280\times 10^{10}\ \Omega$ in the first hour of immersion and gradually decreases to $9.036\times 10^6\Omega$ after 69 days of immersion. Therefore, enamel GP2118-1550F can prevent chloride penetration up to 69 days.

Fig.8 shows the coating surface conditions after 69 days of immersion. It can be seen that GP2118-1550F samples remain intact. However, brown pitting spots can be seen on the surface of GP2118-1500F samples and a large corrosion area can be seen on the surface of GP2118-1450F samples.



(a) GP2118-1450F (b) GP2118-1500F (c) GP2118-1550F

Fig.8. Surface conditions of three types of enamel coatings after 69 days of immersion.

Overall, both the wet process of enamel slurry Tomatec and the dry (electrostatic) process of enamel powder GP2118 can prevent chloride from penetration through the coating. They will thus be used to coat pipe samples in the following experiments.

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

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

The phase composition and microstructure of enamel coatings (Tomatec and GP2118) will be investigated with X-ray diffraction (XRD) and scanning electrons microscopy (SEM).

The short-term corrosion mechanisms of virgin and damaged coatings (Tomatec and GP2118) will be studied and their corrosion resistance will be compared. Impact damage will be introduced to specimens by the free fall of a weight according to ASTM Standard G14. The cohesion of enamel coatings and the enamel-steel adhesion will be determined by pull-off tests.