TiO$_2$-Coated Optical Fibers for Distributed pH Monitoring at High Pressures and Temperatures

SPIE Paper 12532-22

Alexander Shumski
Materials Scientist
NETL Support Contractor

SPIE Defense + Commercial Sensing 2023
May 2, 2023
Disclaimer

This project was funded by the U.S. Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract. Neither the United States Government nor any agency thereof, nor any of its 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

Alexander Shumski$^{1,2*}$, Nathan Diemler$^{1,2}$, Jeffrey Wuenschell$^{1,2}$, Paul Ohodnicki$^{3,4,5}$, Ruishu Wright$^{1}$

$^{1}$National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA
$^{2}$NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA
$^{3}$Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA
$^{4}$Department of Electrical and Computer Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA
$^{5}$Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA, 15261, USA
PH Monitoring is Critical for Wellbore Integrity

Negative impact of wellbore integrity failure:

- **Negative financial consequence:**
  $170B/year due to corrosion in energy/chemical industry\(^2\)

- **Health/environmental risks:**
  - Groundwater contamination
  - Gas leakage to the atmosphere
  - Fluid spills
  - Seepage at the surface
Failure Analysis for Wellbore Integrity

- Pre-production
- Production/storage
  - Mechanical stress/strain
    - Fracture formation within cement
    - Strain on corroded casing (rupture)
  - Geochemical attack
    - Corrosion of casing
      - H$_2$S corrosion (sour)
      - CO$_2$ corrosion (sweet)
    - Microbial corrosion
    - Acid attack
    - Degradation of cement
      - Carbonation
      - Sulfate attack
      - Acid attack

Counts of wells with loss of integrity in Pennsylvania: Results of the survey$^3$

<table>
<thead>
<tr>
<th>Year</th>
<th>Drilled</th>
<th>Failure</th>
<th>Rate of Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>1,609</td>
<td>97</td>
<td>6%</td>
</tr>
<tr>
<td>2011</td>
<td>1,972</td>
<td>140</td>
<td>7.1%</td>
</tr>
<tr>
<td>2012</td>
<td>1,346</td>
<td>120</td>
<td>8.9%</td>
</tr>
</tbody>
</table>

pH monitoring is needed in the wellbore

Failure Analysis for Wellbore Integrity

- **Thermal Gradient**
  - Temperature steadily increases with depth
  - 0.014 °F/ft or 0.026 °C/m

- **Pressure**
  - Hydrostatic pressure
    - 0.43 psi/ft
  - High gas fill pressure
    - 1,000–3,000 psi

Subterranean Gas Storage is Increasing in Significance

Hydrogen Storage Wells Will Likely Require Expansion

- Three types of H\textsubscript{2} storage wells are in use
  - Salt cavern
  - Aquifer
  - Depleted hydrocarbon reservoir
- Most U.S. storage is depleted reservoir
- Conversion of existing storage to pure H\textsubscript{2} is currently insufficient
  - Up to 75% loss of energy storage capacity as pure H\textsubscript{2}
  - 20% H\textsubscript{2}/methane is estimated as equal to current gas storage

[5] Lackey (2023)
Consequences of Gas Storage Wellbore Failure

Aliso Canyon Axial Rupture Site from Blade Energy Partners’ RCA Report

- **Aliso Canyon, Oct–Feb 2015–2016**
  - 109,000 metric tons of CH₄ from corrosion-based rupture of 7 inch casing
  - 8,300 households evacuated
  - Hundreds of lawsuits, tens of thousands of claimants
  - Several hundred million dollars in settlements, fines, and losses

- **Rager Field, November 2022**
  - 1.29 billion cubic feet of methane leaked
  - Integrity issues with the well were identified
  - Resulted in external audits and daily reporting to PA Department of Environmental Protection

TiO$_2$ Sol Gel Process is Used to Prepare Sensor

Sol Gel TiO$_2$ is Dip Coated and Calcined

- Ti(IV) isopropoxide in isopropyl alcohol solution
- +2 eq. acetic acid (2 hours mixing minimum)
- 8x dip coating onto coreless fiber
- Fiber sensor calcined at 500 °C

Polymer Jacket | Multi-Mode Fiber (MMF) | TiO$_2$ Coating | Coreless Fiber | Polymer Jacket

50 cm | 5 cm | 50 cm

[7] https://doi.org/10.1117/12.2618836
Sensor Layouts and Experimental Setup

Transmission Measurements

Optical Backscatter Reflectometry (OBR) Measurements
TiO₂ Coated Optical Fiber pH Sensor Pressurized to 1,000 psi at 80 °C

- High broadband pH response consistent with previously reported TiO₂ fiber sensors
- Pressurization from 1−67 bar (atmospheric to ~971 psi) brings only minor changes in transmission
- Some irreversibility initially noticed during testing

[7] https://doi.org/10.1117/12.2618836
Pressurization to 1,000 psi at 80 °C in Neutral Conditions Causes Irreversibility

- Mild pressure sensitivity observed
- Switching solutions causes a repeatable irreversible increase
  - 125 minutes and 250 minutes
- Does not happen immediately on pressure release
- Damage likely occurs during pressure changes
  - Solution exchange likely removes damaged coating
Pressurization to 1,000 psi at 80 °C in Basic Conditions Shows Reversibility

- Noticeable pressure response
- Unlikely to be direct pressure sensitivity
- Pressure based transmission increase is larger in the first cycle
- Post pressurization showed reversibility when switching back to ambient base and neutral
- Base exposure is known to cause surface degradation\(^7\)

[7] https://doi.org/10.1117/12.2618836
TiO$_2$ Coatings after 1,000 psi Show Obvious Differences by SEM

- As Prepared: A relatively thick and rough outer layer of TiO$_2$ on top of a more consistent undercoating
- High-Pressure Neutral: Severely cracked coating, with a somewhat smooth surface on intact regions
- High-Pressure Base: Rough coating with most of the exterior deposits removed, low cracking
Distributed pH Sensing at Ambient Pressure and at 80 °C

Backscattering in Basic Conditions

Backscattering in Neutral Conditions
Distributed pH Sensing at Elevated Pressure and at 80 °C

- Backscattering in Basic Conditions
- Backscattering in Neutral Conditions

Irreversible baseline decrease when exchanging from high pressure neutral to new neutral solution (Entry 7-8)
Conclusions

- Sol-gel TiO₂-coated optical fiber has been demonstrated for distributed pH sensing at high pH, pressure, and temperatures

- The optical response for TiO₂ is, in general, fairly comparable between ambient and 1,000 psi at 80 °C

- High pH exposure at 1,000 psi further thins and roughens the surface

- High-pressure conditions can irreversibly damage thicker coatings, causing large cracks

- Coating thinning due to base exposure may limit mechanical damage to the surface

- Application of TiO₂ as a pH sensor must account for both pH response and coating thickness behaviors
NETL RESOURCES

VISIT US AT: www.NETL.DOE.gov

@NETL_DOE

@NETL_DOE

@NationalEnergyTechnologyLaboratory