Effect of SiO_2 Morphology on Fe/SiO_2 Coated Optical Fibers for Corrosion Monitoring

IMCS 08-1625

Ruishu Wright, PhD
Research Scientist
Research & Innovation Center
NATIONAL ENERGY TECHNOLOGY LABORATORY

Presented to the 239th ECS Digital Meeting
with the 18th International Meeting on Chemical Sensors (IMCS)

May 30-June 3, 2021

Disclaimer

This project was funded by the United States Department of Energy, National Energy Technology Laboratory, in part, through a site support contract. Neither the United States Government nor any agency thereof, nor any of their employees, nor the support contractor, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Authors and Contact Information

Ruishu F. Wright[a,b], Nathan Diemler[a,b], James C. Egbu[c], Paul R. Ohodnicki, Jr.[d]

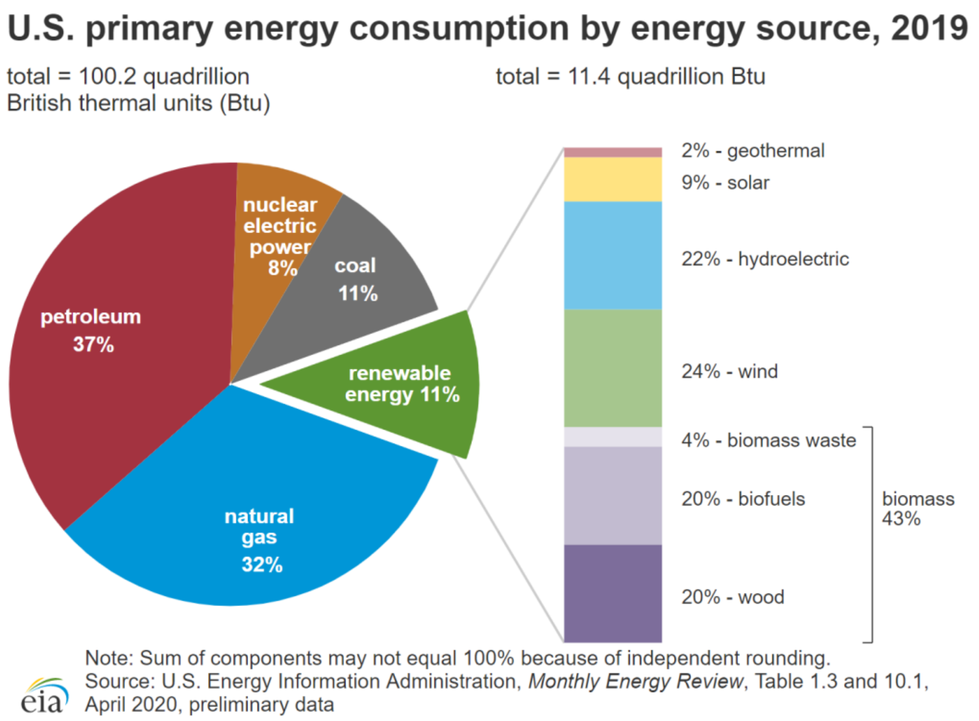
[a]National Energy Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh, PA 15236, USA;
[b]NETL Support Contractor, 626 Cochrans Mill Road, Pittsburgh, PA 15236, USA;
[c]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA;
[d]Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA.

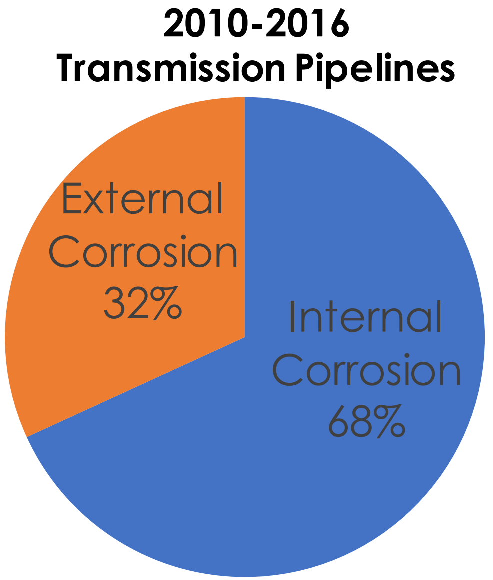
Email: Ruishu.Wright@netl.doe.gov

Outline

- Research background
- Experimental setup
- Results and discussion
- Conclusions

Corrosion in Oil and Gas Infrastructure





Corroded production casing pipe sample from downhole

(University of North Dakota Energy & Environmental Research Center)

- $1.4 billion annually: direct corrosion costs in domestic oil and gas exploration and production in the U.S.
- $589 million: surface piping and facility costs
- $463 million: downhole tubing expenses
- $320 million: capital expenditures related to corrosion.
- **25-30% can be saved** with optimal corrosion management

Ref: Koch, G. H., et al "Corrosion costs and preventive strategies in the United States" (2002).

Corrosion is an Electrochemical Process Causing Mass Loss/Structural Deterioration

NATIONAL ENERGY TECHNOLOGY LABORATORY

Dissolution of CO_2: $CO_2(g) \leftrightarrow CO_2(aq)$

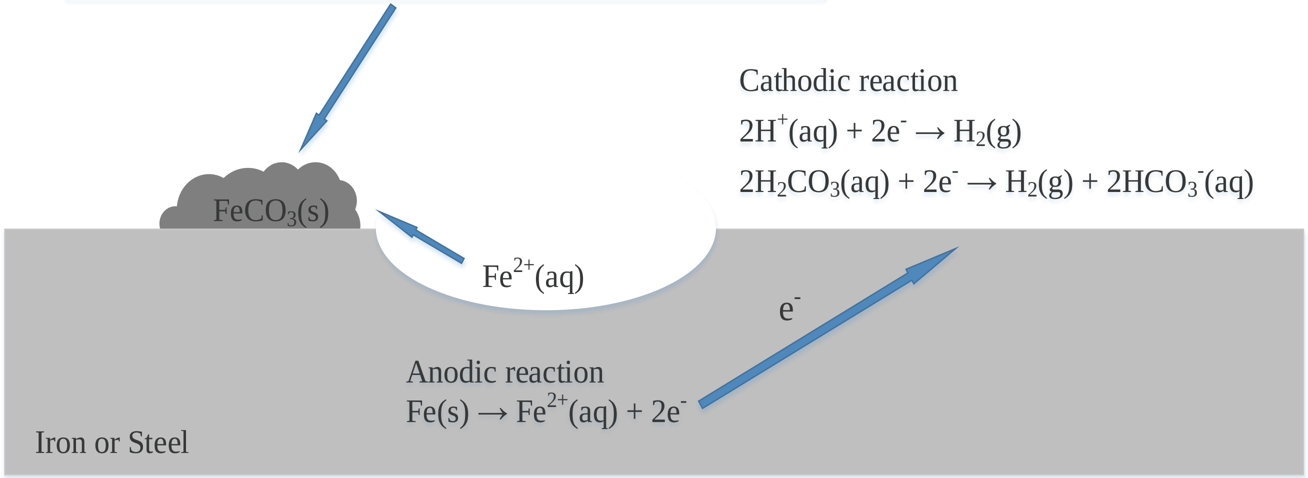
Hydration of CO_2: $CO_2(aq) + H_2O(l) \leftrightarrow H_2CO_3(aq)$

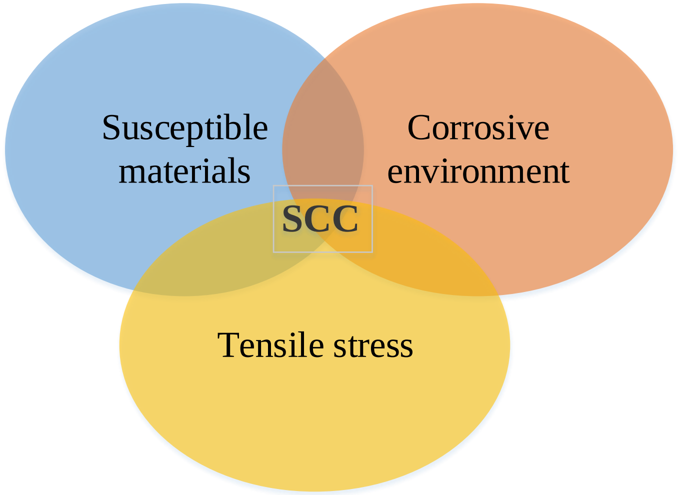
~ 0.2% of $CO_2(aq)$ and quite slow

Dissociation of $H_2CO_3(aq)$:

$H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq)$, pK_1=6.35 at 25 °C

$HCO_3^-(aq) \leftrightarrow H^+(aq) + CO_3^{2-}(aq)$, pK_2=10.33 at 25 °C





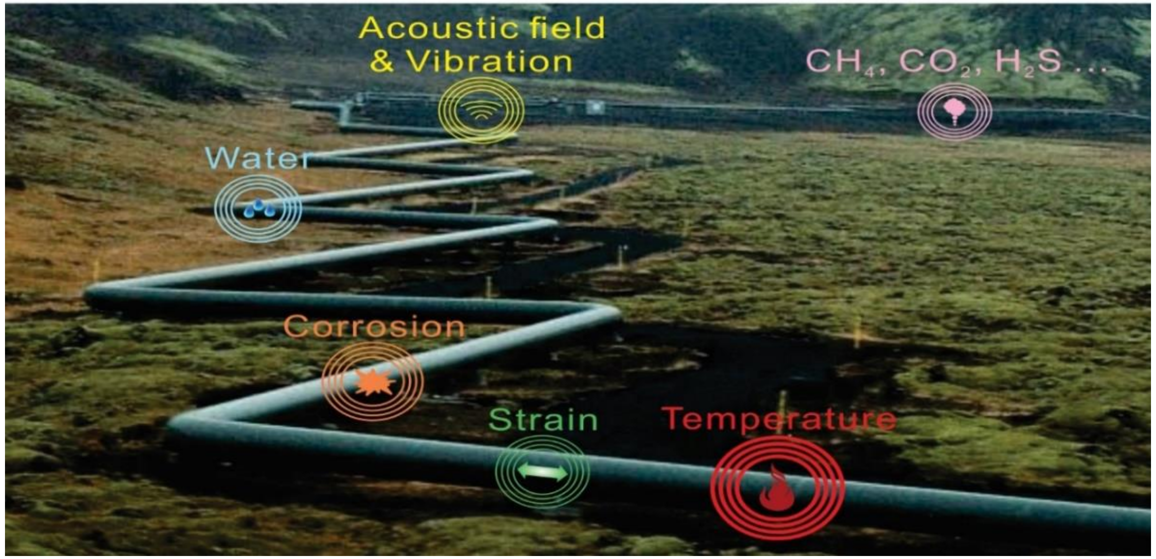
https://corrosion.ksc.nasa.gov/stresscor.htm

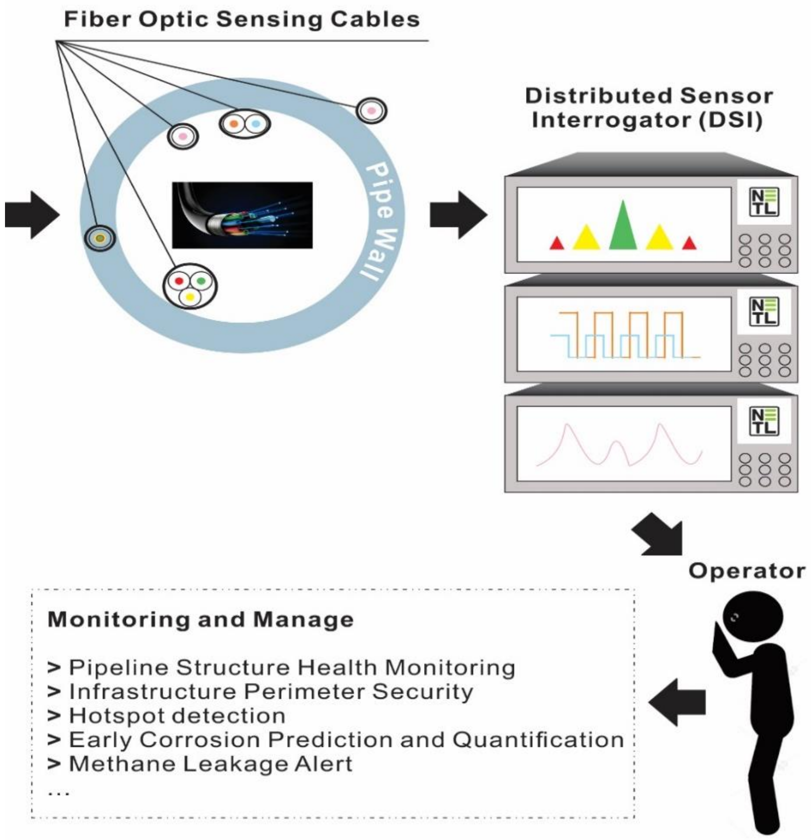
Ref: Jones, D. A., Principles and Prevention of Corrosion, P 237.
Han, J., Nesic, S., Yang, Y., Brown, B., Electrochimica Acta, 2011, 5396-5404.

Optical Fiber Sensor Platform for Natural Gas Pipelines

NATIONAL ENERGY TECHNOLOGY LABORATORY

Pipeline Integrated with Distributed Optical Fiber >100 km





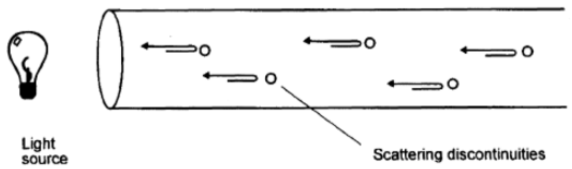
- Early Corrosion Onset Detection
- Methane Leak Detection

A Multi-Parameter, Distributed Optical Fiber Sensor Platform Enabling Reliability & Flexibility

Target Metrics = >100km Interrogation, <1m Spatial Resolution

Distributed Optical Fiber Sensing Principle

Optical Backscatter Reflectometer (OBR) measures the Rayleigh backscattering from the fiber-under-test (FUT).



https://www.samm.com/en/page/86/optical-time-domain-reflectometer-otdr.html

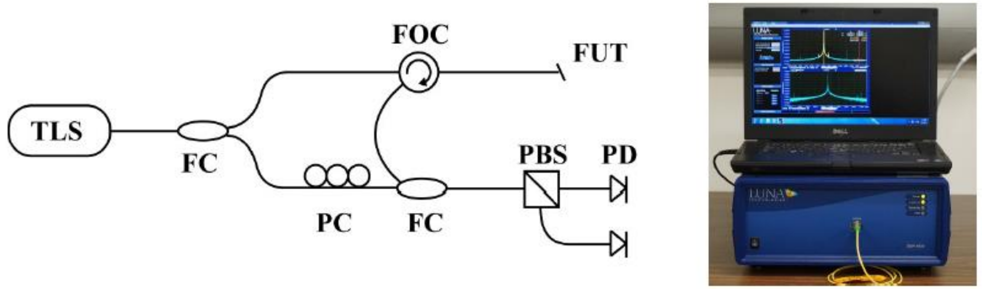
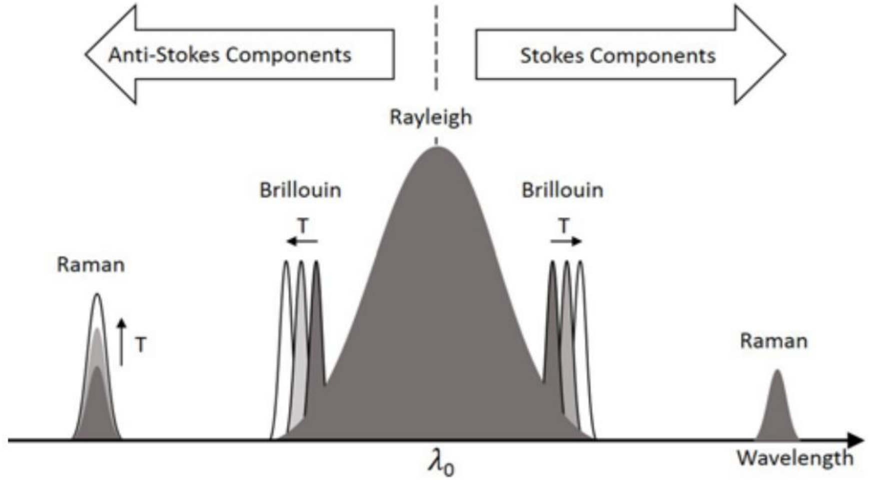


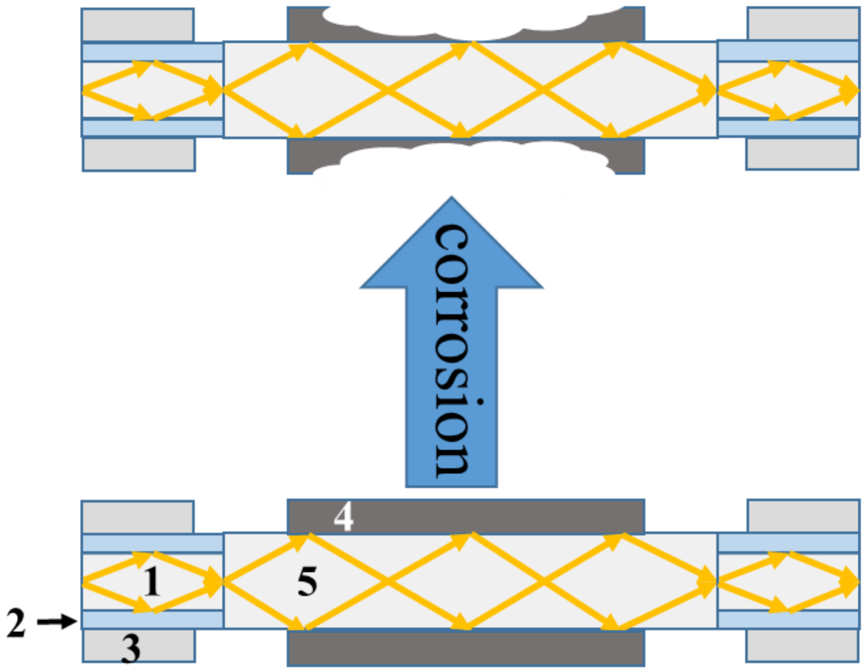
Figure 1 – LUNA OBR 4600 distributed interrogator LEFT: internal components (TLS: tunable laser source, FC: fiber coupler, FOC: fiber optic circulator, PC: polarization controller, PBS: polarizing beamsplitter, PD: photodiode); RIGHT: photo of instrument.

Backscattering enables distributed temperature, strain, and acoustic sensing (DTS, DSS, DAS).



Distributed optical fiber sensors (OFS) enable continuous real-time monitoring over the whole structure with location and sensing information.

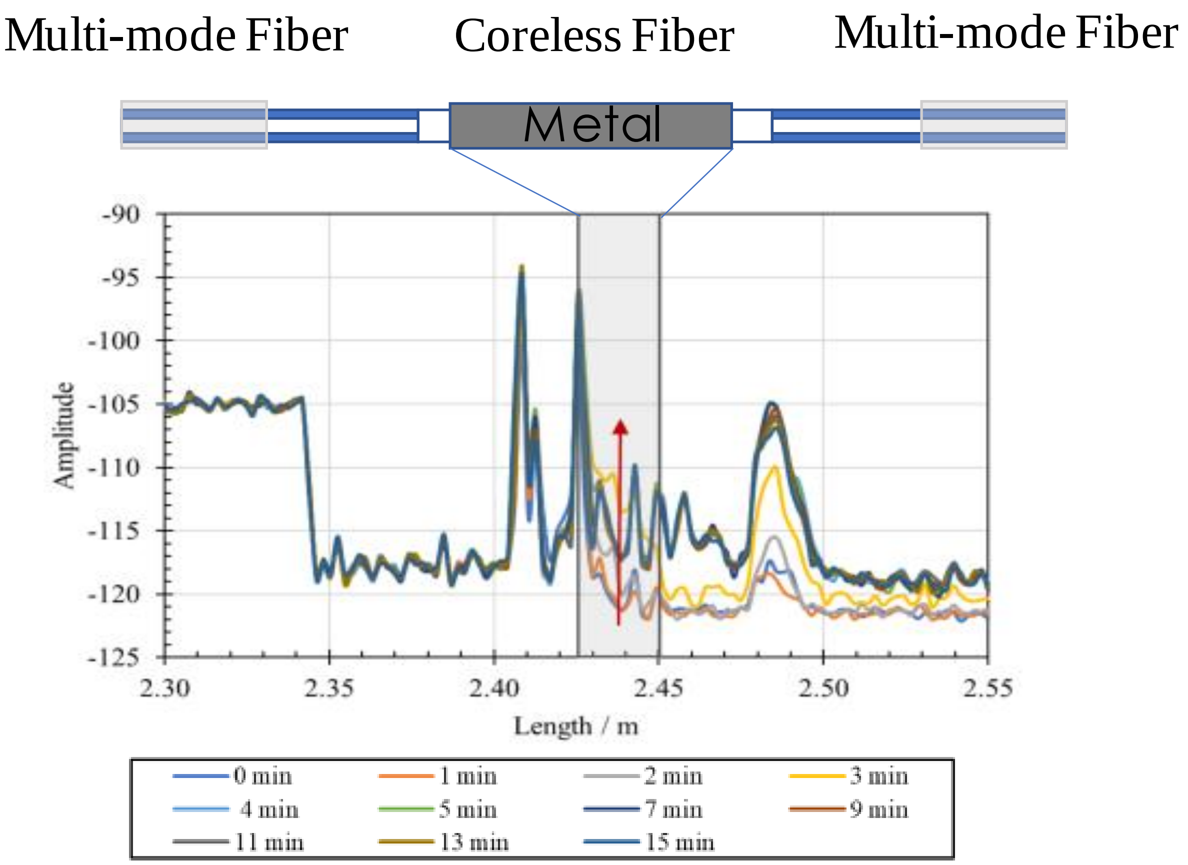
Corrosion Sensing Principle



1—multi-mode fiber core; 2—cladding; 3—polymer jacket; 4—coated metallic film; 5—coreless optical fiber.

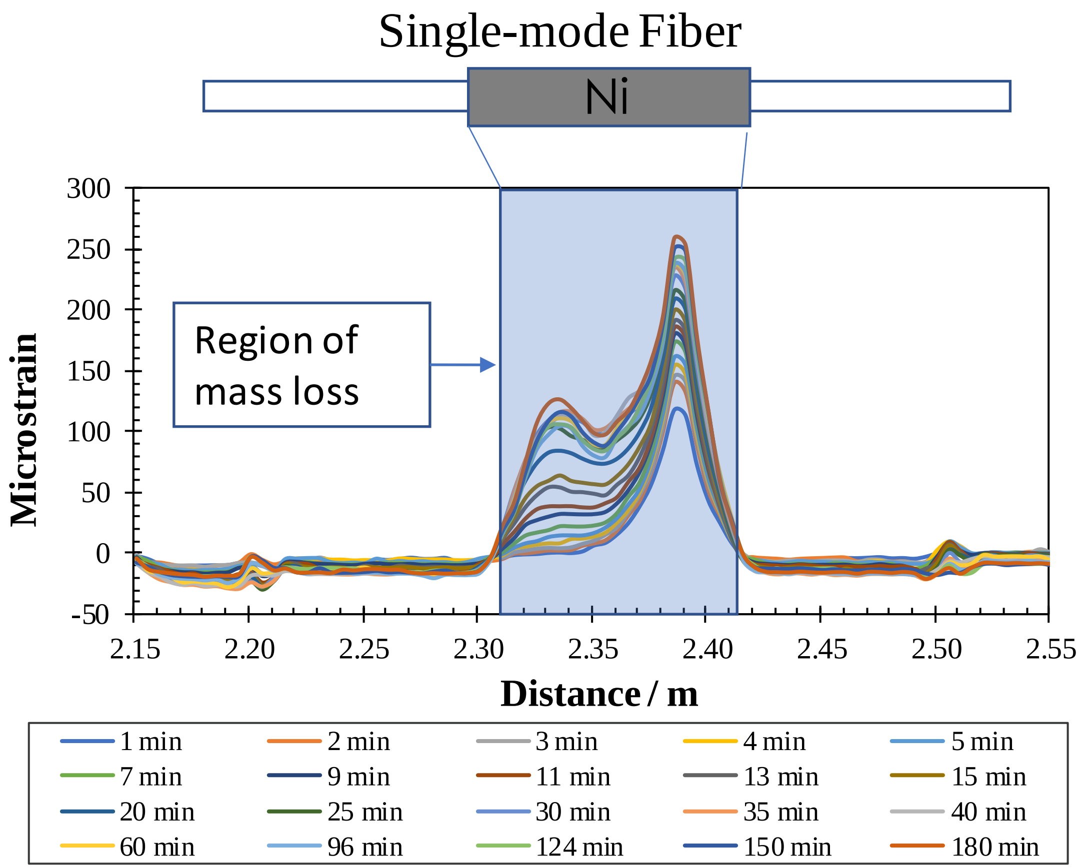
- The metallic thin film leads to broadband light absorption in the evanescent field, which occurs at the interface between the optical fiber and the thin film along the fiber.
- As the metallic film gets thinner, the light absorption of the film decreases; therefore, the light transmission and backscattering increase through the optical fiber.

Optical Fiber Corrosion Sensors From Previous Work



Rayleigh backscattered light increased as corrosion of the metallic film proceeded.

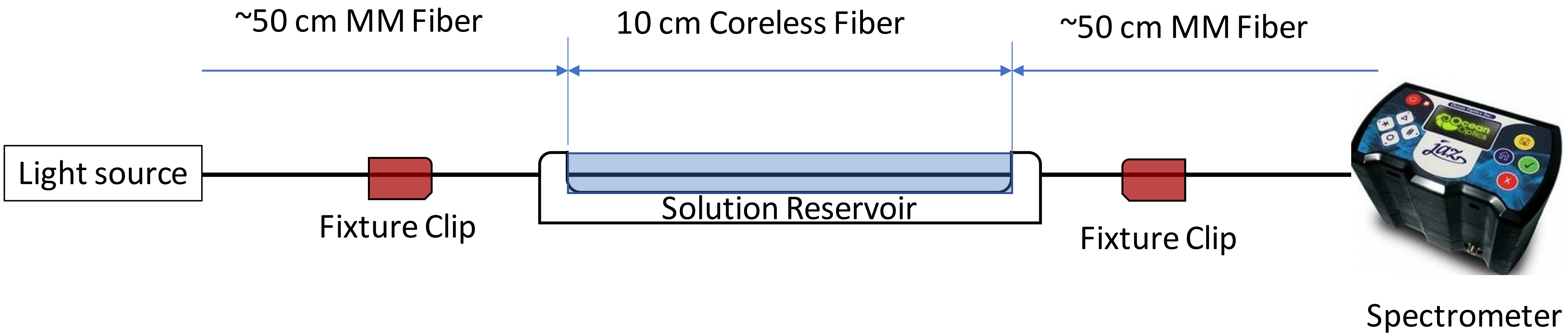
Ref: Wright, et al. *Sensors* 2019, 19, 3964



Microstrain on the fiber increased with mass loss of coated metallic Ni film.

Ref: Wright, et al., *Proc. SPIE 11739, Fiber Optic Sensors and Applications XVII, 117390E*, 2021

Experimental Setup



Schematic diagram of the experimental setup for light transmission measurements in an engraved PTFE holder during electroless plating or metallic film dissolution.

Optical Fiber Preparation and Electroless Plating

NATIONAL ENERGY TECHNOLOGY LABORATORY

➢ TEOS sol-gel recipes for **SiO_2 thin film**

Chemical	Amount	Dip/travel	Dry
DI	1mL	~5 travels of coreless fiber	Overnight
Ethanol	4.5mL		
TEOS	4.5mL		

➢ TEOS sol-gel recipes for **SiO_2 Spheres**

Chemical	Amount	Dip/travel	Dry
DI	1mL	~5 travels of coreless fiber	Overnight
Ethanol	4.5mL		
TEOS	4.5mL		

TEOS: Tetraethyl orthosilicate

➢ Sensitization and Activation (Twice)

Chemical	Amount	Operation
$SnCl_2$	22.6 g/L	30 seconds at room temperature. Rinse in DI water
HCl, conc.	10 mL/L	
$PdCl_2$	0.795 g/L	30 seconds at room temperature. Rinse in DI water
HCl, conc.	5 mL/L	

➢ Electroless plating solutions and conditions

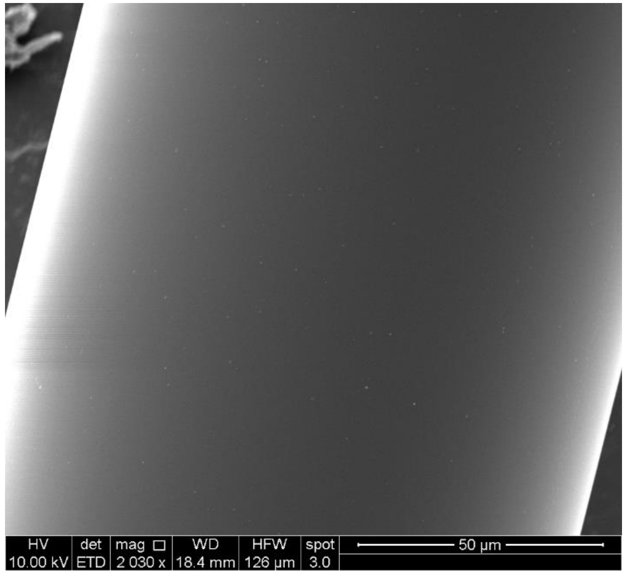
Electroless plating soln.	Fe
Metal source	11 g/L $FeSO_4 \cdot 7H_2O$
Complexing agent	57 g/L $C_6H_5Na_3O_7 \cdot 2H_2O$
Reducing agent	3.0 g/L $NaBH_4$
pH stabilizer	10 g/L H_3BO_3
pH	**10** @ 21.5 ^oC
Solution temperature	21.5 ^oC

Different Morphologies of SiO_2 Layers on Optical Fibers

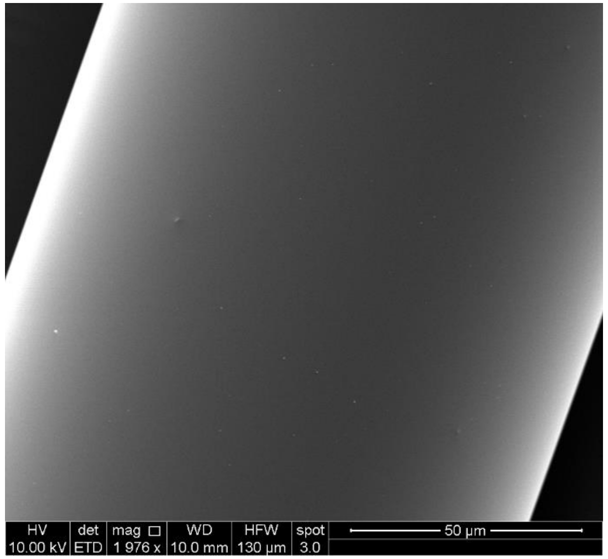
NATIONAL ENERGY TECHNOLOGY LABORATORY

SEM images

Bare fiber

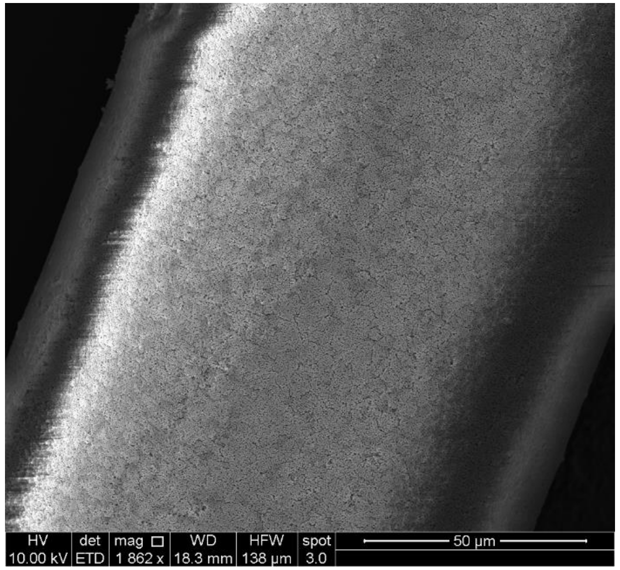


SiO_2 thin film

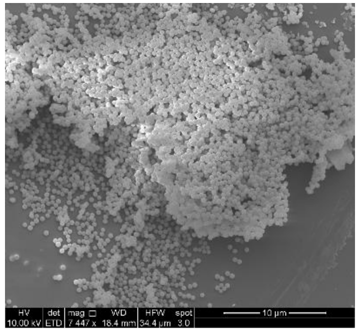


Smooth SiO_2 thin film coating

SiO_2 Spheres



Sphere size: sub-micron



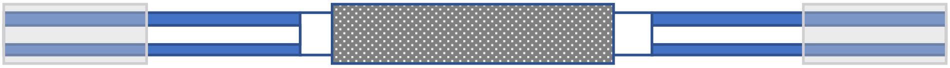
- Different SiO_2 layer morphologies were obtained from different TEOS gel-sol recipes.
- SiO_2 thin film vs SiO_2 spheres.

Fe Plating on SiO_2 Coated Optical Fibers

NATIONAL ENERGY TECHNOLOGY LABORATORY

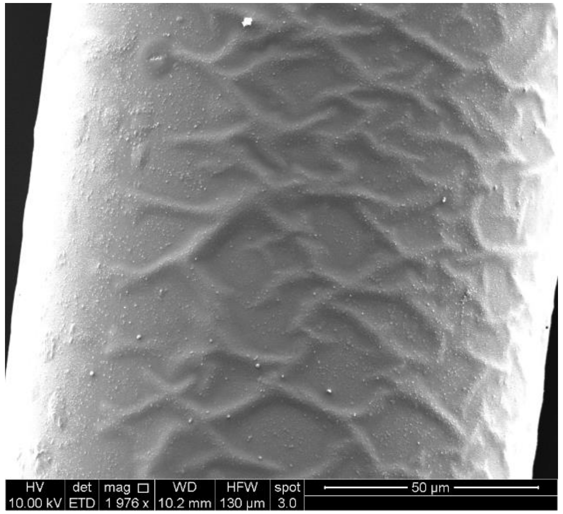
SEM images

Fe on SiO_2 spheres

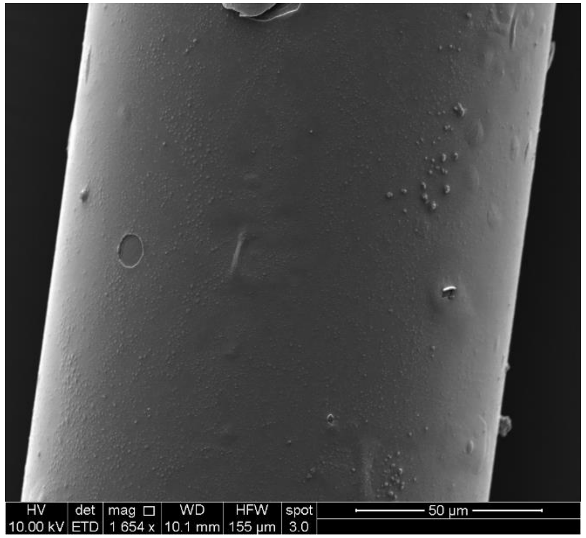


Multi-mode Fiber Coreless Fiber Multi-mode Fiber

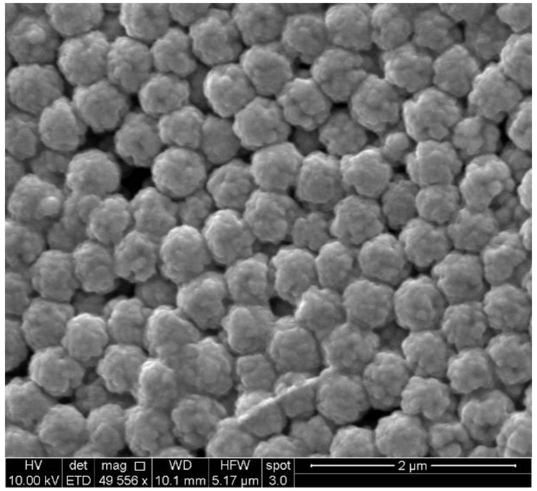
Bare fiber



SiO_2 thin film



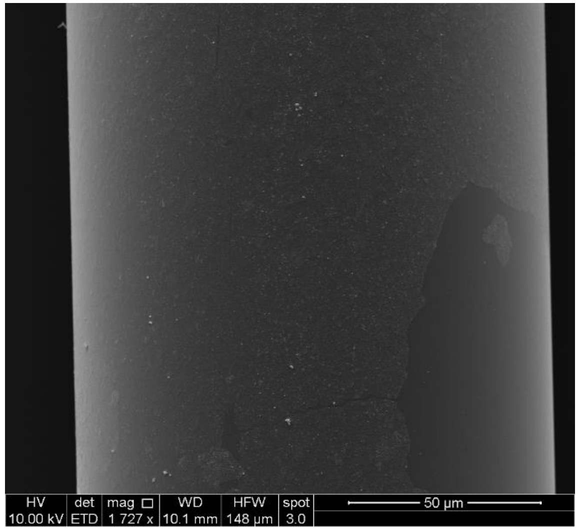
SiO_2 Spheres



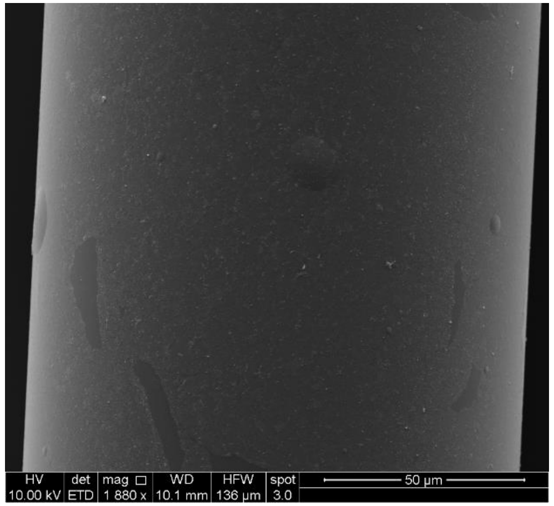
After Fe Dissolution in pH 2.5 Solution

SEM images

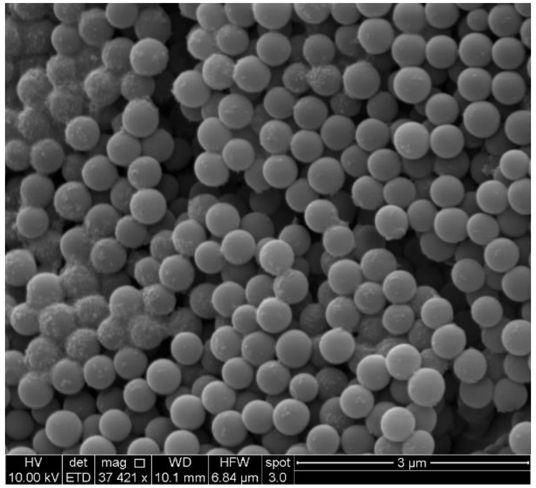
Bare fiber



SiO_2 thin film

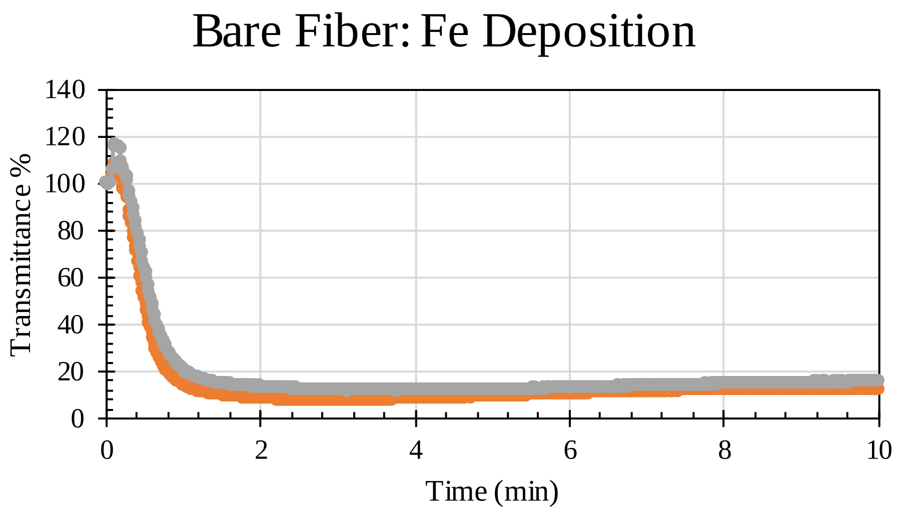


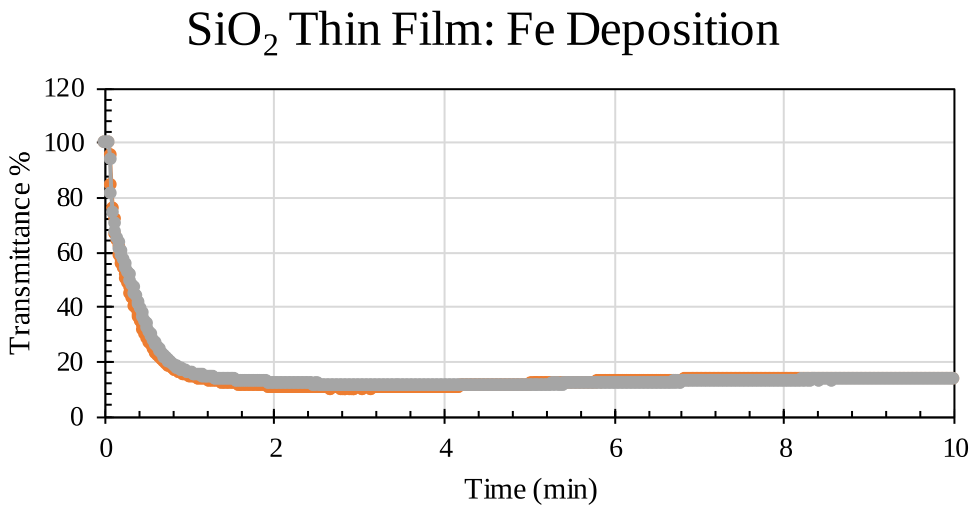
SiO_2 Spheres

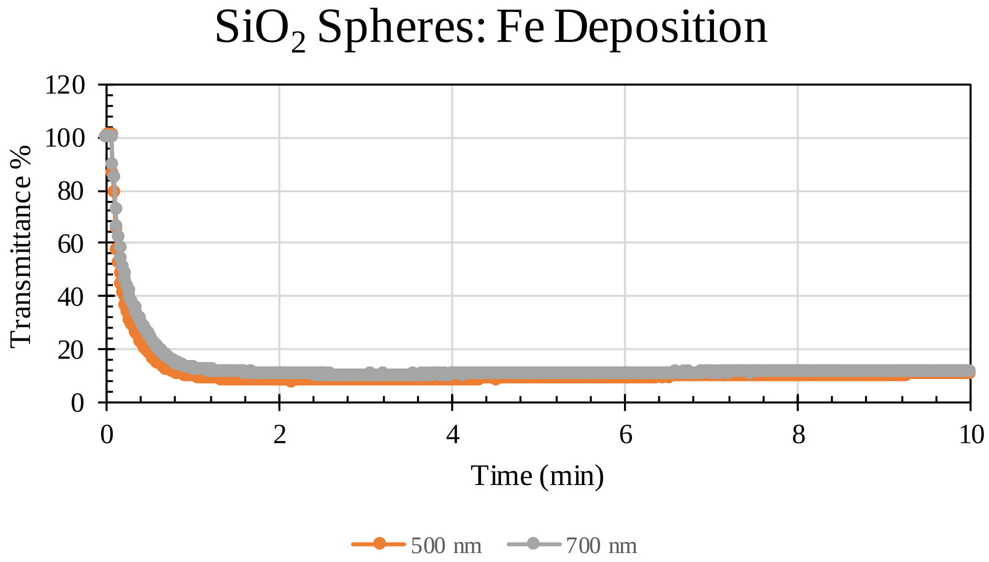


- Fe coating was dissolved in pH 2.5.
- The SiO_2 layer was revealed after Fe dissolution.

T% Decreased as Fe was Coated onto SiO_2 Layers

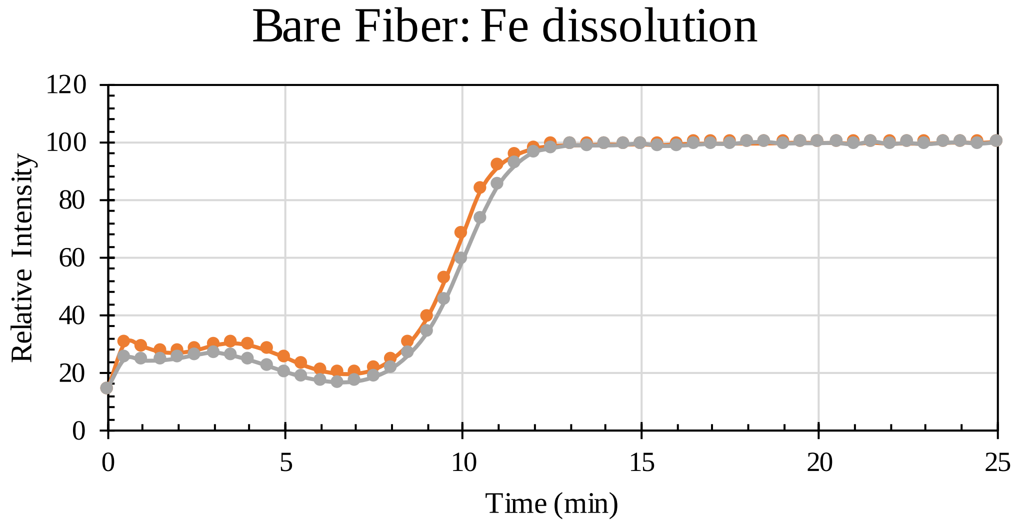


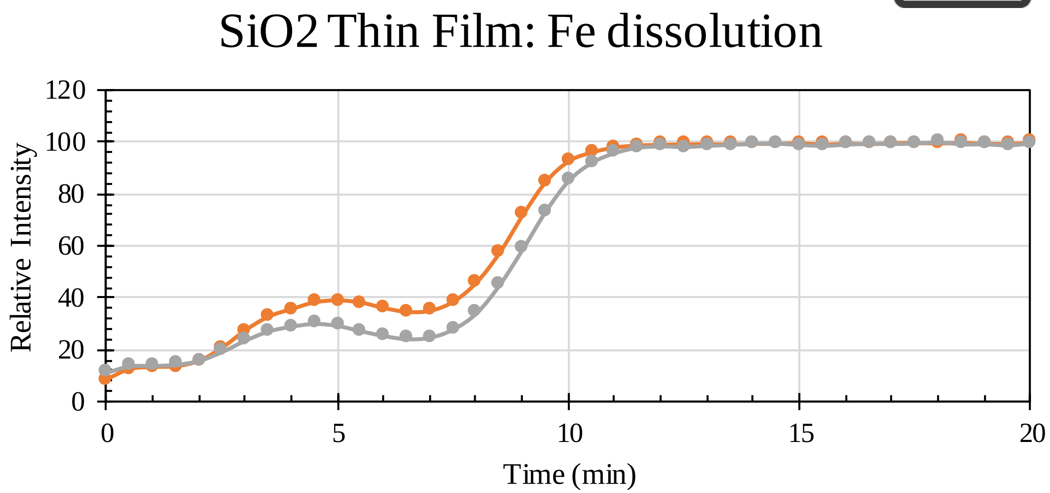


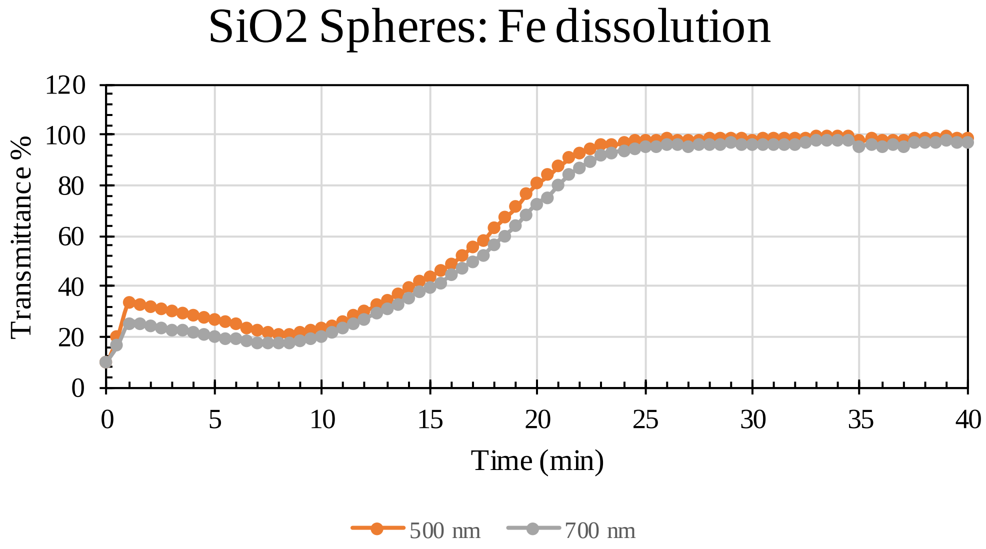


- T% decreased as Fe was deposited onto the SiO_2 coated optical fibers due to the light absorption.
- Different SiO_2 coating morphologies didn't affect the Fe plating induced T% decrease.

T% Increased During Fe Dissolution in pH 2.5 Solutions







- T% increased as Fe was dissolved, which enables corrosion monitoring.
- SiO_2 spheres coating extended the time for Fe coating to fully dissolve, compared to bare fiber and SiO_2 thin film coating.

Conclusions

- The Fe/SiO_2 composite coating was studied as the sensing film where the SiO_2 layer provides roughness/porosity and light coupling and the Fe layer serves as the corrosion sensing element.
- The composite film was prepared through a sol-gel and electroless plating combined process.
- The SiO_2 layer morphology was controlled: SiO_2 thin film and SiO_2 spheres.
- T% decreased after Fe deposited on the fiber due to the light absorption of Fe. Different SiO_2 coating morphologies didn't affect the Fe plating induced T% decrease.
- T% increased as Fe dissolved, which enables corrosion monitoring using the Fe/SiO_2 coated optical fiber. SiO_2 spheres coating extended the time for Fe coating to fully dissolve, compared to bare fiber and SiO_2 thin film coating.

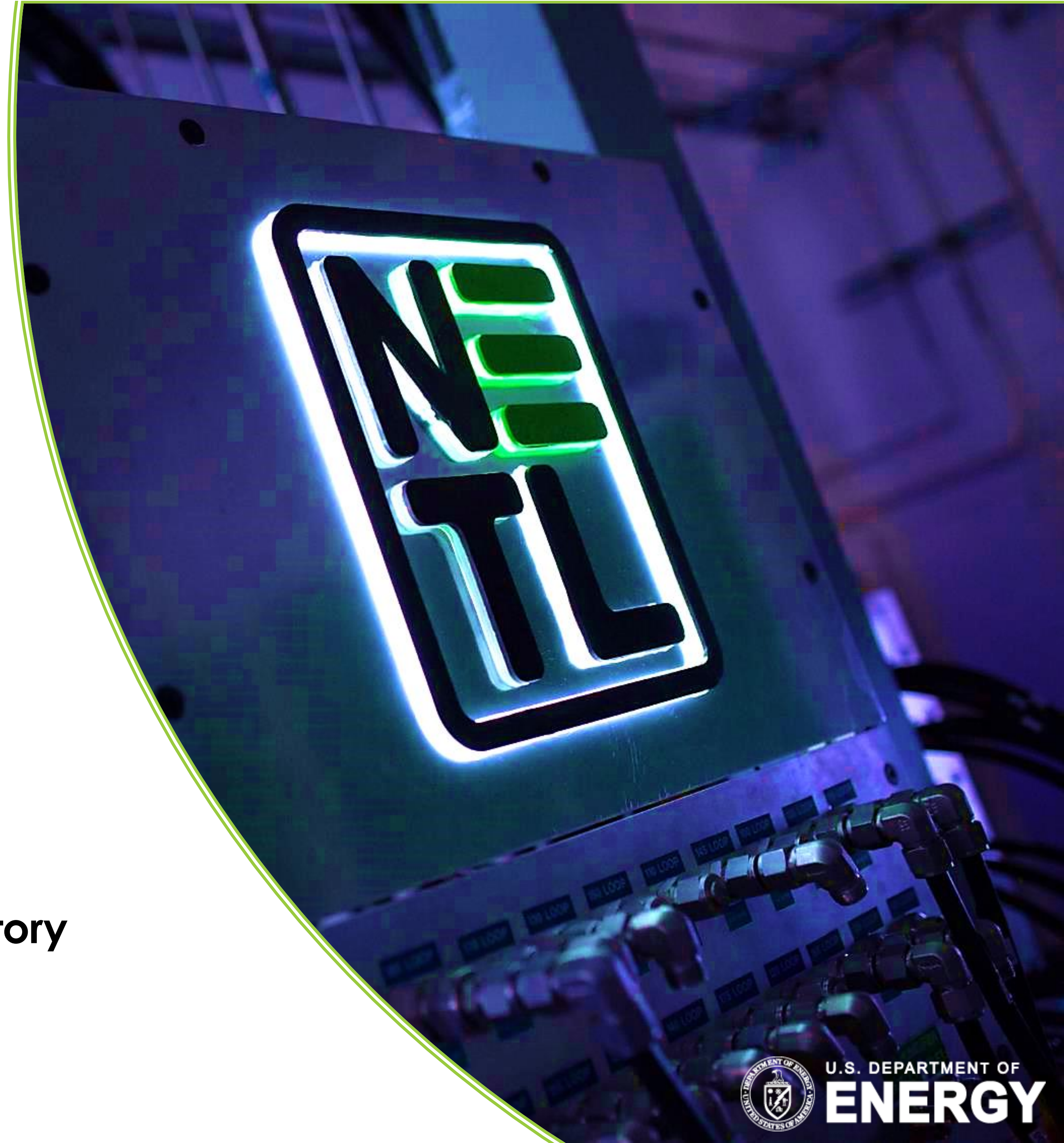
NETL RESOURCES

VISIT US AT: **www.NETL.DOE.gov**

@NETL_DOE

@NETL_DOE

@NationalEnergyTechnologyLaboratory



U.S. DEPARTMENT OF ENERGY