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Pipeline and Hazardous Materials Safety Administration

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An Inorganic Composite Coating for Pipeline Rehabilitation and Corrosion Protection

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Outline

1. Introduction
2. Coating Development
3. Accelerated Corrosion Tests
4. Evaluation of Mechanical Properties
5. Finite Element Analysis
6. Findings and Recommendations

1. Introduction

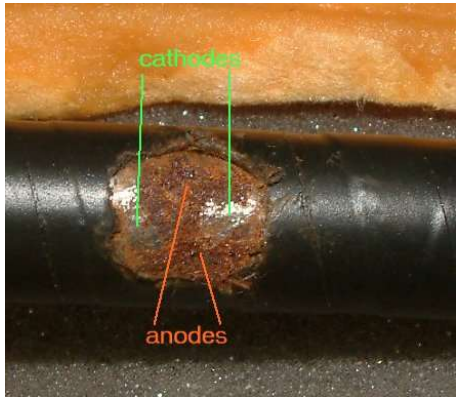
1.1 Pipeline Corrosion and Repair

- Corrosion is the major concern as steel pipes are the most prevalent among pipes in service and for new construction projects.
- Corrosion starts when unprotected steel is exposed to corrosive environment and if undetected would lead to pipeline failure.
- Various types of coatings are used for protection of pipes against corrosive environment.
- Maintenance of pipelines calls for cost-effective repair techniques, such as fiber reinforced composite (FRP) for ease of installation and application against adverse environmental effects.

1.2 Pipeline Coatings

- Pipe sections are usually coated in factories. Majority of coating in pipeline industry are organic-based coatings.
- The coating is susceptible to damage during transportation and installation, such as scratches, gauges, and dents.
- The performance of coating degrades over time due to environmental factors such as heat, freeze/thaw cycles, and UV exposure.

tsb.gc.ca



pipeline-corrosion-control.com

1.3 Objectives

- Develop an inorganic coating system for protection of pipeline from corrosion and mechanical damage and possibly use with composite repair of pipeline
- This research work included the following tasks:
  - Inorganic coating development
  - Accelerated corrosion testing procedure
  - Adhesion strength and durability tests
  - Coating application with carbon fiber reinforced polymer (CFRP)
  - Finite Element modeling of composite repair of pipeline

2. Inorganic Coating Development

2.1 Inorganic Composite Coating

- The composite coating formulations were further modified from an inorganic polymer developed in previous study (Papakonstantinou and Balaguru 2007).
- The earlier study resulted in the development of alkali-alumino-silicate material that can be used for **structure protection and strengthening** using various high strength fibers (Najm et al. 2007; Toutanji et al. 2006).
- The inorganic coating formulation is potassium alumina-silicate, in the class of geopolymer material with general chemical structure:

$$K_n\{-(SiO_2)_z-AlO_{2-}\}_n \bullet wH_2O$$

Where, z>>n and n is the degree of polycondensation; z is 1, 2, and 3; and w is the binding water amount.

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2.2 Features of Inorganic Coating

The specific features of inorganic composite coating include:

- **100% inorganic** nature **without** volatile organic component (VOC)
- The matrix is **water-based**; consequently tools and spills can be cleaned with water. All of the components are **nontoxic** and **no fumes** are emitted during mixing or curing.
- Common application procedures such as **brushing**, **rolling,** and **spraying** are compatible with the matrix.
- The **base coating material is white** and hence **other color** schemes can be easily formulated using pigments.
- The system is **compatible** with *brick, concrete, wood, and steel.*
- **Micro-fiber** can be added to control shrinkage cracking and provide high abrasion resistance
- The coating **will perform up to temperature of 800°F**. Organic coatings could soften at temperatures less than 150°F.

2.3 Fabrication of Inorganic Coating

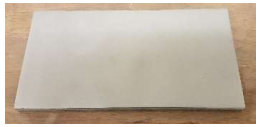
Potassium Silicate solution (Part A)

Metakaolin or Fly ash (Part B)

Carbon Micro-Fiber

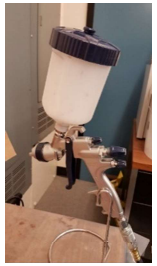
Nano Additives

Mixing Coating components



Steel plate degreasing and sand blasting

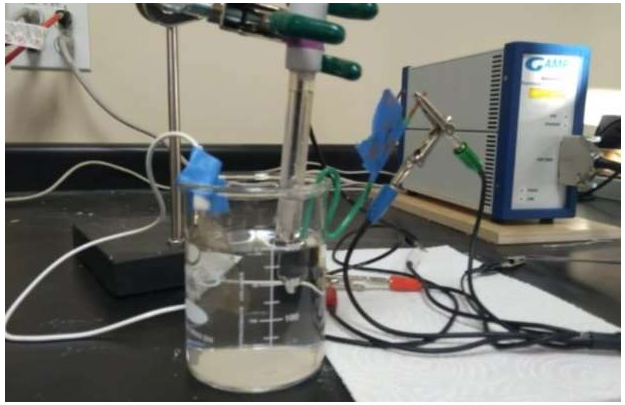
Coating Application

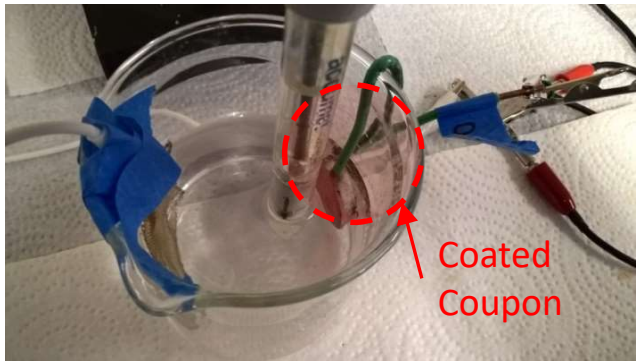


Curing in room temperature (may also be cured in oven to expedite)

2.4 EIS (Electrochemical Impedance Spectroscopy)

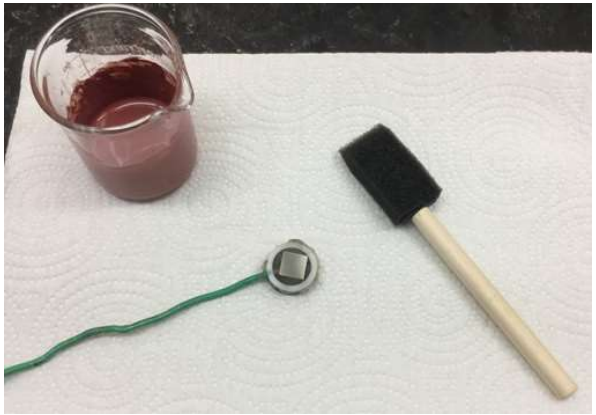
- EIS testing (ASTM G3-14) involves applying small-amplitude alternating current signal into the material over a wide range of frequencies and measuring the responding current and its phase angle shift.
- It compares **relative performance of different coatings**.
- EIS generally give information on the **instantaneous corrosion rate** and may not predict long-term corrosion behavior in the field environment.



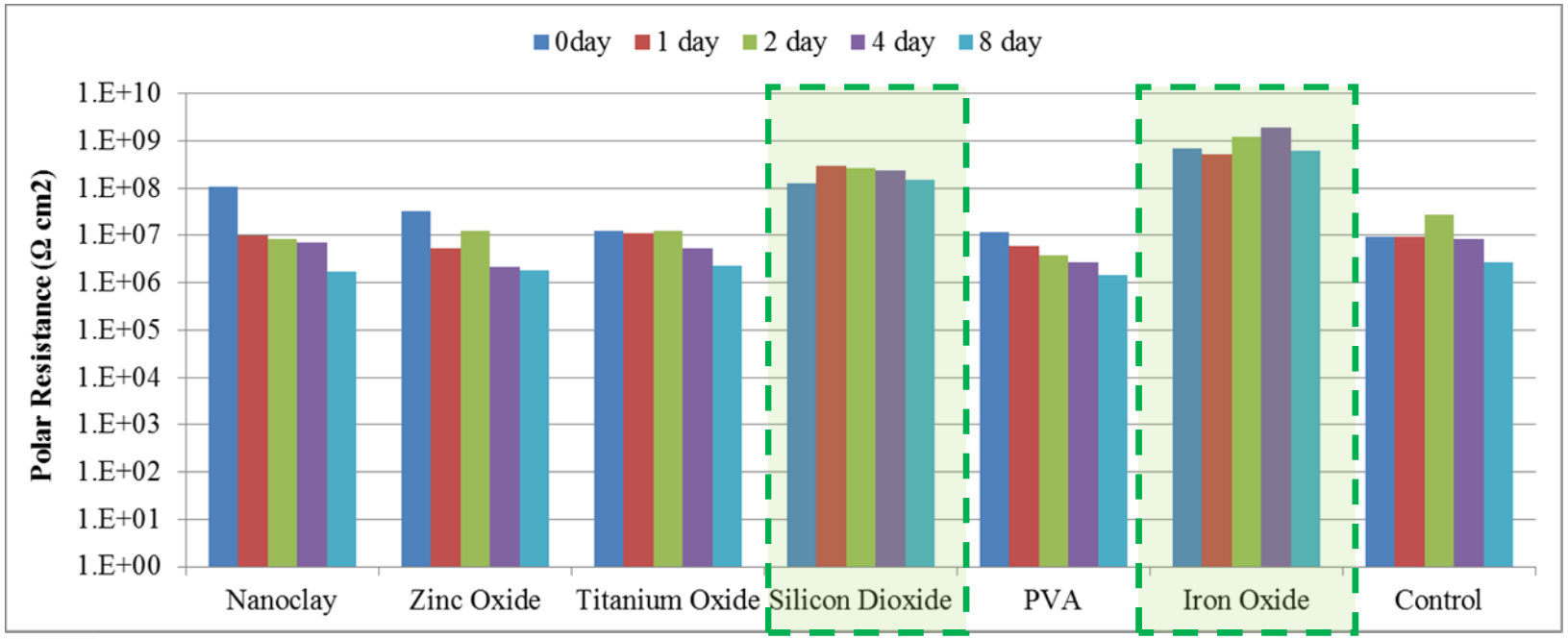


2.5 EIS Test Procedure

- The corrosive environment was prepared by 0.3% aqueous NaCl solutions. The EIS measurements were carried out using Gamry Reference 600 device.
- The first set of steel coupons was prepared with different Nano-materials to **identify the most promising modifier** from various materials.
- The second set of steel coupons was prepared with three different nanomaterials in powder and water dispersion, respectively.



2.6 EIS Test Results



Silicone Oxide and Iron Oxide performed the best

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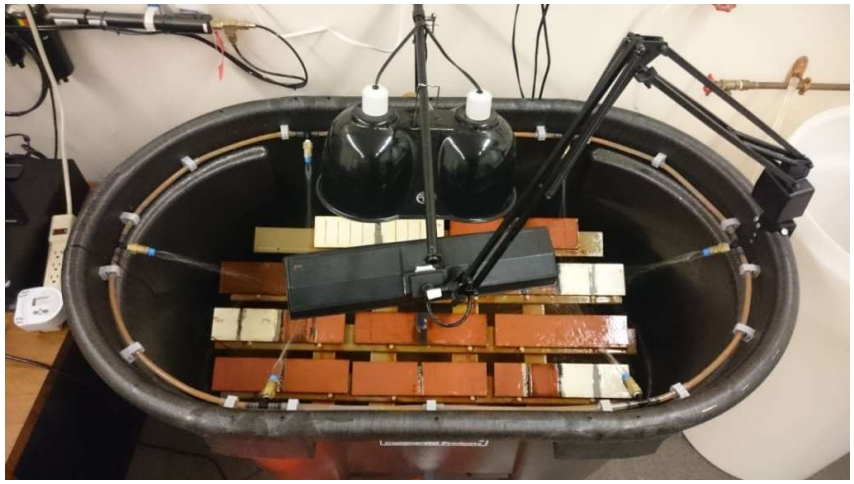
3. Durability and Adhesion Strength Tests

3.1 Accelerated Corrosion Chamber

The components of the chamber include the following:

1. A 100 Gallon chamber (tank)
2. **Nozzles** installed on the perimeter of the chamber to spray salt water
3. A pump that feeds the salt water into the tubing system
4. Infrared light casing containing two **250W infrared bulbs** that can generate heat and dry the specimen.
5. Ultra Violet (UV) light casing containing two Philips T8 15W tubes that radiates UVA/B rays in the range of 350nm wavelength.
6. An inclined rack to hold the steel coupons that had the inclination slope (15º to 30º) according the recommendation from ASTM – B117
7. Timer switches to control the cycles of the actions of UV light, heat, and salt spray
8. Temperature and humidity meter



3.2 Accelerated Corrosion Procedure

Proposed Testing Cycle:

- 12 hours of freezing, The lowest temperature during freezing was -23°C (-10°F)
- 4 hours UV radiation + infrared heating. The infrared light induced temperature on black surface probe was up to 60°C
- 8 hours of salt water spray

3.3 Pull-Off Strength Test

Probes and specimens:

- The steel coupons that were used in the accelerated corrosion test were chosen to have the dimension of 12×4×0.5 inches.
- The **coating thickness** was measured using PosiTest DFT coating thickness gauge.
- The adhesion strength of coating was evaluated according to **ASTM-D7234** and measured with the PosiTest AT-M Manual Adhesion Tester by Defleskowas using 14-mm dimeter dollies.

3.4 Accelerated Corrosion Test Results

First batch results:

- Coating systems:
  - The first was ***three-layer*** coating with two inorganic coating layers with one nano-film layer (proprietary product) in the middle.
  - The second and third ones were inorganic coating with **organic coatings on top**, which were hi-solids polyurethane purchased from Sherwin Williams.
  - The thickness range of coatings was between **160-180 µm**
- After cycles:
  - After 30 Days of cycles: The changes of **pull-off strength were found not to be significant**
  - The failure patterns at the interface indicated that **no corrosion happened at the interface between coating and steel plate.**

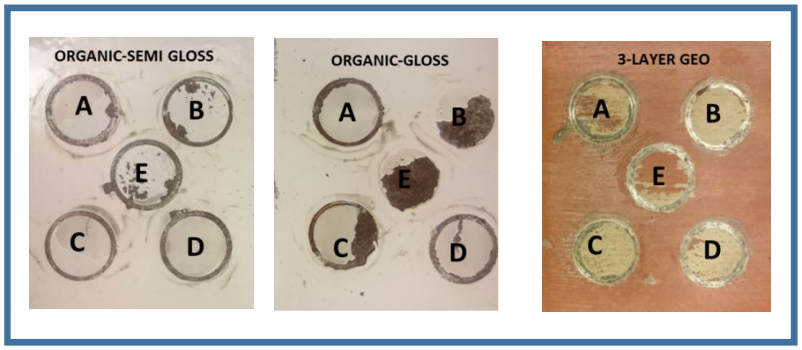
3.4 Accelerated Corrosion Test Results

Summary of Pull-off Strengths and Interface Failure Patterns (1st batch)

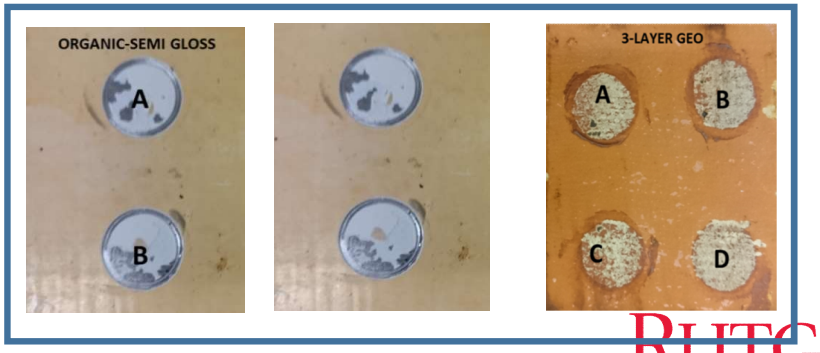
Corrosion System	Pull-off Strength (MPa) and Failure Pattern*								
	Before Corrosion Cycle					After One Month of Corrosion Cycle			
	A	B	C	D	E	A	B	C	D
3 - Layer Inorganic	9.61	6.28	8.06	7.07	4.14	6.59	5.18	3.65	5.06
	CF	CF	CF	CF	CF	CF	CF	CF	CF
Organic on top - Gloss	13.33	10.27	12.65	13.38	7.65	16.13	18.29	/	/
	AF-GD	AF-CS	AF-GD	AF-GD	AF-CS	AF-GC	AF-GC	/	/
Organic on top - Semi Gloss	17.74	15.08	12.52	12.65	13.63	17.27	15.07	/	/
	CF	CF	CF	AF-GD	CF	CF	CF	/	/

*CF: Cohesive failure in the coating; AF-CS: Adhesive failure (coating-steel)
AF-GD: Adhesive failure (glue-dolly); AF-GC: Adhesive failure (glue-coating)

Before Cycles



After Cycles



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3.4 Accelerated Corrosion Test Results

Second batch results:

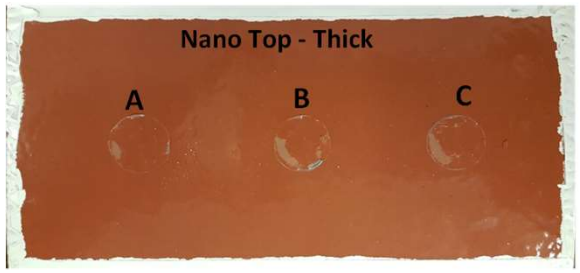
- Coating systems:
  - The first was inorganic coating with 3M sol-gel on top (150 µm average coating thickness).
  - The second and third ones were inorganic coating topped with nano-film with two different thicknesses (150 µm and 210 µm average coating thickness).
- After cycles:
  - The pull-off strength increased after 30-day corrosion cycle, which was probably due to the **continuous curing effect of coating**
  - It was found that the sample with 3M sol-gel performed well after 30-day cycles, but developed powder residue at the surface after 60-day cycles

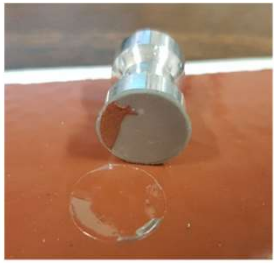
3.4 Accelerated Corrosion Test Results

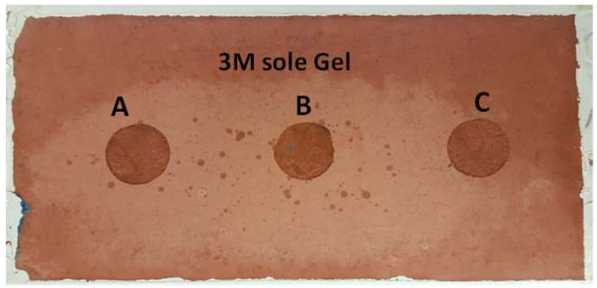
Summary of Pull-off Strengths and Interface Failure Patterns (2nd batch)

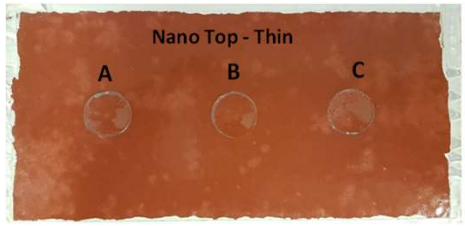
Inorganic Coating System	Pull Off Strength (MPa) and Failure Pattern*								
	Before corrosion cycle			After 30-day corrosion cycles			After 60-day corrosion cycles		
	A	B	C	A	B	C	A	B	C
3M Sol-Gel on top	3.73	4.26	4.17	9.01	8.13	10.92	N/A (due to powder surface)		
	CF	CF	CF	CF	CF	CF			
Nano-film on top (thin)	9.75	9.04	8.8	17.85	15	15.36	16.47	14	8.9
	NA	NA	NA	AF-GC	AF-GC	CF	AF-GC	AF-GC	AF-GC
Nano-film on top (thick)	4.74	4.46	4.15	16.47	13.85	13.99	8.56	7.32	7.29
	CF	CF	CF	AF-GC	AF-GC	AF-GC	AF-CS	AF-CS	AF-CS

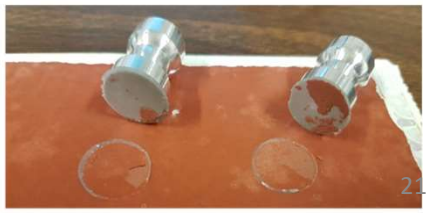
*CF: Cohesive failure in the coating; AF-CS: Adhesive failure (coating-steel)
AF-GD: Adhesive failure (glue-dolly); AF-GC: Adhesive failure (glue-coating)











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3.5 Nano-Modification of Coating

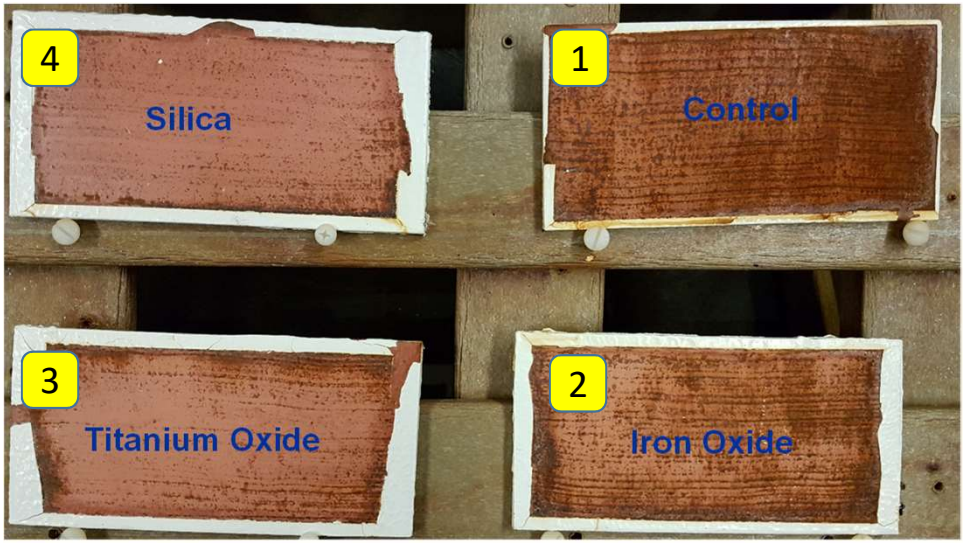
First nano-added batch results:

- Coating systems:
  - Three water-based nano-additives were mixed with inorganic coating:
    - 20% iron oxide
    - 30% titanium oxide
    - 30% silica (in weight)
  - The **water amount from the solutions of nano-additives was accounted for** so that the total water content in the coating mix remained unchanged
  - **Two specimens for each coating system** in addition to two control specimens were prepared (**total 8 specimens**)

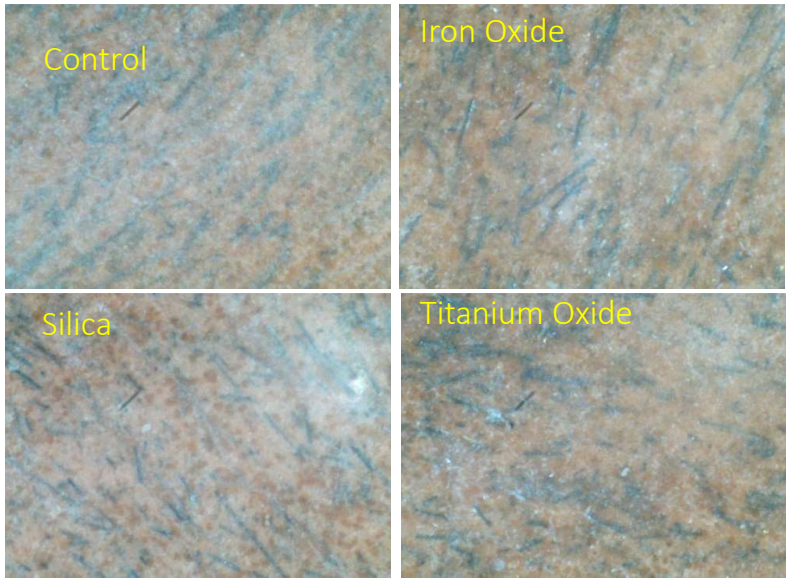
3.6 Accelerated Corrosion Test Results – Nano-modified Coating

- After cycles:
  - Blistering appeared in the following order:
    1. Control specimen
    2. Iron oxide
    3. Titanium oxide
    4. Silica

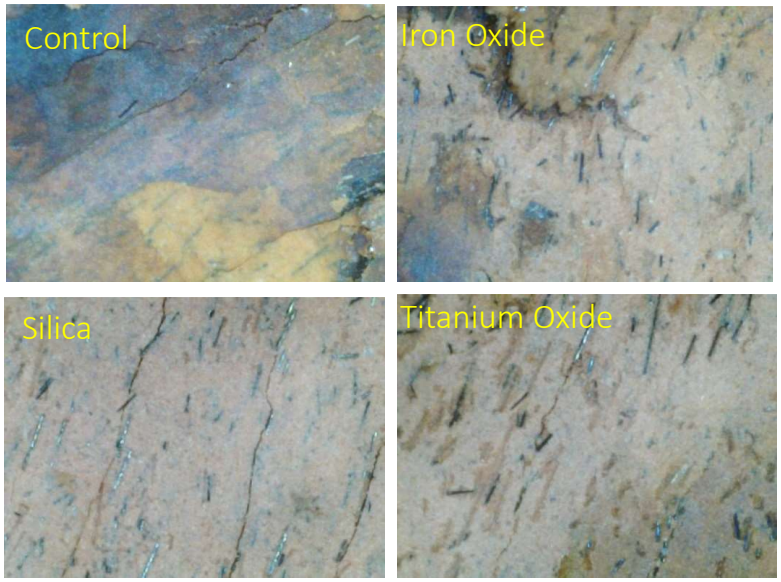
- **Groove marks** from **foam brush** may have also contributed to concentration of corrosion along the grooves



3.6 Accelerated Corrosion Test Results – Nano-modified Coating



Before Cycles



After Cycles

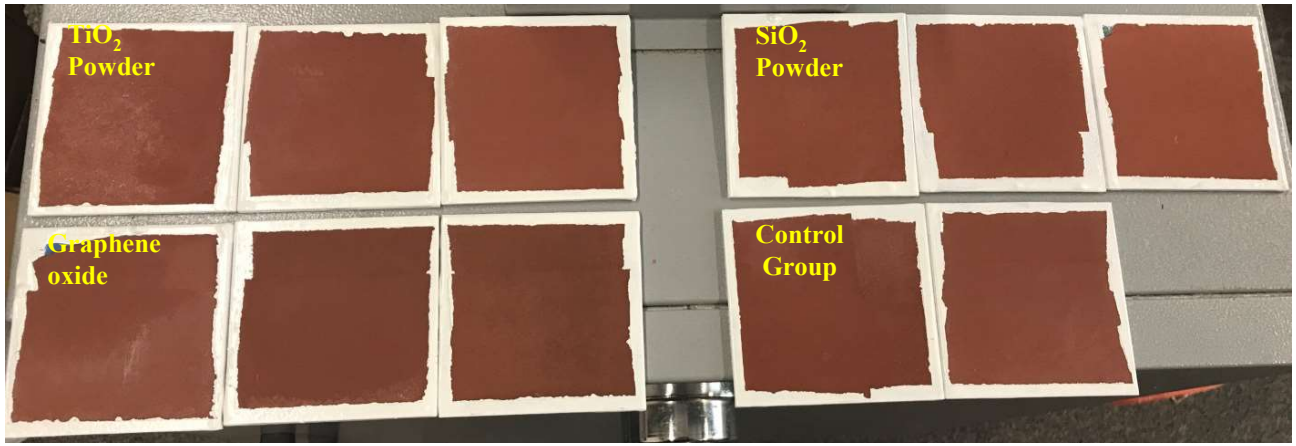
- After cycles:
  - Microscopic images of surface showed no crack before corrosion cycles.
  - After corrosion cycles rust developed within micro-cracks.

3.6 Accelerated Corrosion Test Results – Nano-modified Coating

Second nano-added batch results:

- Coating systems:

Additives	Nano Contents
TiO_2 powder	1%, 3%, 5%
SiO_2 powder	1%, 3%, 5%
Graphene oxide	1%, 3%, 5%



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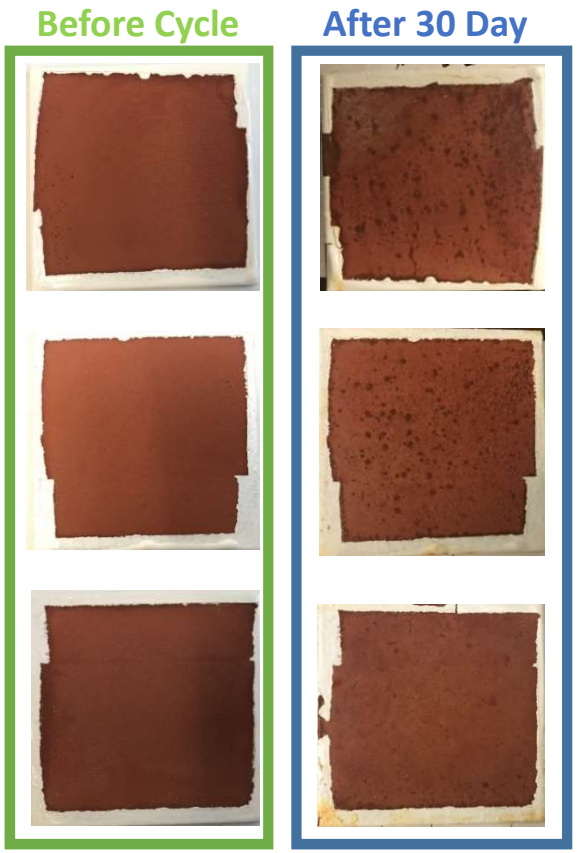
3.6 Accelerated Corrosion Test Results – Nano-modified Coating

Pull-Off Strength Test Results (after 30-day corrosion test)

Samples	Bonding strength (MPa)			Average (MPa)
TiO_2 1%	2.95	3.68	4.19	**3.61**
TiO_2 3%	3.95	2.84	3.58	**3.46**
TiO_2 5%	3.47	3.68	-	**3.58**
SiO_2 1%	4.55	4.52	-	**4.54**
SiO_2 3%	3.36	4.16	3.95	**3.82**
SiO_2 5%	3.7	3.98	-	**3.84**
Graphene oxide 1%	4.51	4.37	4.05	**4.31**
Graphene oxide 3%	3.11	3	3.39	**3.17**
Graphene oxide 5%	4.01	3.54	3.37	**3.64**



TiO_2 3%

SiO_2 3%

Graphene oxide 3%

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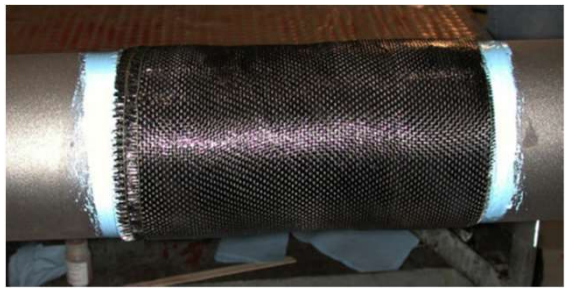
4. Coating Application with CFRP

4.1 Coating Application with CFRP

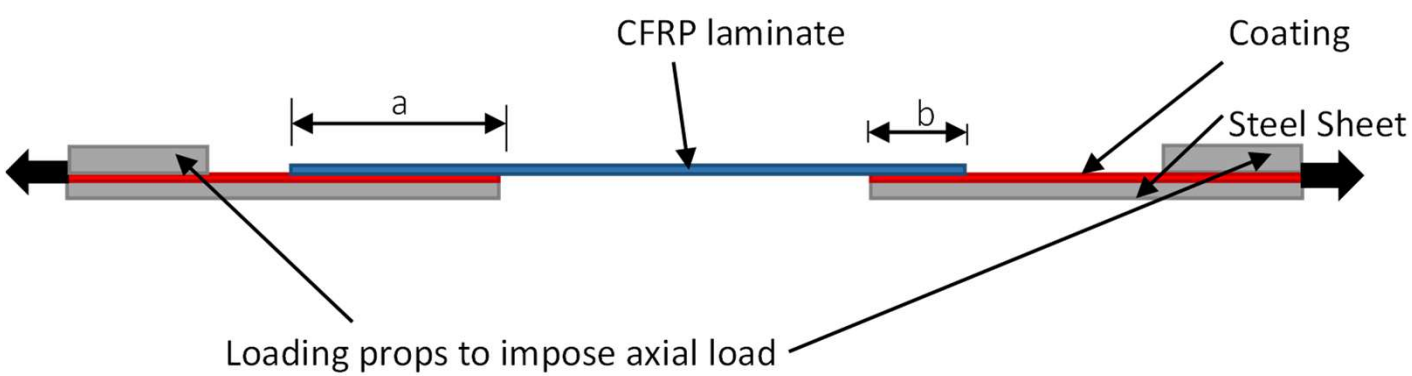
- Traditional repair of pipeline in cases of pipe damage and thickness loss has been cutting and replacing of defective section.
- Application of CFRP has emerged as a less expensive alternative.
- Direct contact between carbon fiber and steel may induce **galvanic corrosion** (Tavakkolizadeh and Saadatmanesh 2001).
- Inorganic coating can be used as the intermediate layer between CFRP and steel.



Duell et al. 2008

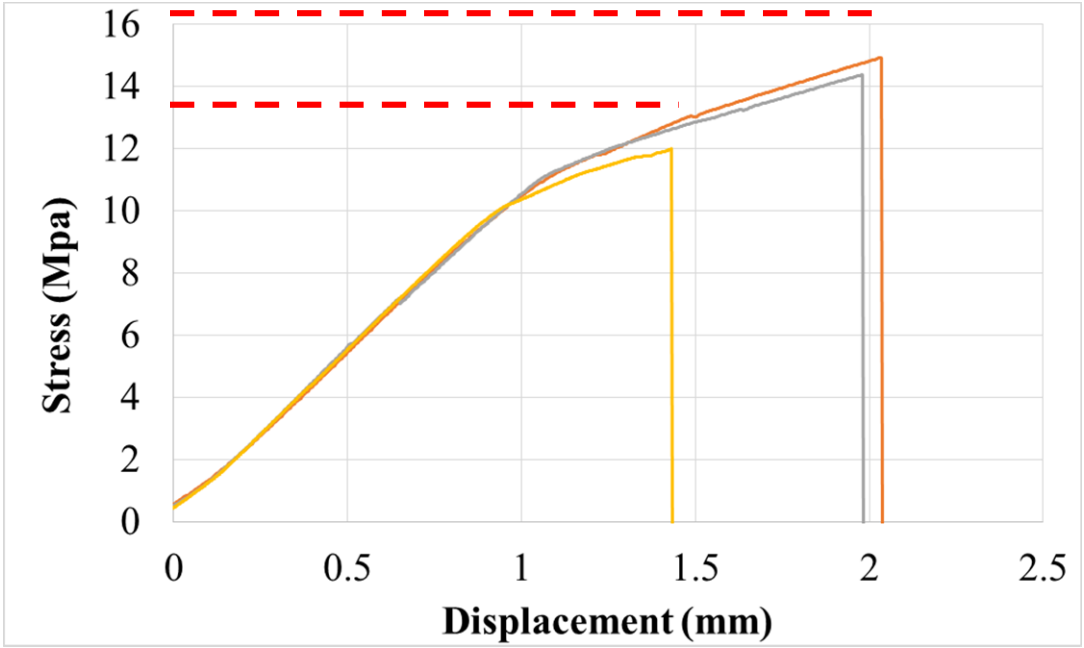
4.2 Shear Strength between CFRP and Steel

- Interface Stress Transfer: Modified lap shear tests were conducted to measure the shear bonding strength between CFRP and steel with and without coating

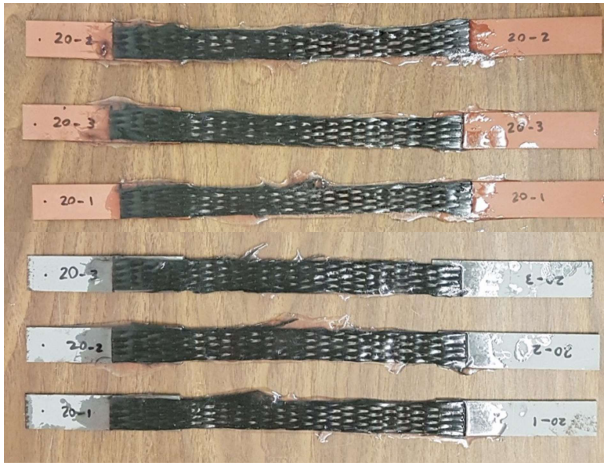


4.3 Shear Strength Results

- Carbon Fabric: Medium weight unidirectional carbon fabric (DowAksa CFU20T)
- Saturant resin : DowAksa CarbonBond 300-HT
- Observed bond strength range (12-14 Mpa) for 20mm bond length was in agreement with manufacturers datasheet.

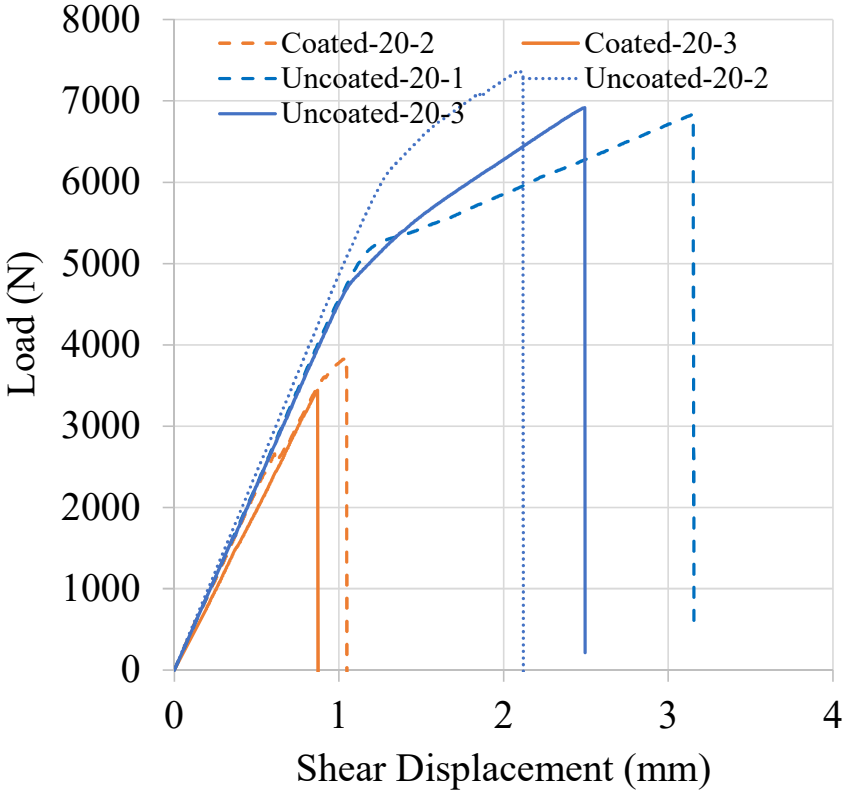


4.4 Shear Strength between CFRP and Coating



Ultimate Bond Strengths for Coated and Uncoated Specimens

Specimen	Ultimate load (N)	Bond strength (MPa)
Coated-20-2	3650	**9.1**
Coated-20-3	3440	**8.6**
Uncoated-20-1	6836	**17.1**
Uncoated-20-2	7336	**18.3**
Uncoated-20-1	6913	**17.3**



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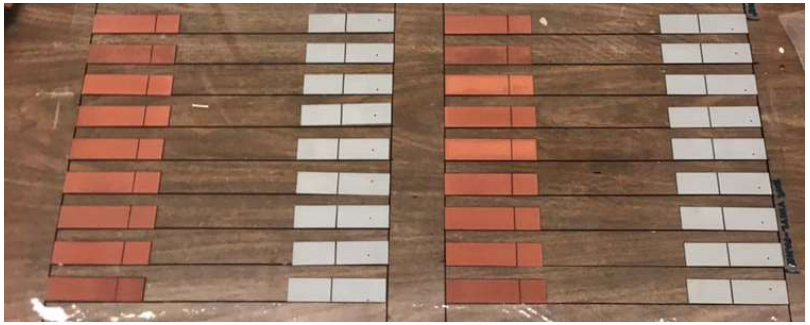
4.5 Shear Strength between CFRP and Nano-modified Coating

- For these series of tests 30mm bond length was selected.
- Specimens were cured for 10 days in room temperature and later placed in the oven at 60°C (150 °F) for 48 hours.
- To ensure failure occurs at the intended location opposite side was not coated and had 50mm bond length.



4.5 Shear Strength between CFRP and Nano-modified Coating

Shear Strengths Measurements for Samples with SiO_2

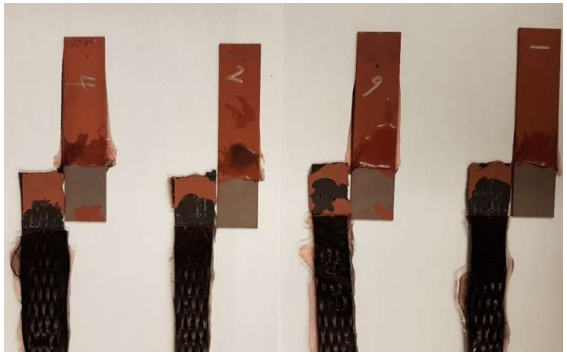
SiO2 Nano Compositions	Shear Strength (MPa)	Average Strength (MPa)
1% - S11	8.7	**7.25**
1% - S6	5.8	
3% - S1	7.0	**7.7**
3% - S2	8.4	
5% - S5	9.4	**10.5**
5% - S10	11.7	

Bond Strengths Measurements for Samples with TiO_2

TiO2 Nano Compositions	Shear Strength (MPa)	Average Strength (MPa)
1% - S15	3.7	**4.0**
1% - S16	4.4	
3% - S8	6.4	**6.4**
3% - S14	6.5	
5% - S3	7.7	**6.7**
5% - S20	5.6	

Bond Strengths Measurements for Samples with graphene oxide

Graphene-Oxide Nano Compositions	Shear Bond Strength (MPa)	Average Strength (MPa)
1% - S12	5.0	**5.8**
1% - S21	6.6	
3% - S4	5.5	**5.5**
3% - S22	6.5	
5% - S9	5.5	**5.7**
5% - S17	5.8	

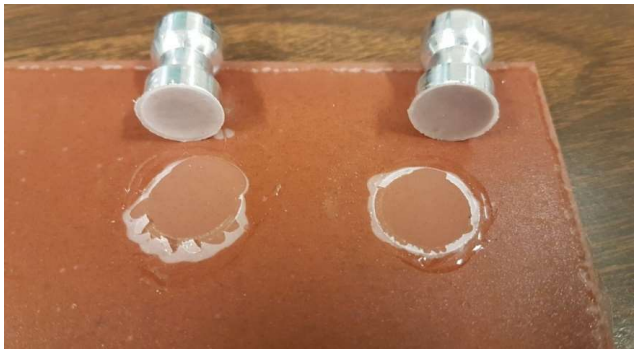


4.6 Pull-Off Strength between CFRP Resin and Coating

- Same saturant resin used in fabrication of CFRP laminates (*DowAksa CarbonBond 300H)* was used in this test. Saturant resin was applied over the coated steel plate.
- Thickness measurements were repeated on top of the coating and the average thicknesses were 144 and 152µm on two specimens.

Pull-Off Strength of Saturant Resin on Coated Specimen

Sample	Pull Off Strength (MPa)			
	1	2	3	**Average**
1	5.4	5.1	NA	**5.25**
2	5.2	4.6	5.2	**5.03**



5. Finite Element Analysis of Composite Repair

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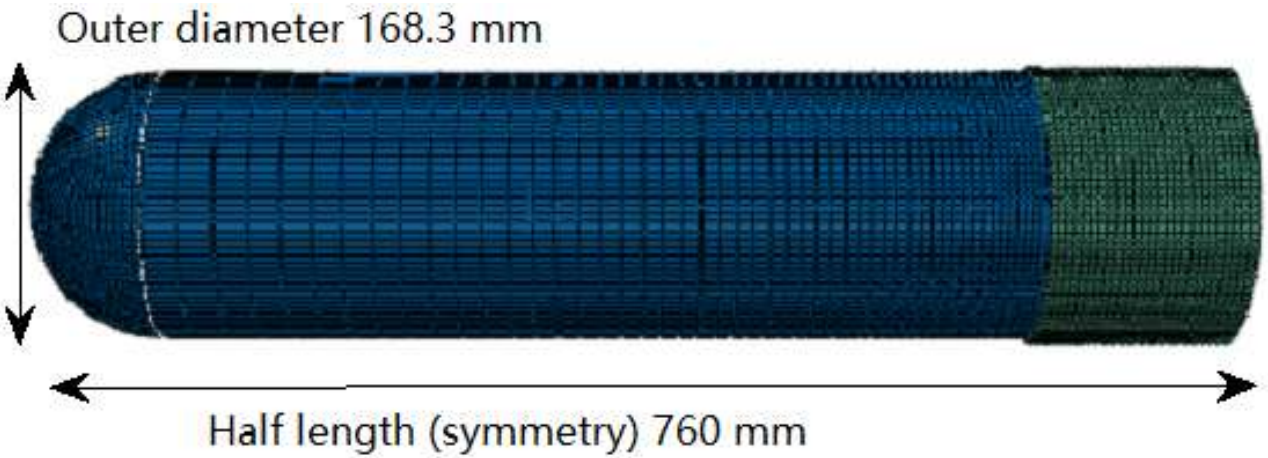
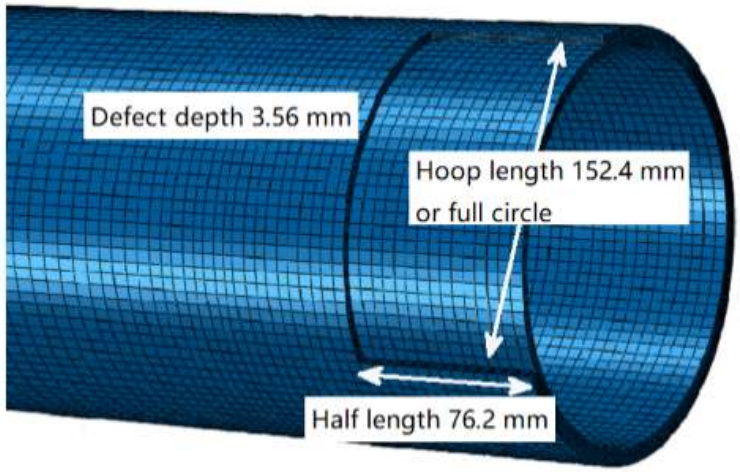
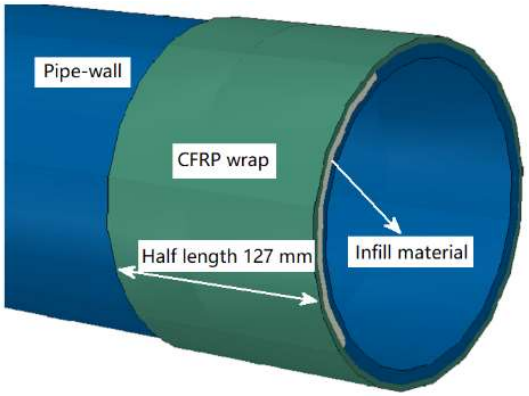
5.1 Finite Element Modeling

- The primary objective of analytical study is to evaluate mechanical behavior of the defected pipeline **repaired with carbon fiber reinforced polymer (CFRP) and the inorganic coating as intermediate layer**.
- Two repair methods were evaluated:
  - Full encircle **wrap**
  - **Patch** with various hoop lengths
- Burst pressure was observed when Von-Mises stress reached ultimate strength of steel. **Design pressure was 18.5 MPa**. In practice, the MAOP cannot exceed the lowest value among design pressure, test pressure, MAOP during five years preceding the applicable date of pipeline, and the maximum safe pressure determined by the operator (49 CFR 192.619).

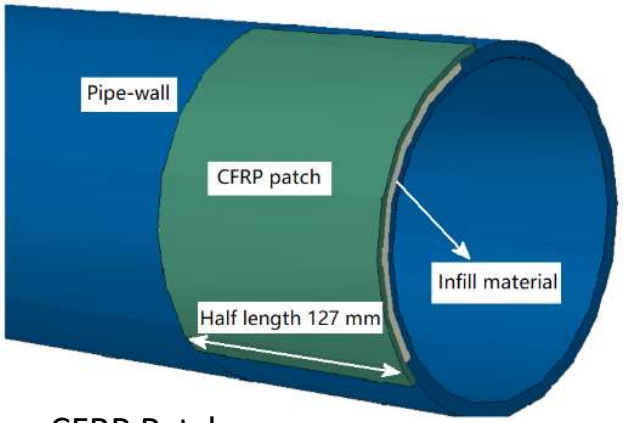
5.2 Model Size and Mesh







Full CFRP Wrap



CFRP Patch

5.3 Material Properties

Material	Properties*			
	Linear (below yield)		**Nonlinear (above yield)**	
Steel	Young's Modulus	207 GPa	Yield Stress (MPa)	Plastic Strain
			301	0.0000
			317	0.0029
			374	0.0138
			412	0.0207
	Poisson's Ratio	0.3	482	0.0386
			534	0.0575
			596	0.0862
			648	0.1222
Epoxy	Young's Modulus	1.74 GPa	Yield Stress	33 MPa
	Poisson's Ratio	0.45	Tangent Modulus	0.87 GPa
CFRP	Young's Modulus	E_1 5.5 GPa (radial)	Poisson's Ratio (assumed)	ν_{12} 0.1
		E_2 49 GPa (hoop)		ν_{13} 0.4
		E_3 23.4 GPa (axial)		ν_{23} 0.4
	Shear Modulus	G_{12} 29.6 GPa		
		G_{13} 0.69 GPa		
		G_{23} 0.69 GPa		
	Ultimate Hoop Strength	576 MPa		

*Adopted from (Duell et. al 2008)

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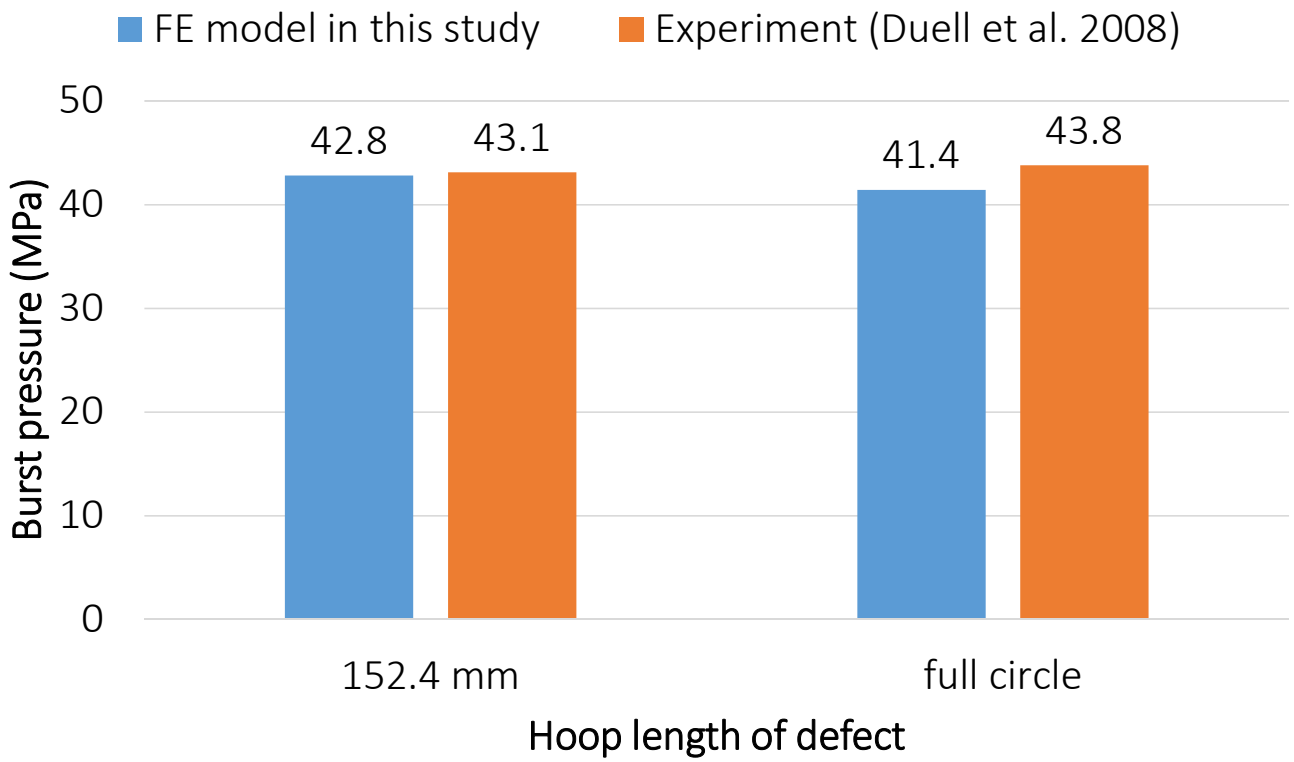
5.4 FE Model Validation



Duell et al. 2008

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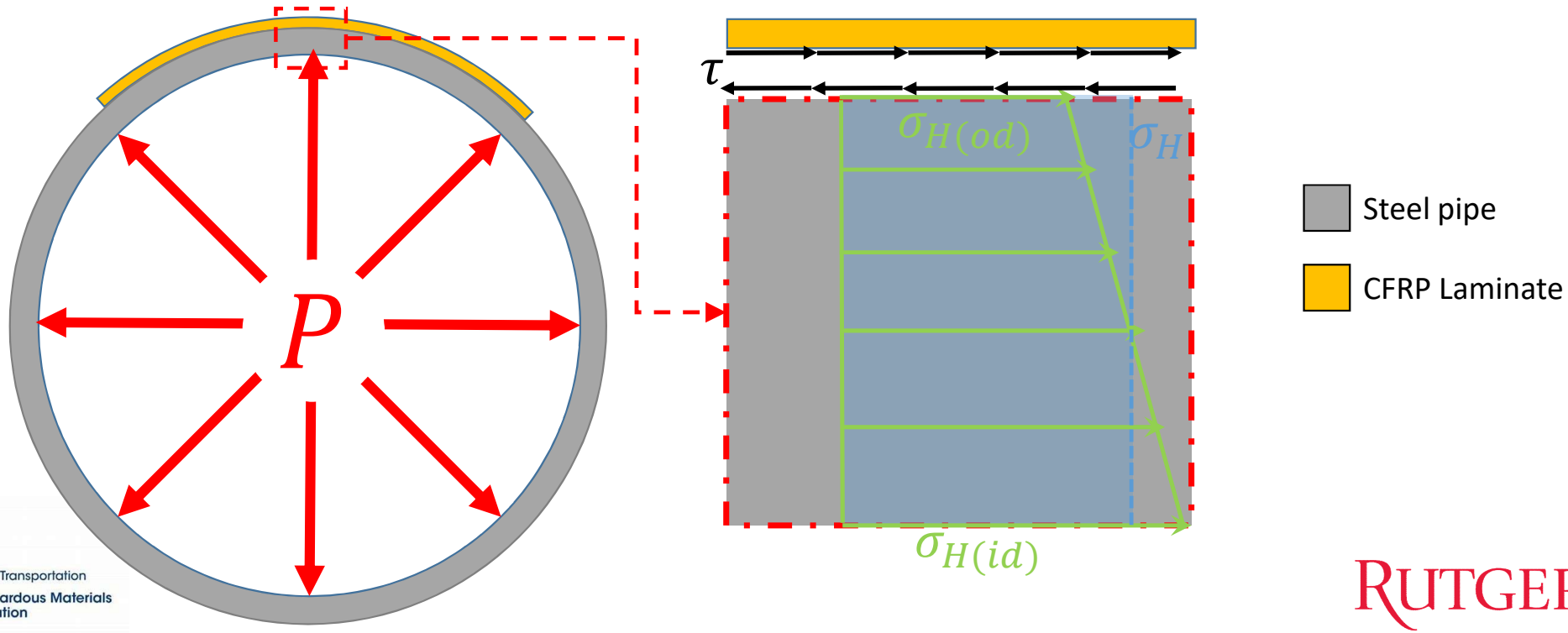
5.5 Stress in Pipeline with Composite Repair

P: Internal Pressure of Pipeline

$\sigma_{H(od)}$: hoop stress at outer diameter σ_H: Hoop Stress τ: Shear stress between CFRP laminate and steel



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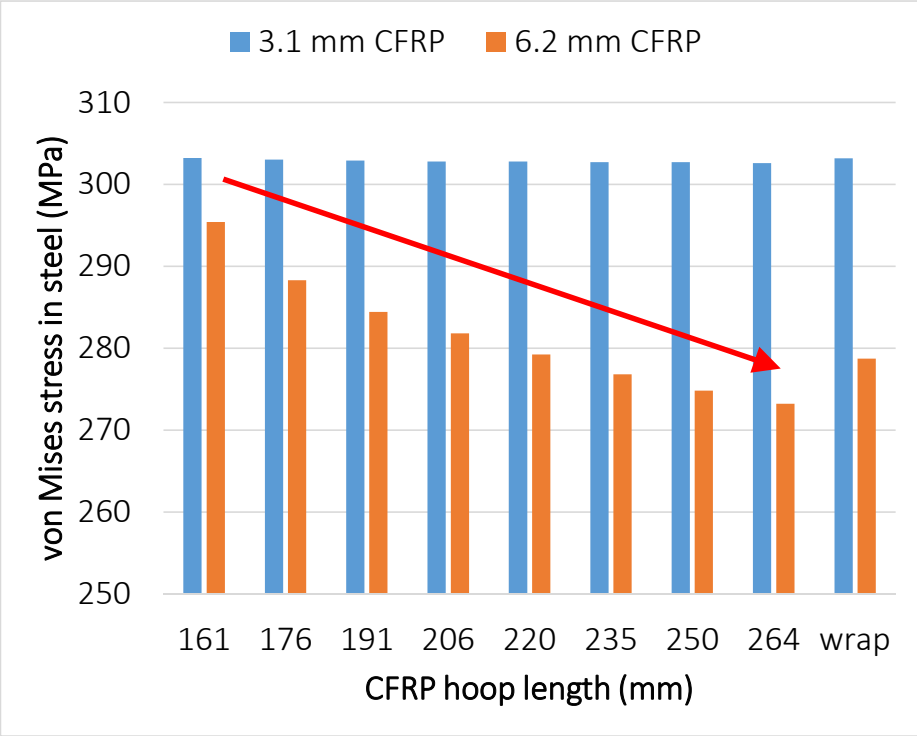
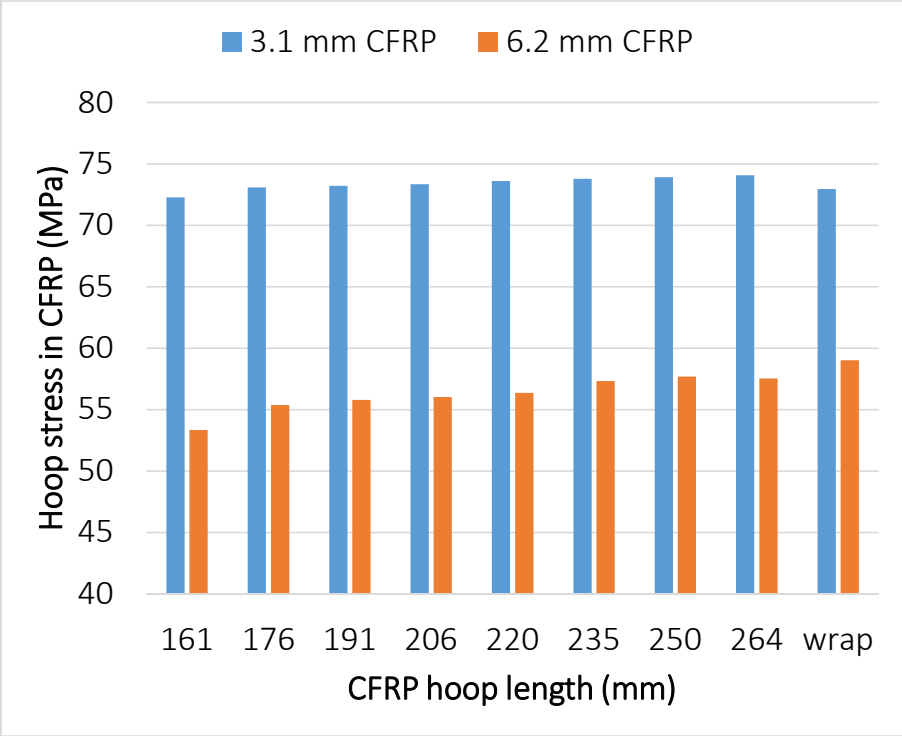
5.6 Sensitivity Analysis of Patch Size



Stress in Steel



Hoop Stress in CFRP layer

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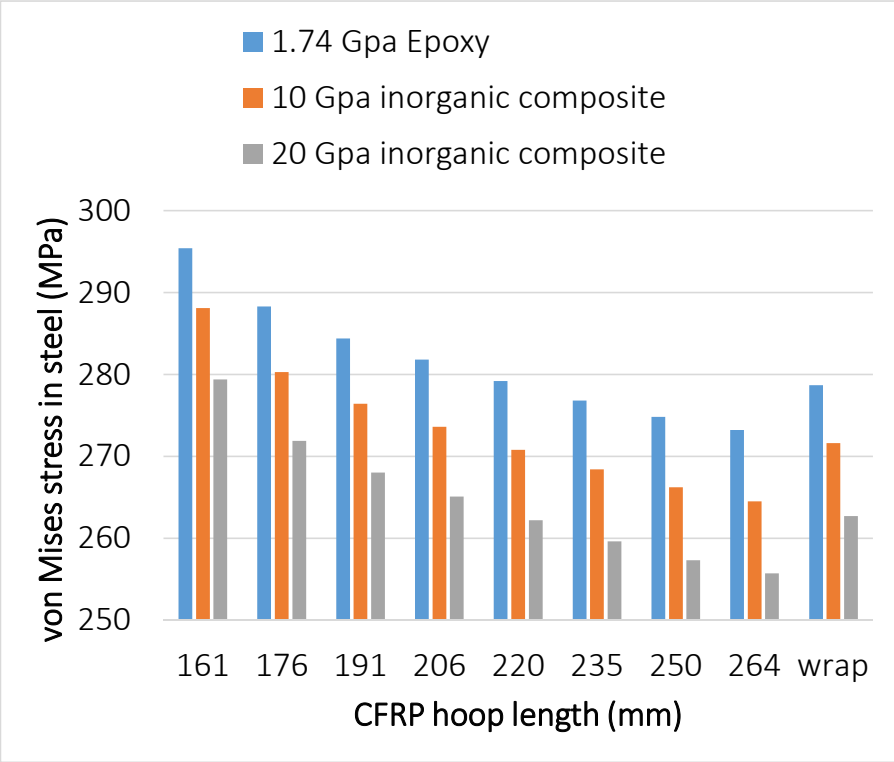
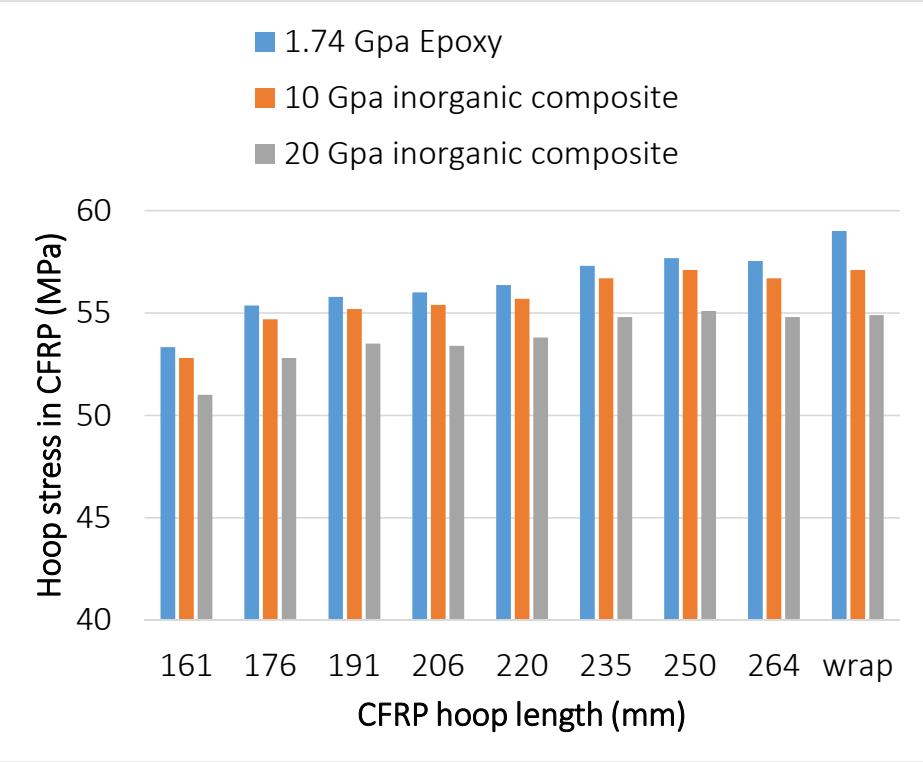
5.6 Effect of Infill Material Modulus





Stress in Steel

Hoop Stress in CFRP layer

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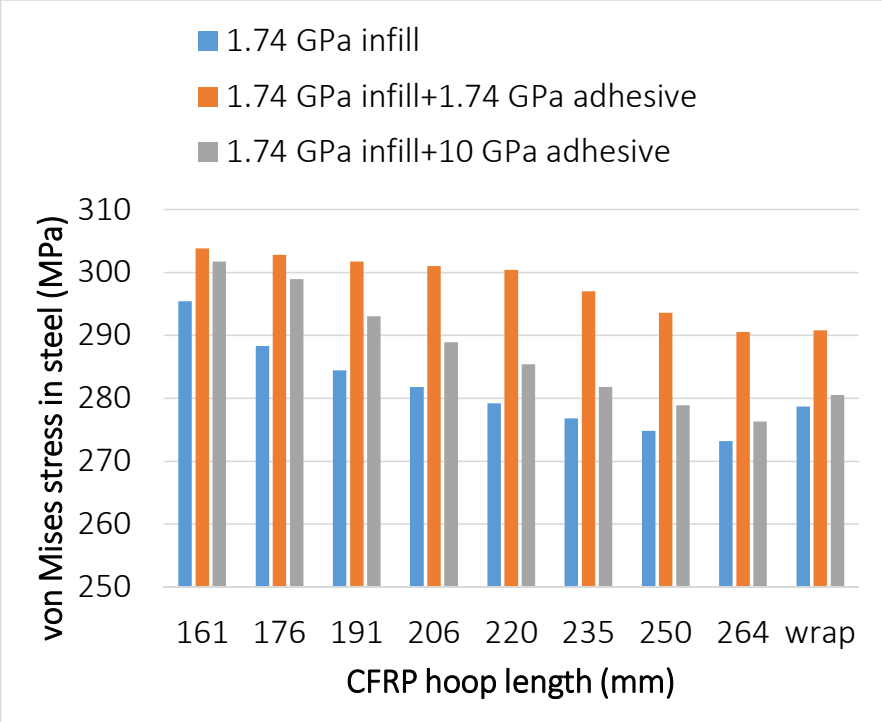
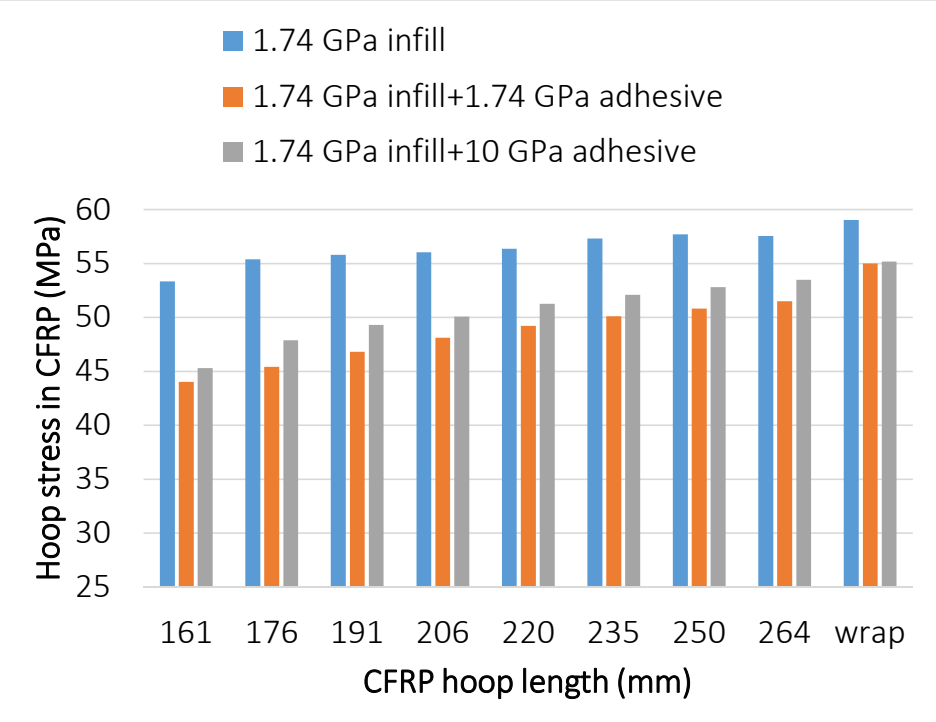
5.7 Effect of Adhesive Layer





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Stress in Steel

Hoop Stress in CFRP layer

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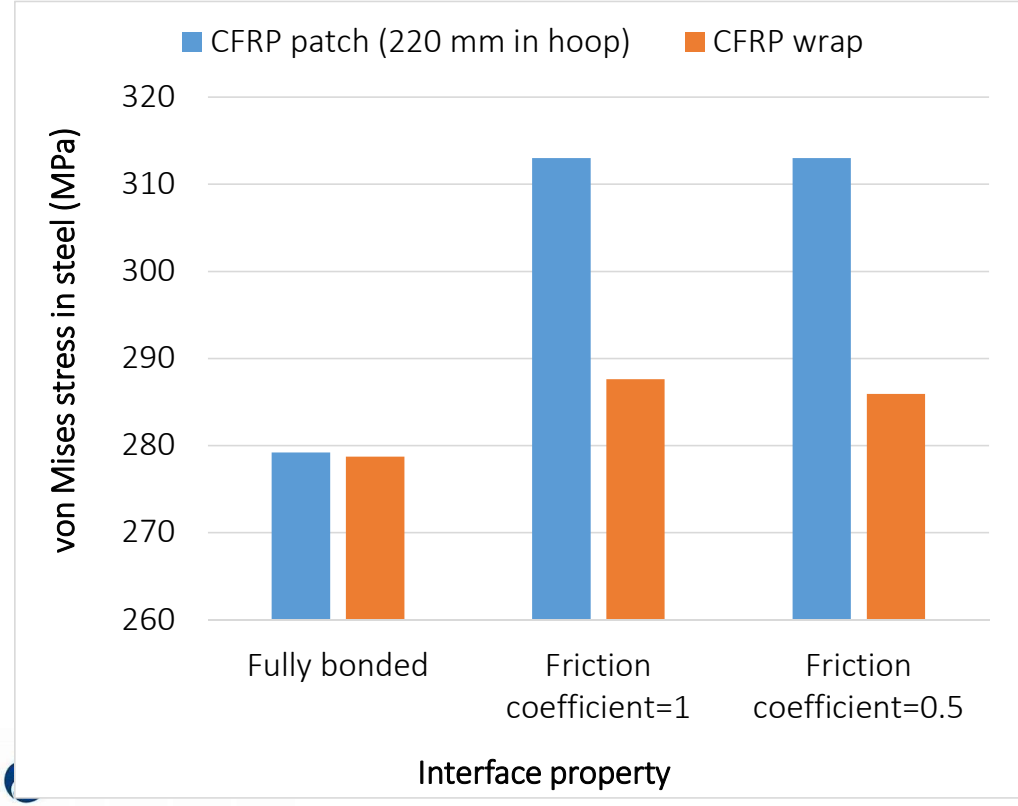
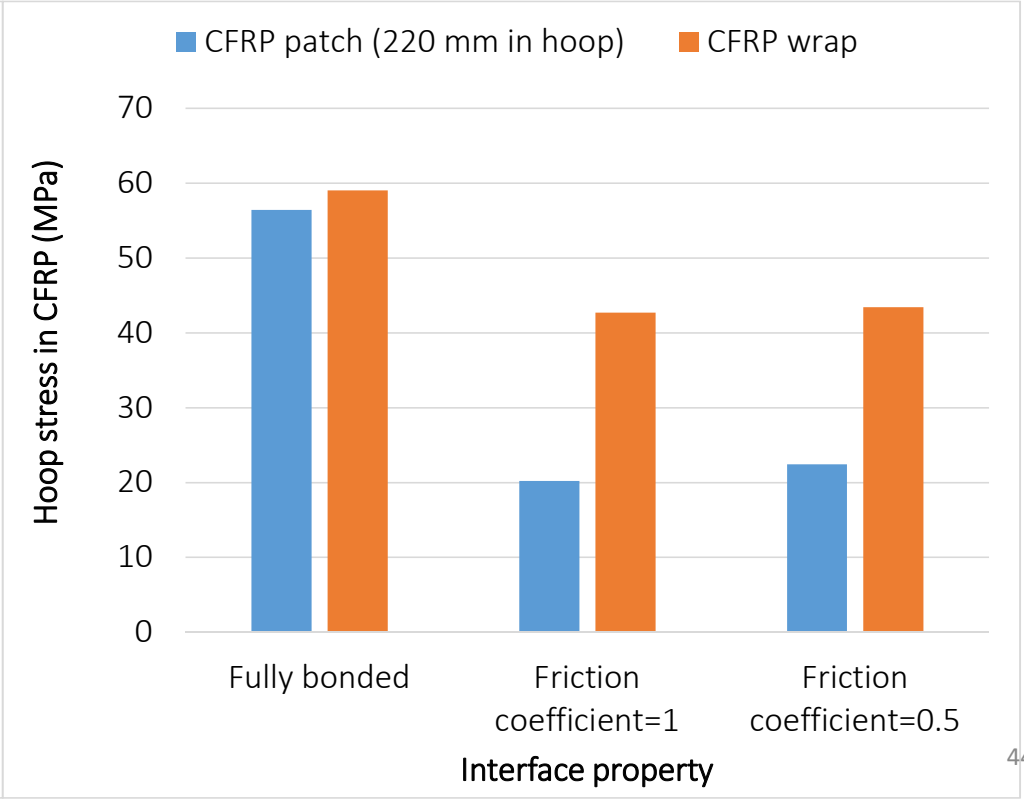
5.8 Effect of Layer Interface Friction



Stress in Steel



Hoop Stress in CFRP layer

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6. Findings and Recommendations

6.1 Findings

- The inorganic composite coating was developed using alkali activation and microfiber in the class of geopolymer material.
- A customized corrosion chamber was built to achieve an accelerated corrosion process including slat water spray, infrared and UV radiation cycles, and freezing.
- The **observations** for performance of nano-additives in terms of **interface bonding strength** were **consistent with corrosion resistance (visual observation)** in accelerated corrosion tests.
- Among different nanomaterials used for coating modification, **nano silica** showed relatively better performance in terms of corrosion resistance and interface bonding with steel substrate.
- Variations in performance were observed for nano-modified coating, depending on **coating thickness** and the **type and content of nano-material.**

6.1 Findings

- The inorganic coating can be used with CFRP for composite repair of pipeline.
- Two different repair strategies, namely wrap and patch repair were considered. The analysis findings show that **patch repair can be used for composite repair** of pipeline defects due to corrosion-induced thickness loss in the pipe wall.
- The maximum von Mises **stress in the pipe wall** and **hoop stress in the CRFP** are affected by the **modulus of infill material** and the **adhesive layer** between CFRP and pipe wall.
- The **bonding condition** between CFRP and pipe wall is critical to reduce the maximum stresses in the patch repair.

6.2 Recommendations

- Geopolymer is one type of green materials that can be synthesized from silicate- and aluminate-bearing materials. The properties of geoplymer-based inorganic coating depend on the **composition of raw materials and curing condition**.
- Future research need be conducted to **optimize the formulation** of coating matrix and improve corrosion resistance.
- **Hybrid coating** is recommended to improve the performance of coating system for pipeline application. This could be achieved by using **inorganic coating as primer** and the organic coating as top layer to combine the advantages of both coatings.

Thank You!

Questions and Comments

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