Potential Utilization of Geopolymers for Oil Well Cementing Operations

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Outlines

- Past, Present, and Future of Oil Wells in Norway
- Geopolymers as an Alternative Material
- Placeability - Rheological Determination
- Physical Observation
- Properties of the Geopolymers
- X-ray Crystallography
- Microstructure Characterization
- Long-Term Durability Analysis
- Summary
Materials for Oil Well Cementing

- Two new materials were developed:
  - Aplite-based geopolymers
  - Norite-based geopolymers
Oil Wells in Norway - Since 1966 until June 2015

Total No. of drilled wells
5579

No. Of development wells
4037

No. Of exploration wells
1542

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Oil Wells

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## Alternative Plugging Materials

### Portland Cement as the Prime Material

- Concerns regarding Portland cement
  - Shrinkage
  - Possible gas influx (permeability)
  - Instability at high temperatures
  - Instability in corrosive environments
  - Well conditions (rock formation type, thermal cycling, etc.)
Alternative Material, Norsok-D010

- Characteristics of a suitable alternative material:
  - Ensure bonding to steel,
  - Impermeable,
  - Non-shrinking,
  - Able to withstand mechanical loads/impact,
  - Resistance to chemical/substances (H₂S, CO₂ and hydrocarbons),
  - Not harmful to the steel tubulars integrity,
  - Provide long-term integrity (eternal perspective).
Alternative Plugging Materials

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cements / ceramics (setting)</td>
<td>Portland cement, aluminosilicate, borate cements, hardening</td>
</tr>
<tr>
<td>B</td>
<td>Grouts (non-setting)</td>
<td>Sand or lime, bentonite, barite plugs, calcium carbonate</td>
</tr>
<tr>
<td>C</td>
<td>Thermosetting polymers and composites</td>
<td>Resins, epoxy, polyester, acrylics, thermosets, fibre reinforcements</td>
</tr>
<tr>
<td>D</td>
<td>Thermoplastic polymers and composites</td>
<td>Polyethylene, polypropylene, polylamide, PTFE, Peek, PMMA, PC and polycarbonate, including fibre reinforcements</td>
</tr>
<tr>
<td>E</td>
<td>Elastomeric polymers and composites</td>
<td>Natural rubber, neoprene, nitrile, EPDM, FKM, FFKM, silicone rubber, polyurethane, PUE and swelling rubbers, including fibre reinforcements</td>
</tr>
<tr>
<td>F</td>
<td>Formation</td>
<td>Claystone, shale, salt.</td>
</tr>
<tr>
<td>G</td>
<td>Gels</td>
<td>polymer gels, polysaccharides, starches, silicate-based gels, clay-based gels, diesel / clay mixtures</td>
</tr>
<tr>
<td>H</td>
<td>Glass</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Metals</td>
<td>Steel, other alloys such as bismuth-based materials</td>
</tr>
</tbody>
</table>
Geopolymers

- How do I produce the geopolymers?
Placeability - Consistency

- Reaction
  - Dissolution
  - Coagulation
  - Polycondensation

- RAS

Atmospheric consistometer of the aplite-based geopolymers with different mix ratios.

Atmospheric consistometer of the aplite-based geopolymers with different dosages of retarder.
Shear stress vs. shear rate for Na- and K-containing aplite-based geopolymers at ambient condition.

Shear stress vs. shear rate for fly ash- and aplite-based geopolymers at ambient condition.
Physical Observations

- Color changes
  - Chemical indicator of the geopolymers

- Cracks
  - Water evaporation

(a) cured at ambient pressure and temperature for 7 days,
(b) cured at 87°C and ambient pressure for 7 days, and
(c) cured at 87°C and ambient pressure for 365 days.
Properties of the Geopolymers - UCS

- The aplite-based geopolymers cured at ambient pressure and 87°C.
  - 6M KOH

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Properties of the Geopolymers - UCS

- Retarder Effect
  - Similar compressive strength
  - Dissolution

Uniaxial compressive strength of the aplite-based geopolymers cured at 90°C and 2000 psi.
Properties of the Geopolymers - CCM

- Estimated dynamic mechanical properties of the aplite-based geopolymers at 87°C and 1000 psi by using MPro.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slurry Density (g/cc)</th>
<th>Poisson’s Ratio</th>
<th>Bulk Modulus (kpsi) [GPa]</th>
<th>Young’s Modulus, E (kpsi) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1.90</td>
<td>0.28</td>
<td>746 [5.14]</td>
<td>1063 [7.33]</td>
</tr>
<tr>
<td>8</td>
<td>1.93</td>
<td>0.15</td>
<td>404 [2.78]</td>
<td>107 [0.74]</td>
</tr>
<tr>
<td>9</td>
<td>1.89</td>
<td>0.28</td>
<td>1057 [7.28]</td>
<td>1371 [9.45]</td>
</tr>
</tbody>
</table>

- Measured dynamic mechanical properties of the aplite-based geopolymers at 90°C and 2000 psi by using triaxial compression cell.

<table>
<thead>
<tr>
<th>Mix design</th>
<th>Bulk modulus</th>
<th>Young’s modulus</th>
<th>Poisson’s ratio</th>
<th>Axial creep (%) [t=7021 min]</th>
<th>Radial creep (%) [t=7021 min]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kpsi [GPa])</td>
<td>(kpsi [GPa])</td>
<td>[t=7021 min]</td>
<td>[t=7021 min]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>241.0 [1.66]</td>
<td>207.2 [1.43]</td>
<td>0.016</td>
<td>2.09</td>
<td>0.86</td>
</tr>
<tr>
<td>2*</td>
<td>222.3 [1.53]</td>
<td>238.0 [1.65]</td>
<td>0.015</td>
<td>2.00</td>
<td>0.88</td>
</tr>
<tr>
<td>3</td>
<td>221.2 [1.53]</td>
<td>213.1 [1.47]</td>
<td>0.018</td>
<td>2.23</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*Average values from two tests.
Properties of the Geopolymers

- **Ultrasonic Cement Analyzer (UCA)**
  - Custom algorithms shall be developed.

- **pH measurements**
  - Slurry’s pH value: 14
  - pH value of the geopolymer: 11.5-12.5

- **Shrinkage determination**
  - Autogenous shrinkage < 1%
  - Drying shrinkage ≈ 5%

- **Permeability measurements**
  - 0.007-0.040 micro-Darcy
Additional Studies

- Besides the previously mentioned investigations:
  - Effect of curing temperature:
    - Ambient temperature
    - Elevated temperature
  - Effect of activator:
    - Alkali solution
    - Alkali silicate solution
    - Alkali solution and alkali silicate solution
  - Influence of GGBFS:
    - Early strength development:
      - Amorphous content
      - Calcium and Magnesium content
      - C-S-H and C-A-S-H
X-ray Crystallography of the Geopolymers

- Aplite rock-based geopolymers K-silicate solution to alkali solution ratio of 1.

XRD pattern of Na-containing geopolymer cured at ambient temperature for 28 days.

XRD pattern of K-containing geopolymer cured at ambient temperature for 28 days.

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Microstructure Analysis of the Geopolymers

- Aplite rock-based geopolymers

(Top left) BSE image and elemental EDX maps for the most abundant elements in the geopolymer: Si, Al, O, Ca, Fe, Na, K, and Mg.
Long-Term Durability of the Geopolymers

- Aplite rock-based geopolymers
  - Ageing temperature: 100°C
  - Ageing pressure:
    - brine and crude oil: 7250 psi
    - \( H_2S \): 145 psi
Long-Term Durability of the Geopolymers

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  - Ageing pressure:
    - brine and crude oil: 7250 psi
    - \(H_2S\): 145 psi

<table>
<thead>
<tr>
<th></th>
<th>Ageing Pressure (MPa)</th>
<th>1-month</th>
<th>3-months</th>
<th>6-months</th>
<th>12-months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>50</td>
<td>-0.4±0.2</td>
<td>0.0±0.3</td>
<td>-0.9±0.1</td>
<td>-0.3±0.1</td>
</tr>
<tr>
<td>Brine</td>
<td>50</td>
<td>4.3±0.2</td>
<td>3.9±0.4</td>
<td>3.6±0.2</td>
<td>3.0±0.7</td>
</tr>
<tr>
<td>(H_2S)</td>
<td>1</td>
<td>3.1±2.0</td>
<td>1.1±1.0</td>
<td>-7.0±2.0</td>
<td>-10.5±3.0</td>
</tr>
</tbody>
</table>

Measured weight changes (%) of the geopolymers.

<table>
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<th></th>
<th>Ageing Pressure (MPa)</th>
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<th>6-months</th>
<th>12-months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>50</td>
<td>-0.1±0.6</td>
<td>-0.4±0.7</td>
<td>*</td>
<td>-1.0±1.5</td>
</tr>
<tr>
<td>Brine</td>
<td>50</td>
<td>7.0±1.0</td>
<td>5.0±2.0</td>
<td>6.5±1.5</td>
<td>3.5±1.5</td>
</tr>
<tr>
<td>(H_2S)</td>
<td>1</td>
<td>5.4±1.0</td>
<td>11.0±4.0</td>
<td>4.0±2.0</td>
<td>0.9±0.6</td>
</tr>
</tbody>
</table>

Measured volume changes (%) of the geopolymers.
Summary

- The particle size of the source material significantly affects the reactivity and properties of the geopolymers.
- Na-containing geopolymeric systems show a markedly higher viscosity than potassium-containing systems.
- The setting time could effectively be adjusted by the addition of retarders.
- A lower concentration of alkali solution can result in a higher strength for geopolymer than a higher concentration of alkali solution when combinations of Na- and K-containing systems are used as activators.
A higher curing temperature of the mixes with higher concentration of alkali solution may activate a consecutive reaction, which could reduce the strength of geopolymers.

The X-ray patterns indicated the formation of the zeolite phase for potassium-containing systems.

Long-term durability experiments show a further reaction after six months of curing takes place and increases the compressive strength and tensile strength of the aplite-based geopolymers that were exposed to crude oil and brine.
The long-term exposure of geopolymers to H$_2$S deteriorates both the compressive strength and tensile strength of the geopolymers. After six months of curing, as a result of the consecutive reaction, phase(s) is formed which increases the compressive and tensile strengths while interacting with H$_2$S.

Low permeability, favorable compressive strength, high pH value, and low shrinkage factor of geopolymers are key factors that could indicate a bright future for the geopolymer technology.
List of Publications


Acknowledgement

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