# Optical Fiber-based Corrosion Sensor with Fe/$SiO_2$ Composite Coating

NATIONAL ENERGY TECHNOLOGY LABORATORY

**ECS Abstract #120158**

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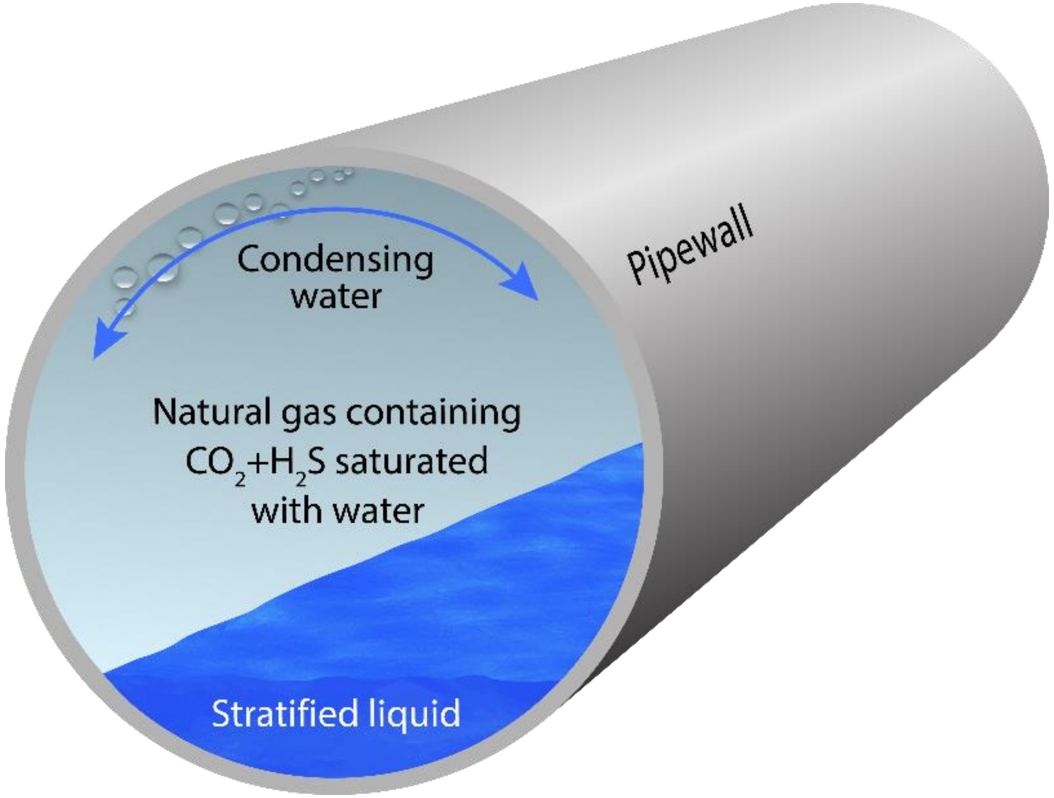
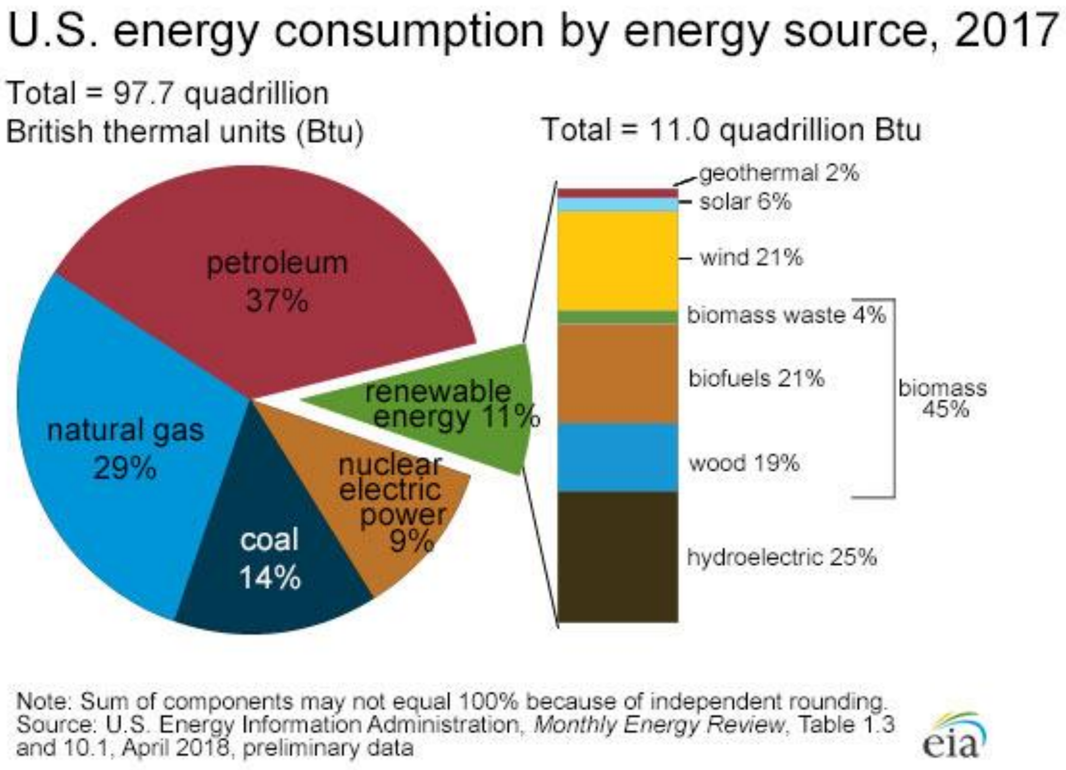
# Outline

- ➢Research Background
- ➢Experimental Procedure
- ➢Results and Discussion
- ➢Conclusions
- ➢Acknowledgment and Disclaimer

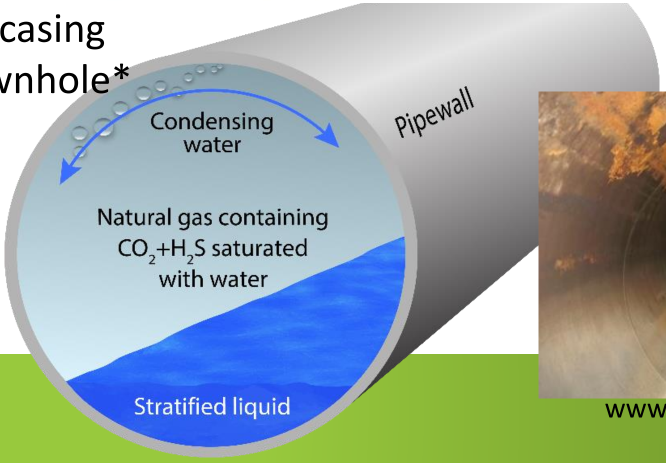


# Corrosion in Oil and Natural Gas Industry




- $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.


Corroded production casing pipe sample from downhole*




Top-of-line corrosion in Natural gas transmission pipeline

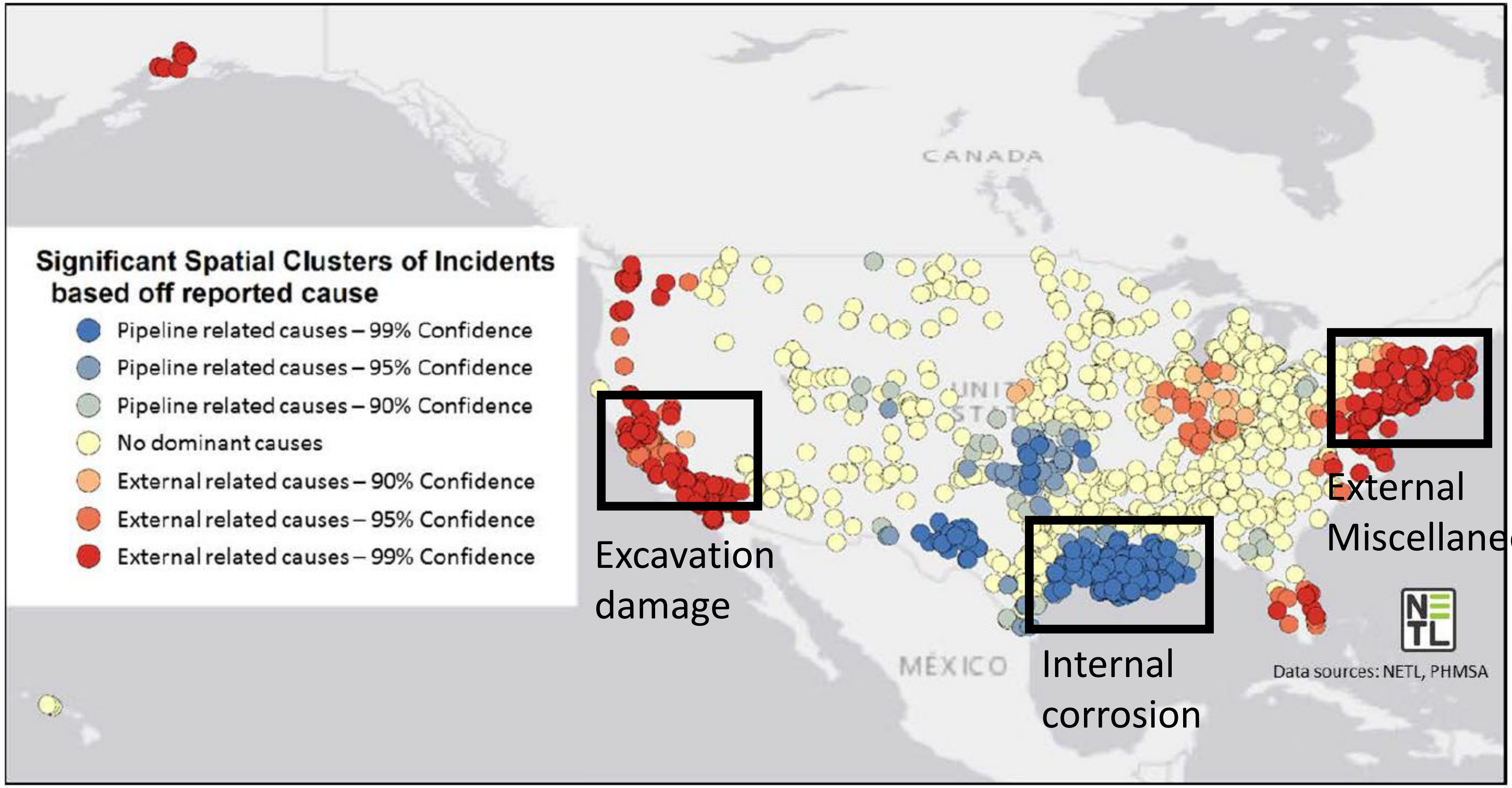
www.corrosionpedia.com

Koch, G. H., Brongers, Michiel, P. H., Thompson, N. G., Virmani, Y. P. and Payer, J. H., "Corrosion costs and preventive strategies in the United States" (2002).

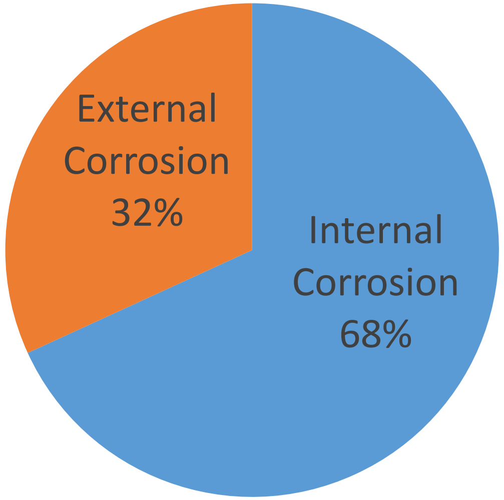
* University of North Dakota Energy & Environmental Research Center.

# Corrosion in Natural Gas Pipelines

- 528,000 km of Natural Gas Transmission & Gathering Pipelines in U.S.
- ~ $4.5 billion Corrosion-related Annual Cost to monitor, replace, and maintain these assets.




**2010-2016 Transmission Pipelines**



# Corrosion is an electrochemical process that causes mass loss and structural deterioration

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

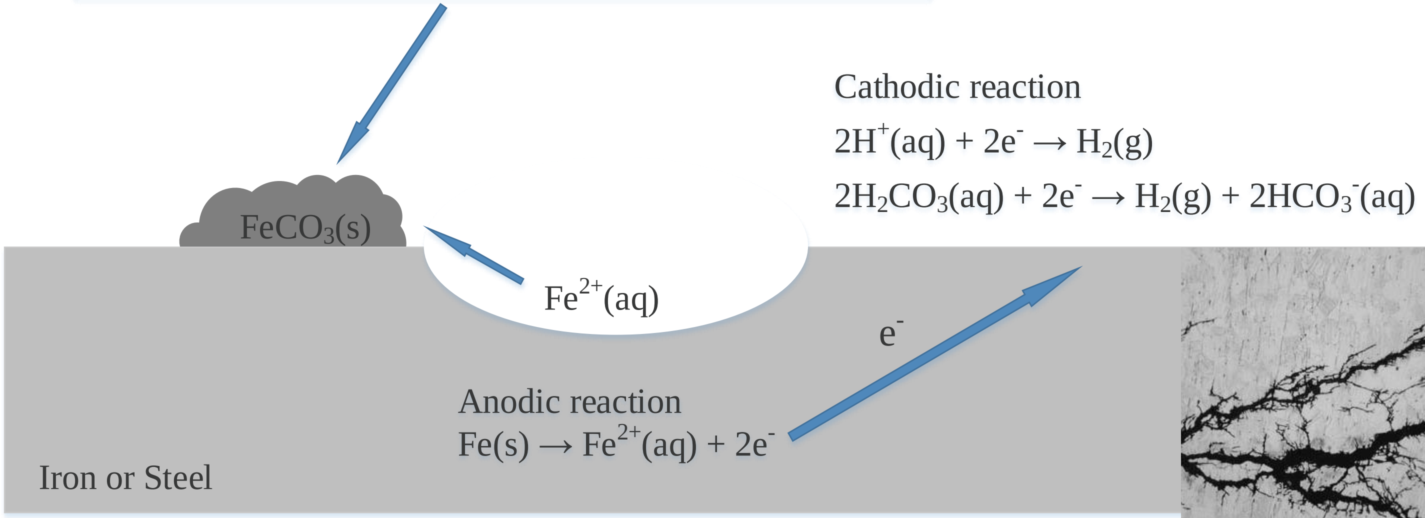
Hydration of $CO_2$: $CO_2(aq) + H_2O(l) \leftrightarrow H_2CO_3(aq)$

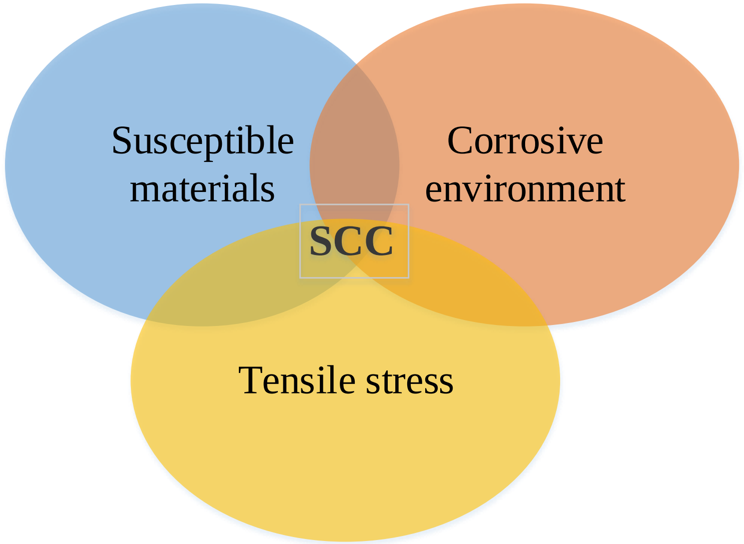
~ 0.2% of $CO_2(aq)$ and quite slow

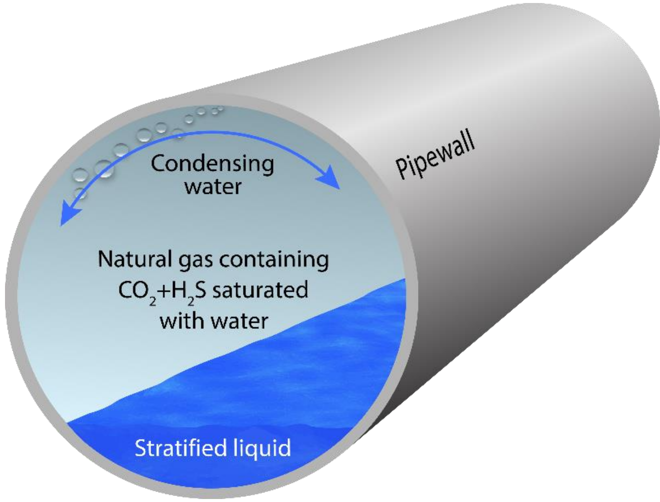
Dissociation of $H_2CO_3(aq)$:

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

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



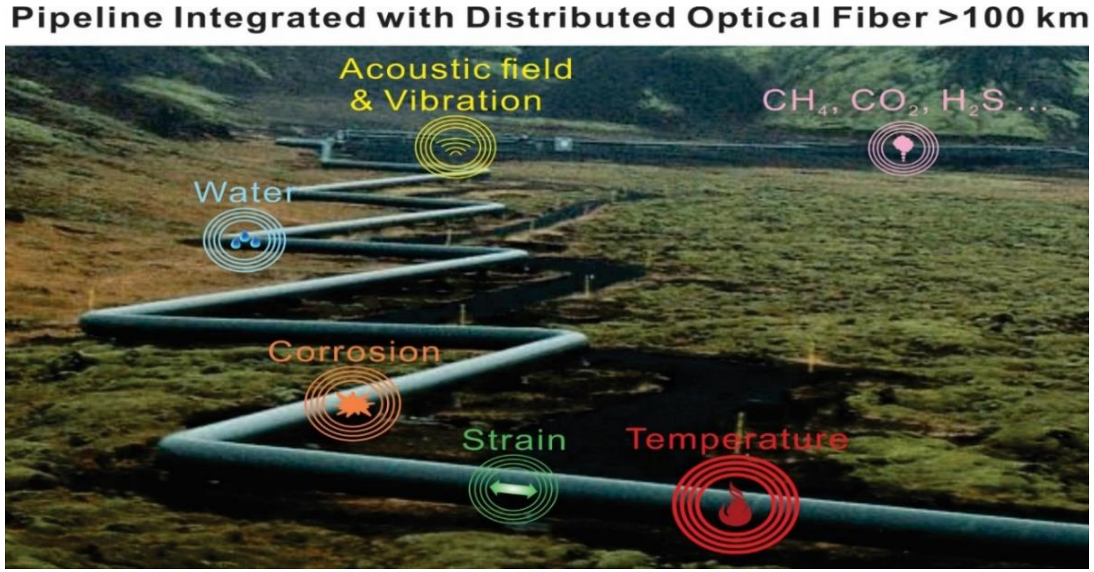



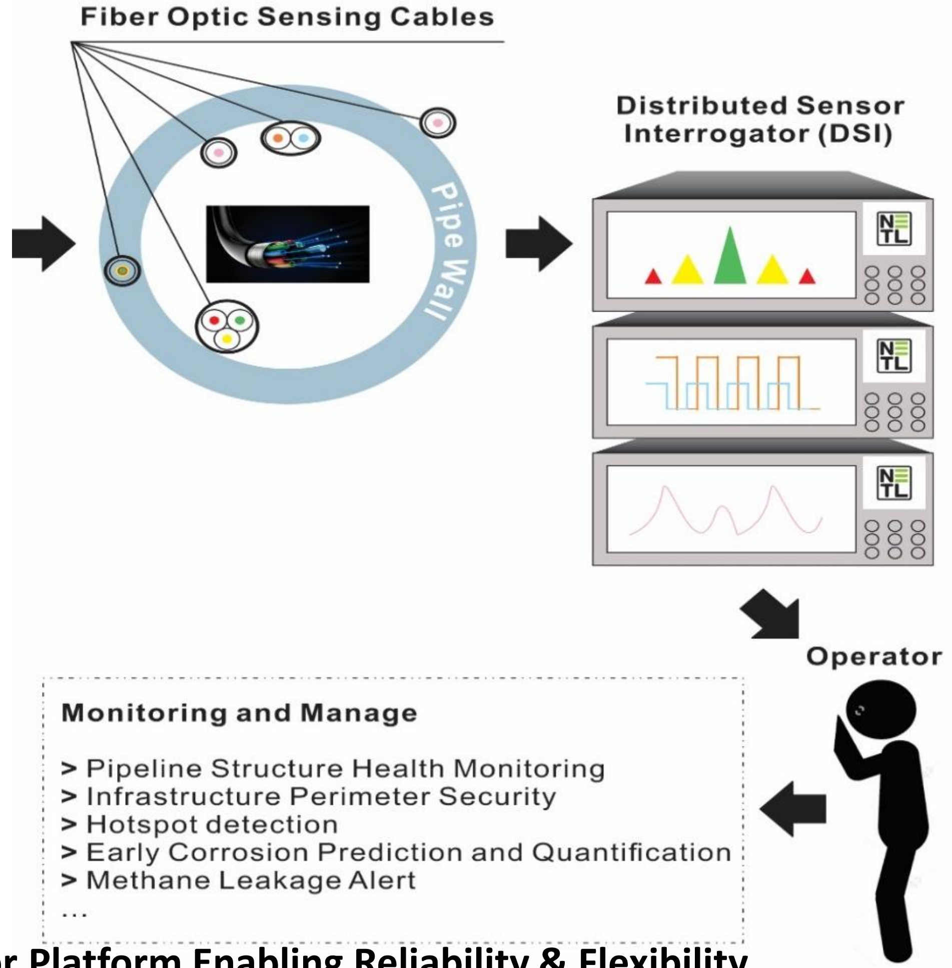






Jones, D. A., Principles and Prevention of Corrosion, P 237.
Han, J., Nesic, S., Yang, Y., Brown, B., Electrochimica Acta, 2011, 5396-5404.
https://corrosion.ksc.nasa.gov/stresscor.htm

# Optical Fiber Sensor Platform




Emphasis Within NETL Research & Innovation Center:

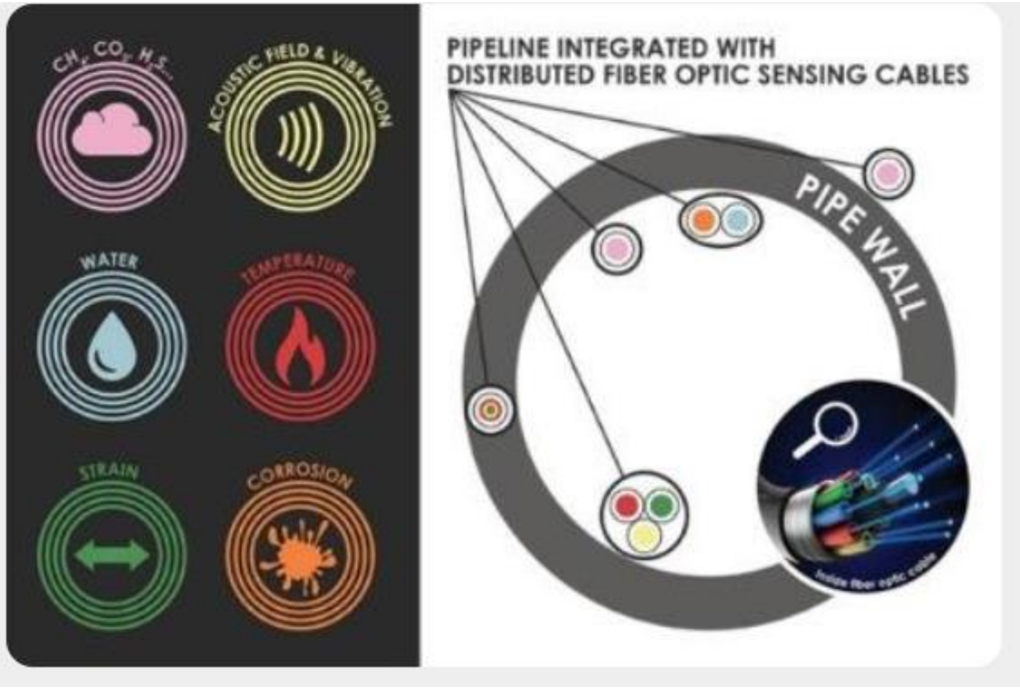
- Optimize Interrogation System (Range, Resolution, Cost)
- Early Corrosion On-Set Detection
- Methane Leak Detection & In-Pipe Gas Composition Monitoring

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

**Target Metrics = >100km Interrogation, <1m Spatial Resolution, Cost ~$30k (<$0.30 / m)**

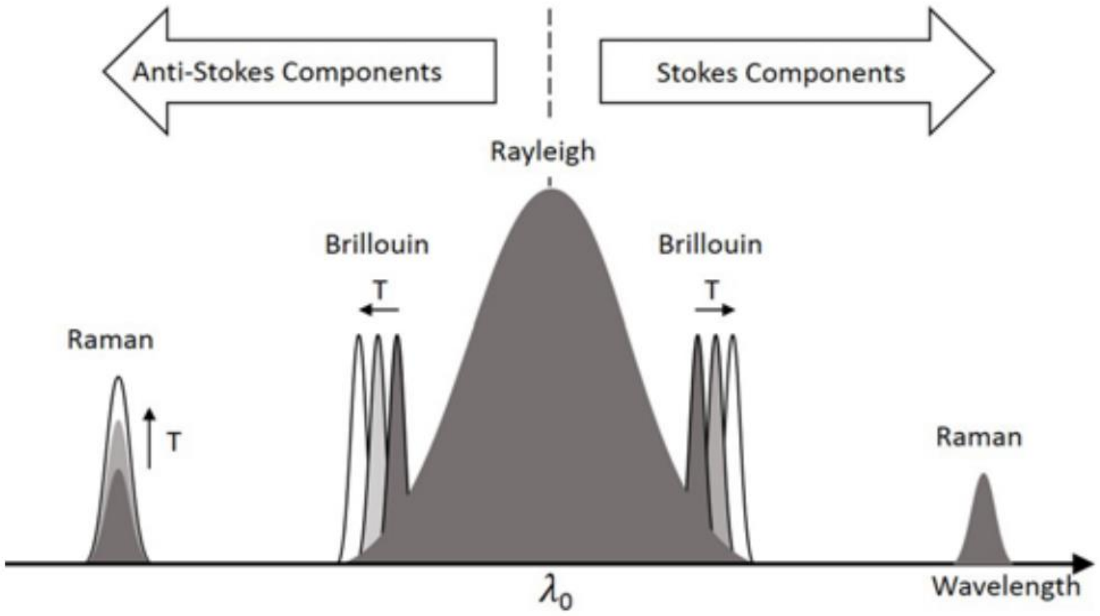
# Optical fiber sensors

- **Advantages of optical fiber sensors (OFS)**
  - nondestructive monitoring
  - in-situ distributive measurements
  - small size, flexibility, geometric versatility, light weight
  - inherent immunity to electromagnetic interference (EMI)
  - compatibility to optical fiber data communication systems
  - improved safety in the presence of flammable gas environments as compared to electrical based sensors
  - can be functionalized with specific sensing materials

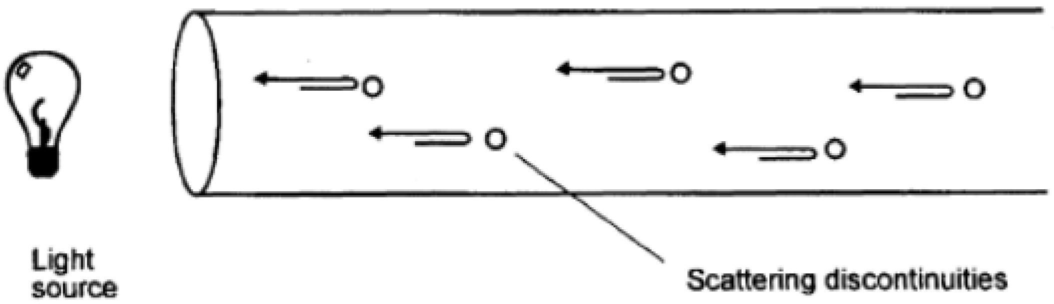



http://www.materialsperformance.com/news/2018/09/fiber-optic-sensors-prevent-corrosion-of-natural-gas-pipelines

# Distributed OFS sensing principle




Distributed temperature, strain, and acoustic sensing (DTS, DSS, DAS)



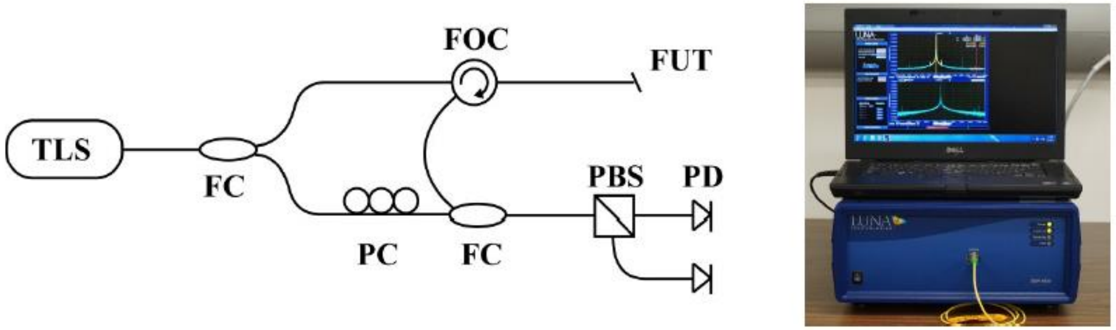




Figure 1 – LUNA OBR 4600 distributed interrogator LEFT: internal components (TLS: tunable laser source, FC: fiber coupler, FOC: fiber optic circulator, PC: polarization controller, PBS: polarizing beamsplitter, PD: photodiode); RIGHT: photo of instrument.

Optical backscatter reflectometer (OBR)

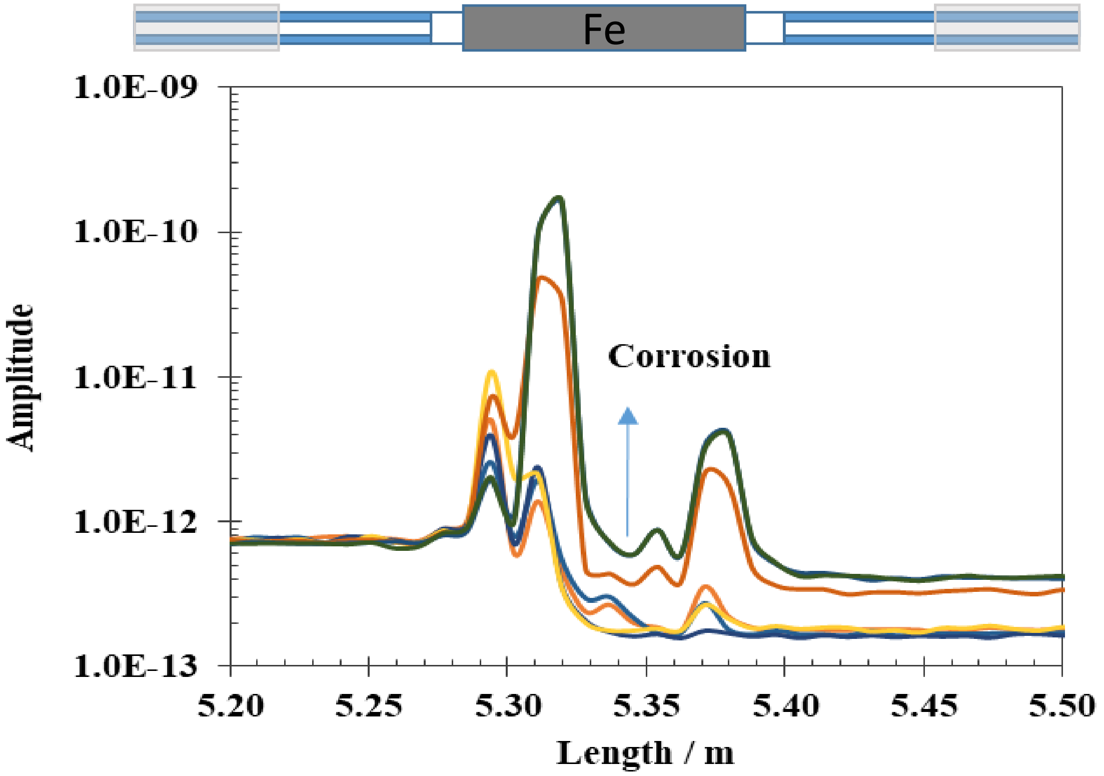
- Distributed OFS enables continuous real-time monitoring over the whole structure at a reduced cost per length unit.



Joe, H.-E., Yun, H., Jo, S.-H., Jun, M. B. G. and Min, B.-K., Int. J. Precis. Eng. Manuf. Technol. **5**(1), 173–191 (2018).

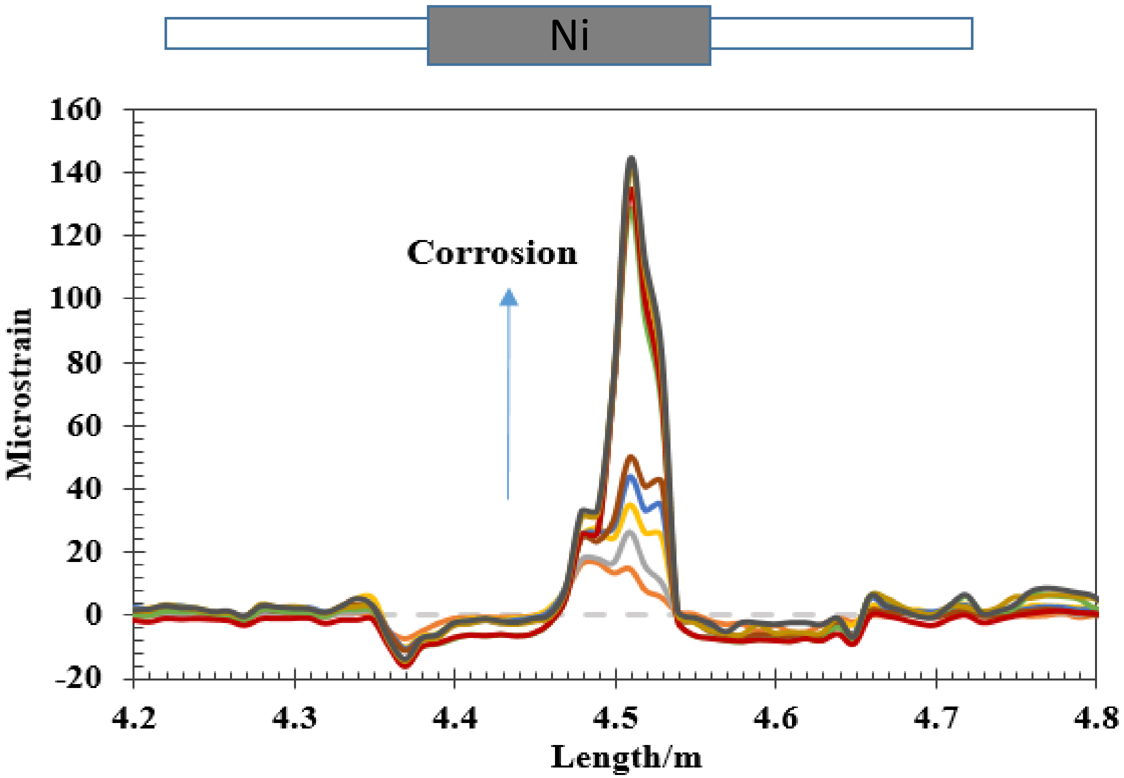
# Corrosion sensors from previous work

Multi-mode Fiber Coreless Fiber Multi-mode Fiber




Rayleigh backscattered light increased as corrosion of Fe film proceeded

Single-mode Fiber

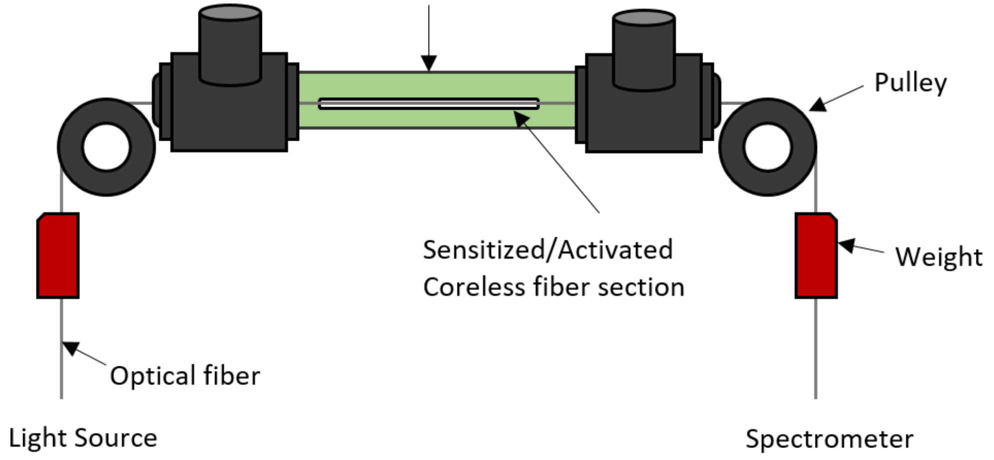



Microstrain on the fiber increased with mass loss of coated metallic Ni film.

Proc. SPIE 10973, Smart Structures and NDE for Energy Systems and Industry 4.0, 109730N.

NACE CORROSION, 2019, No. 13499.

# Experimental Setup




Transmission measurement during the Fe plating onto and dissolution from the $SiO_2$ coated optical fiber.

# Fe/$SiO_2$ Composite Coating Preparation

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TEOS sol-gel for dip coating to form $SiO_2$ layer

| Chemical | Amount | Stir Hot plate T | Dip/travel | Calcination |
|---|---|---|---|---|
| DI | 1mL | 60 °C for 3h | ~25 travels of coreless fiber | Up, 3h; 600 °C, 2h; Cool,3h |
| Ethanol | 4.5mL | | | |
| TEOS | 4.5mL | | | |

Cleaning and Prep

| Chemical | Amount | Operation |
|---|---|---|
| Acetone | 100% | <5min, Sliding |
| DI water | Rinse | Air dry |
| NaOH | 10M, 50C | <5min, Sliding in PTFE plate |
| DI water | Rinse | Air dry |

Sensitization & Activation

| Chemical | Amount | Operation |
|---|---|---|
| SnCl2 | 22.6g/L | Stir, 30mL<br>Immerse, 20min at 50C |
| HCl, conc. | 10mL/L | |
| PdCl2 | 0.795g/L | Stir, 30mL<br>Immerse, 20min at 50C |
| HCl, conc. | 5mL/L | |

Fe Electroless Plating

| Chemical | Amount | Operation |
|---|---|---|
| FeSO4·7H2O | 11g/L | Stir, 30mL |
| C6H5Na3O7·2H2O (Sodium Citrate) | 57g/L | Stir, 30mL |
| H3BO3 | 10g/L | Stir, 30mL |
| NaOH | 1.2M to pH 9.8@22C | Drops |
| NaBH4 | 3.0g/L | Added the last |

# Fe plating on sub-micron $SiO_2$ spheres

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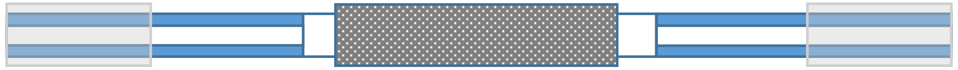
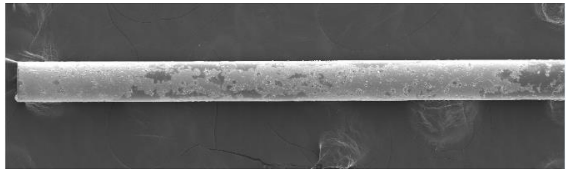
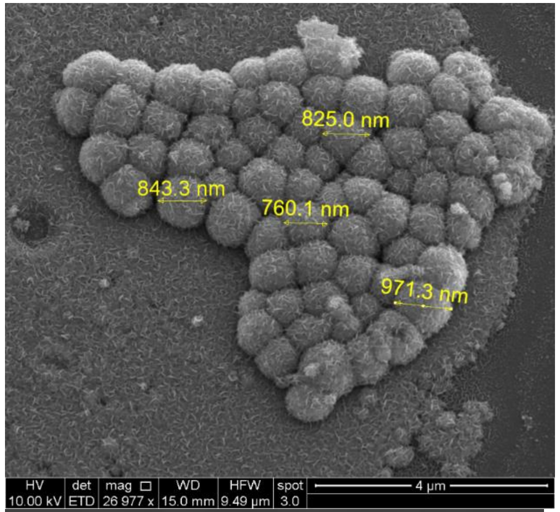
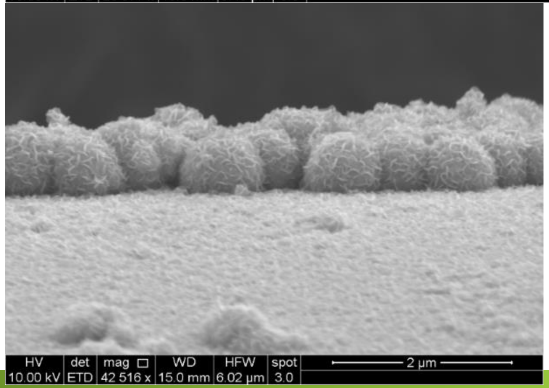
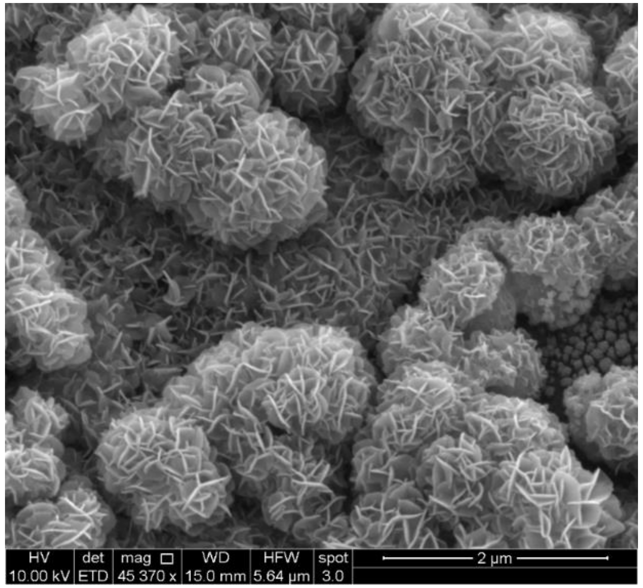
**Fe on $SiO_2$ spheres**

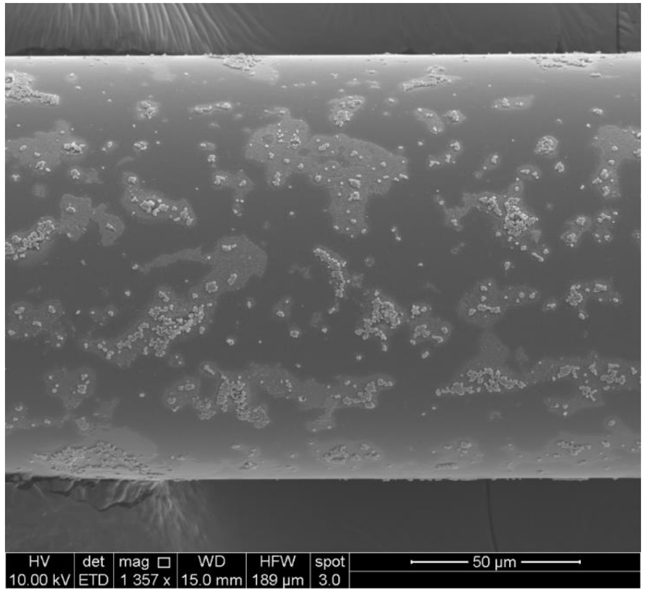




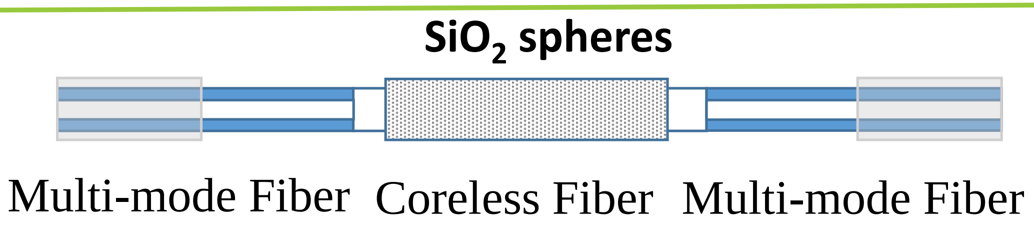



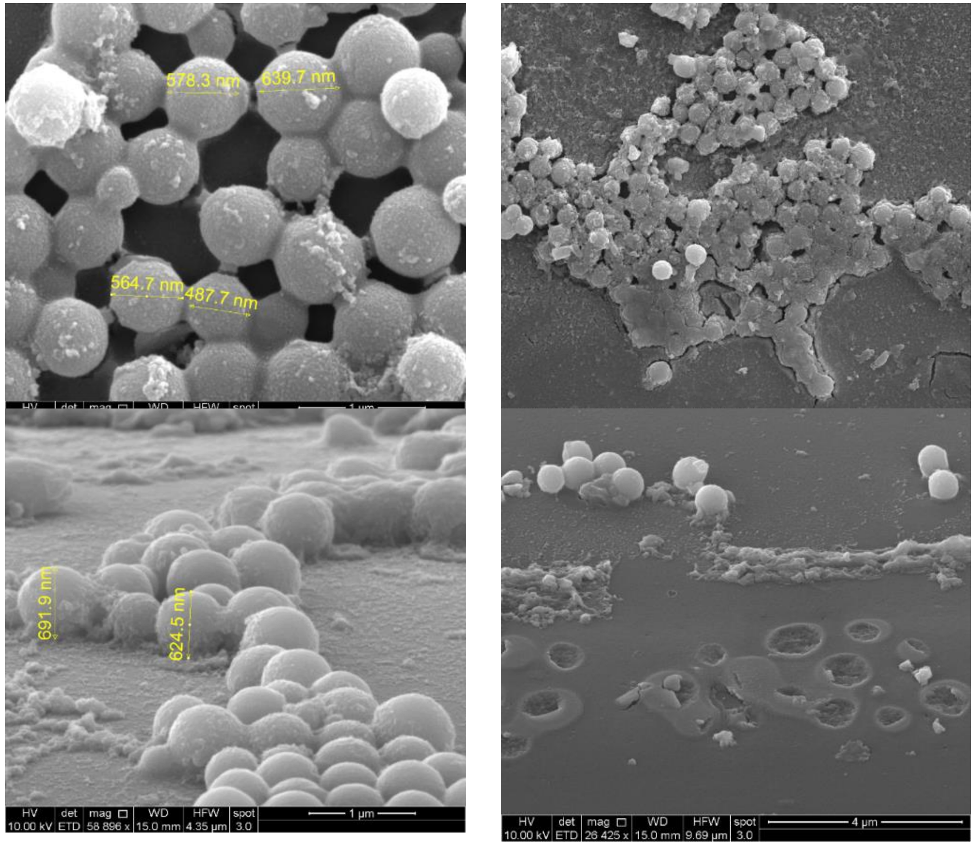



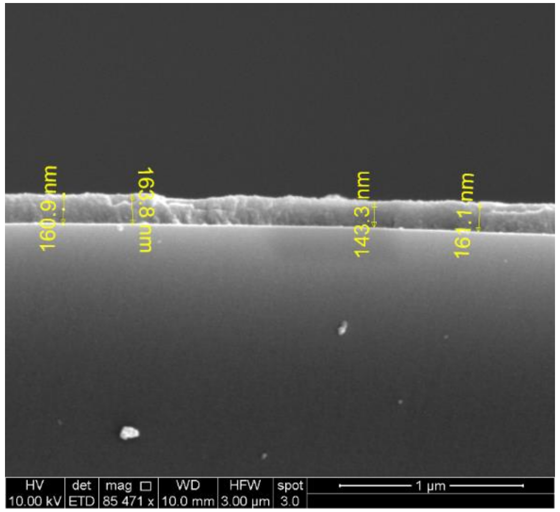

- Fe coated SiO2 spheres with about hundreds of nm thickness. (~1h)
- Honeycomb-like Fe coating.

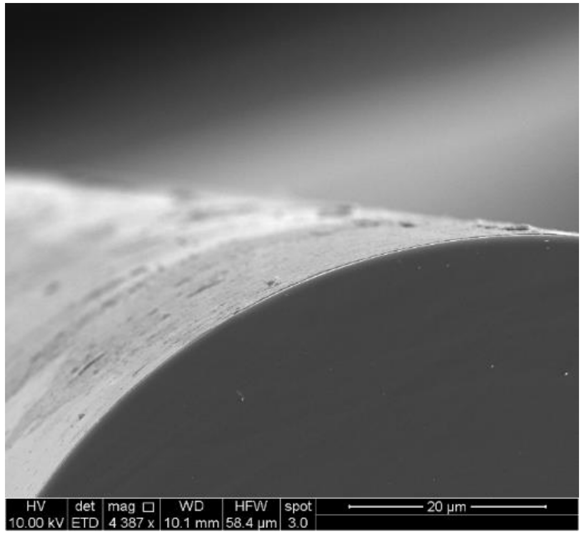
- The patches of Fe coating indicates that SiO2 spheres/coating facilitated Fe plating.

# After Fe dissolution in pH2 (SEM)



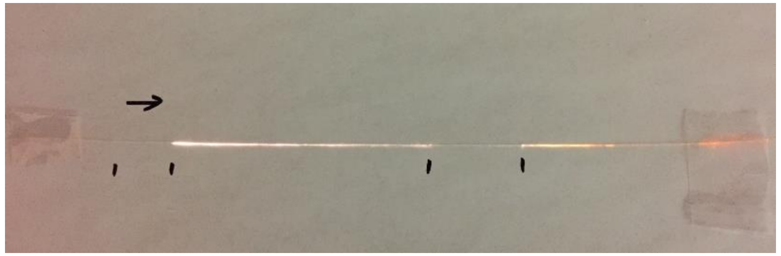



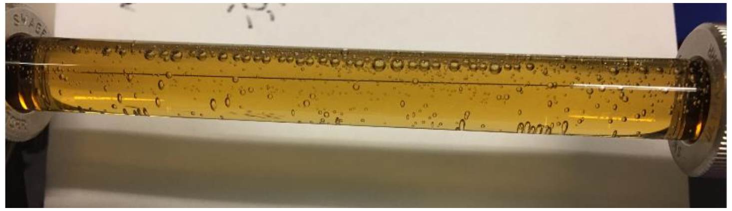



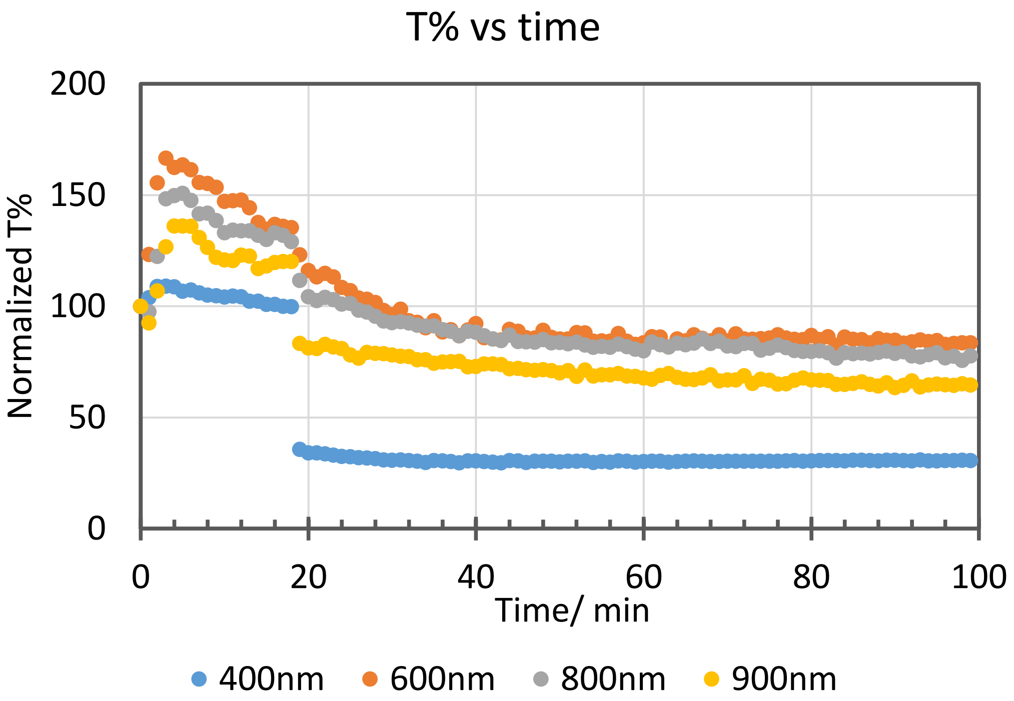




- Fe coating was dissolved in pH 2.
- A ~150nm uniform coating was observed in the cross-section. Porous $SiO_2$ or residual Fe?

# T% decreased during Fe plating

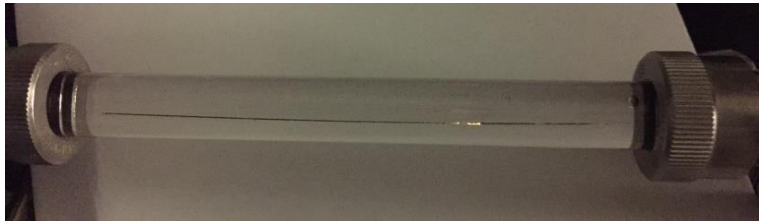


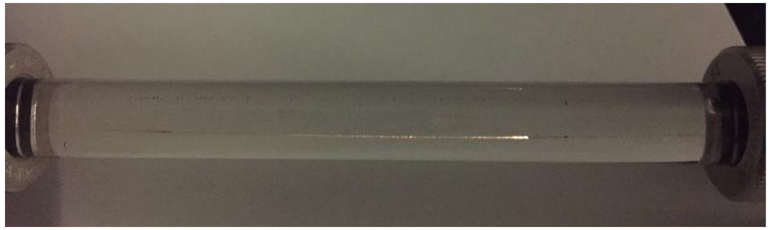


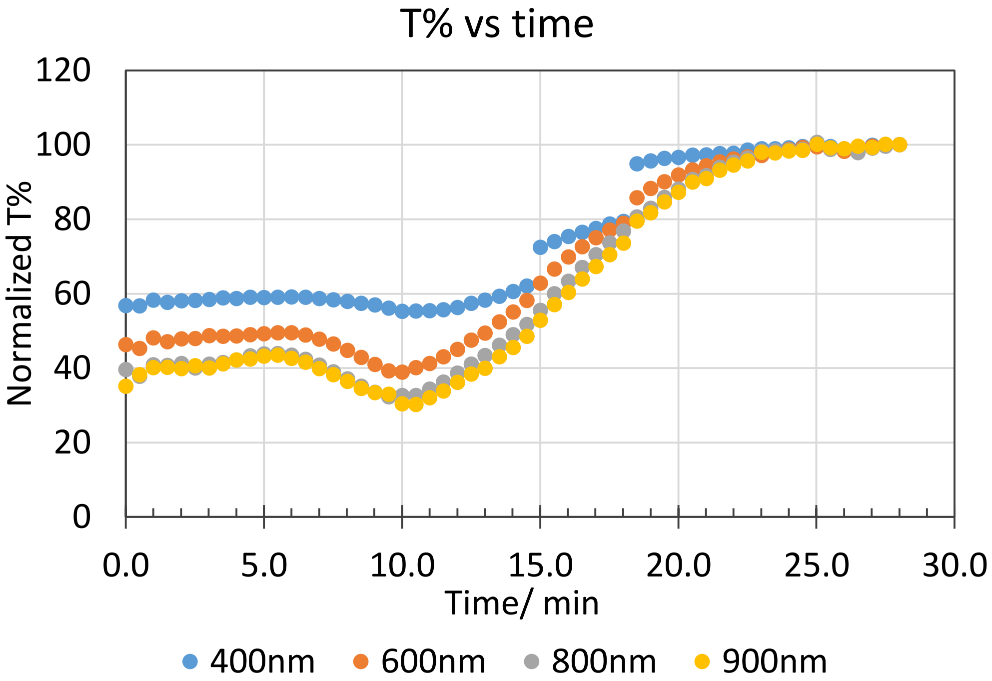



- T% increased in the first 2 mins, probably due to the $H_2$ gas formation on the surface at the early stage of Fe plating.
- T% then decreased after Fe deposited on the fiber due to Fe light absorption.
- For the wavelengths of 600nm and 800nm, T% became relatively stable after 60min.
- Wavelengths of 400nm and 900nm were affected more by the integration time because of low SNR.

# T% increased during Fe dissolution in pH 2








- T% increased as Fe dissolved, which enables corrosion monitoring.

# Conclusions

- A Fe/$SiO_2$ composite film 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 with potential for mass production.
- T% decreased after Fe deposited on the fiber due to light absorption of Fe film.
- T% increased as Fe dissolved, which enables corrosion monitoring using this Fe/$SiO_2$ coated optical fiber.

# Acknowledgments

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# Disclaimer

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# Thank you!

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