Calcined Polyethyleneimine-Coated Optical Fibers for Distributed pH Monitoring at High Pressures and Temperatures

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Subterranean Hydrogen Storage

- **Hydrogen Storage**
  - Pure H₂ and mixed CH₄
  - Expansion of current gas storage capacity required

- **Three Well Types**
  - Depleted reservoir
  - Aquifer
  - Salt cavern

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

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

[1] Lackey et al. (2023)
[6] Goodman Hanson et al. (2022)
## Energy Infrastructure Wellbore Conditions

<table>
<thead>
<tr>
<th>Application</th>
<th>Depth</th>
<th>Average Temperature</th>
<th>Pressure</th>
<th>pH Range*</th>
<th>Dissolved Solids</th>
<th>Common Ions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Storage</td>
<td>200-2,000 m</td>
<td>25-100 °C</td>
<td>5-35 MPa</td>
<td>3-6</td>
<td>10,000-70,000 mg/L</td>
<td>Sulfides, CO₂/Carbonate, Cl⁻, Na⁺, K⁺, H₂O⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Fe²⁺/³⁺</td>
<td>[3–5]</td>
</tr>
<tr>
<td>H₂ and H₂/CH₄ Blend Storage</td>
<td>200-2,000 m</td>
<td>25-100 °C</td>
<td>5-30 MPa</td>
<td>4-9.5</td>
<td>10,000-70,000 mg/L</td>
<td>Sulfides, CO₂/Carbonate, Cl⁻, Na⁺, K⁺, H₂O⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Fe²⁺/³⁺</td>
<td>[2–4, 7–9]</td>
</tr>
<tr>
<td>Geothermal</td>
<td>3,000-4,000 m</td>
<td>&gt;90 °C** 150-300 °C</td>
<td>~30-50 MPa</td>
<td>Most 5-9, acidic 2.5-4</td>
<td>2,000-50,000 mg/L</td>
<td>Silicates, SO₄²⁻, CO₂/Carbonate, NO₃⁻, Cl⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺</td>
<td>[10–16]</td>
</tr>
<tr>
<td>Oil/Natural Gas</td>
<td>1,000-10,000 m</td>
<td>&lt;150 °C*** &lt;70 MPa***</td>
<td>3-9.5</td>
<td></td>
<td>10,000-200,000 mg/L</td>
<td>Sulfides, SO₄²⁻, CO₂/Carbonate, Cl⁻, Na⁺, K⁺, H₂O⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Fe²⁺/³⁺</td>
<td>[2, 9, 17, 18]</td>
</tr>
</tbody>
</table>

* On average, pH range is highly dependent on local geology
** For certain low temperature coupled layouts
*** Some HPHT wells are potentially much higher

- Previous sensor ranges were narrower
  - Gas storage requires at least 4-9.5
  - Cement focus was primarily 8-13
- Acid range of interest for geochemistry
  - Corrosion and microbes
- Example: Aliso Canyon, Oct–Feb 2015–2016\(^{19}\)

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Old Sol Gel Process Optimized for High pH

Sol Gel TiO₂ is Dip Coated and Calcined

- Effective pH range is either 8-12 or 8-4 for TiO₂
- Cannot discriminate between pH 12 and 4 reliably

[21] https://doi.org/10.1117/12.2618836
Polyethylenimine Requires Minimal Processing

Apply Commercial Polymer Solution and Calcine

- Calcination ends solubility issues, but is not yet fully characterized

Branched Polyethylenimine

Calcination at 500 °C

pH Sensitive Carbonized Coating, Currently Undergoing Investigation

50 cm

Polymer Jacket

Multi-Mode Fiber (MMF)

Calcined Polymer Coating

Coreless Fiber

Polymer Jacket

5 cm

1 cm

50 cm

1 cm
Sensor Layouts and Experimental Setup

Two Fiber Layouts in the Same Reactor for Point and Distributed Measurements

Transmission (Point) Measurements

Distributed Measurements

<table>
<thead>
<tr>
<th>Temperature Conditions</th>
<th>Pressure Conditions</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 °C and 80 °C</td>
<td>0 psig to 950 psig</td>
<td>2-12</td>
</tr>
</tbody>
</table>

- Transmission and Distributed Sensing
  - Forward propagating vs. backscattered light

[22] Lu, 2019
Transmission for pH Sensing at 20 °C

• Citrate buffer titration allowed for reversible sensing
• pH responds relatively linearly at slightly acidic to neutral ranges
• Basic conditions are always higher transmission than acidic
Transmission for pH Sensing at 80 °C

- Similar response to ambient temperature conditions observed
- Higher linearity observed for several responses
- Increased response from first titration (blue) to subsequent (orange/black)
Distributed Backscattering for pH Sensing at 80 °C

- Backscattering decreases at high pH alongside higher transmission
- Again, low pH range is less sensitive than the neutral to basic range
PEI Pressurization to 66 bar (950 psi) at 80 °C

- Color coding used to represent pH + pressure conditions
- Fluctuations from pressure are strong
PEI Pressurization to 66 bar (950 psi) at 80 °C

- Color coding used to represent pH + pressure conditions
- Fluctuations from pressure are strong
- Uncoated fiber does not show large pressure changes, indicating that this is coating related
Assessing Post Pressurization Stability and Damage

- pH response was maintained relatively well after retreating the fiber and attempting recalibration.
- Cracking occurs, and wrinkling produced during calcination is maintained.

Post-Pressure pH Calibration at 0 barg 80 °C and 600 nm

\[ y = 6.9545x + 126.78 \]
\[ R^2 = 0.93 \]
Conclusions

• A coating produced from polyethylenimine calcined at 500 °C is pH sensitive from pH 2-12, with the best sensitivity from pH 4-11

• Transmission increases with pH, and integrated backscattering decreases with pH with relatively high linearity

• Drift occurs at high pressures in the 800-1,000 psi range, but does not impact the pH sensing trends

• Coatings can be applied from commercially available solutions, requiring minimal preparation beyond calcination

• The exact composition of the calcined pH sensitive coating is currently undergoing further study
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