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

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Materials for Oil Well Cementing

- Two new materials were developed:
  - Aplite-based geopolymers
  - Norite-based geopolymers

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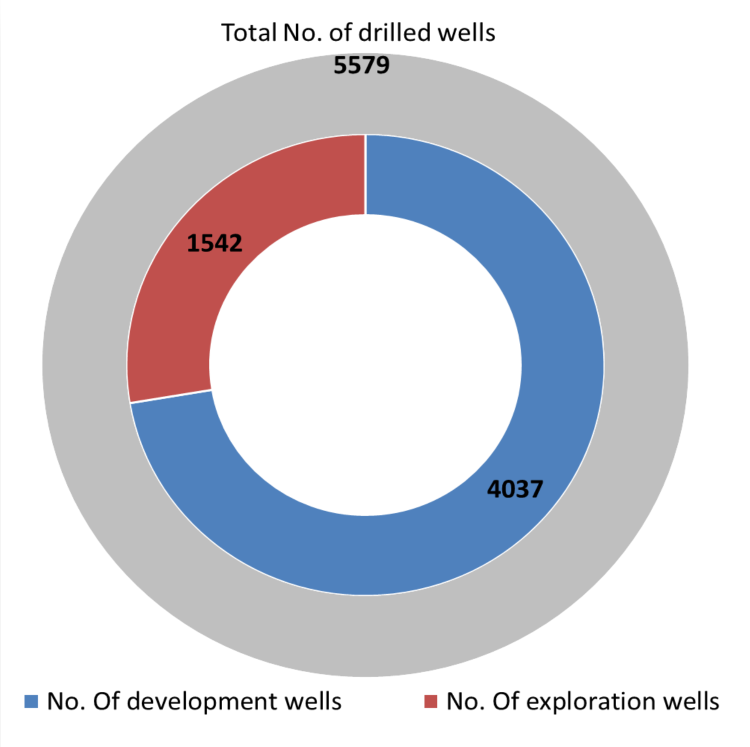
Oil Wells in Norway - Since 1966 until June 2015



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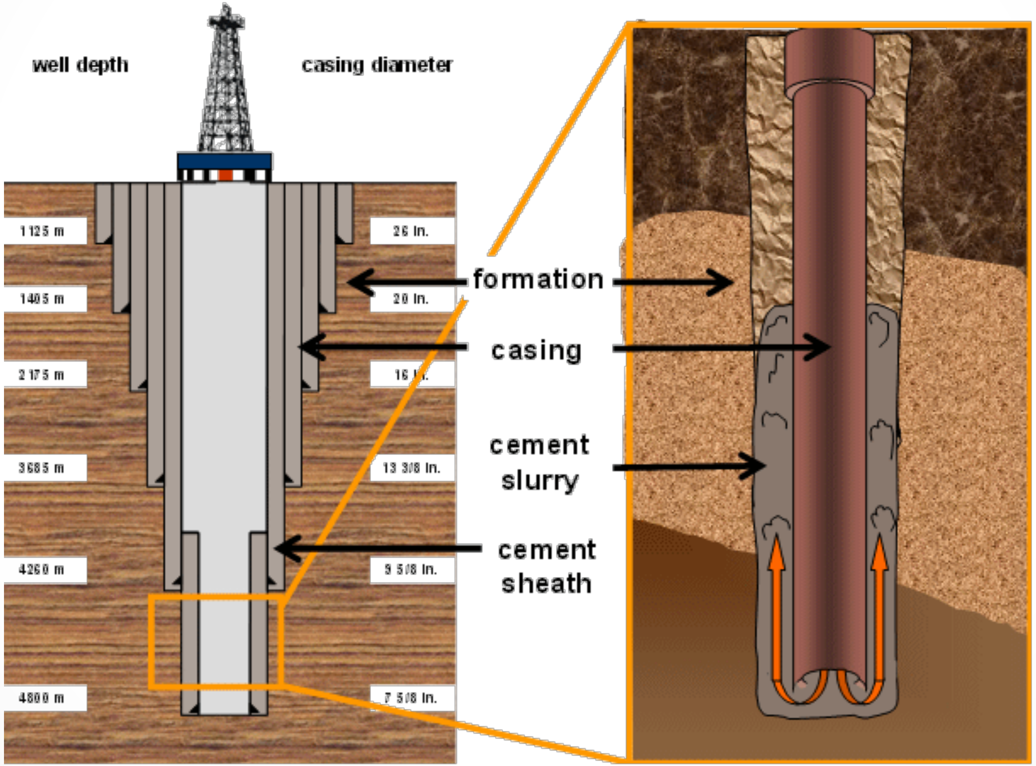
Oil Wells



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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.)

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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 (H_2S, CO_2 and hydrocarbons),
  - Not harmful to the steel tubulars integrity,
  - Provide long-term integrity (eternal perspective).

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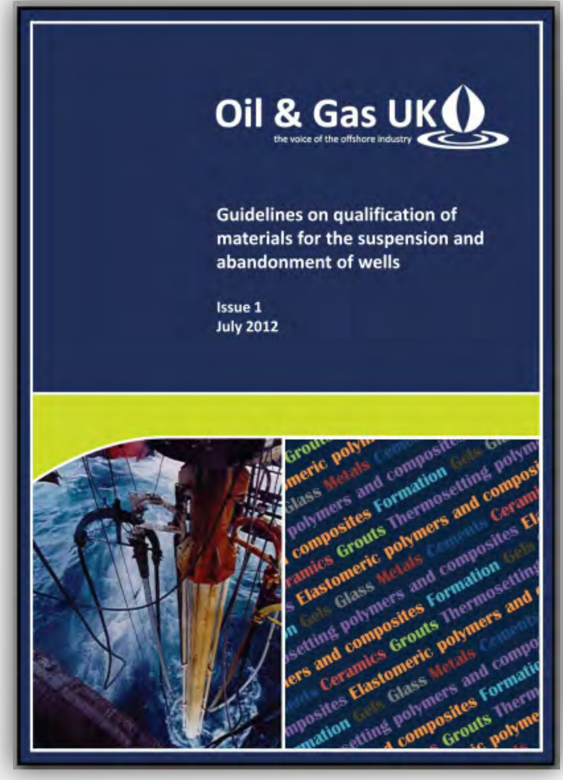
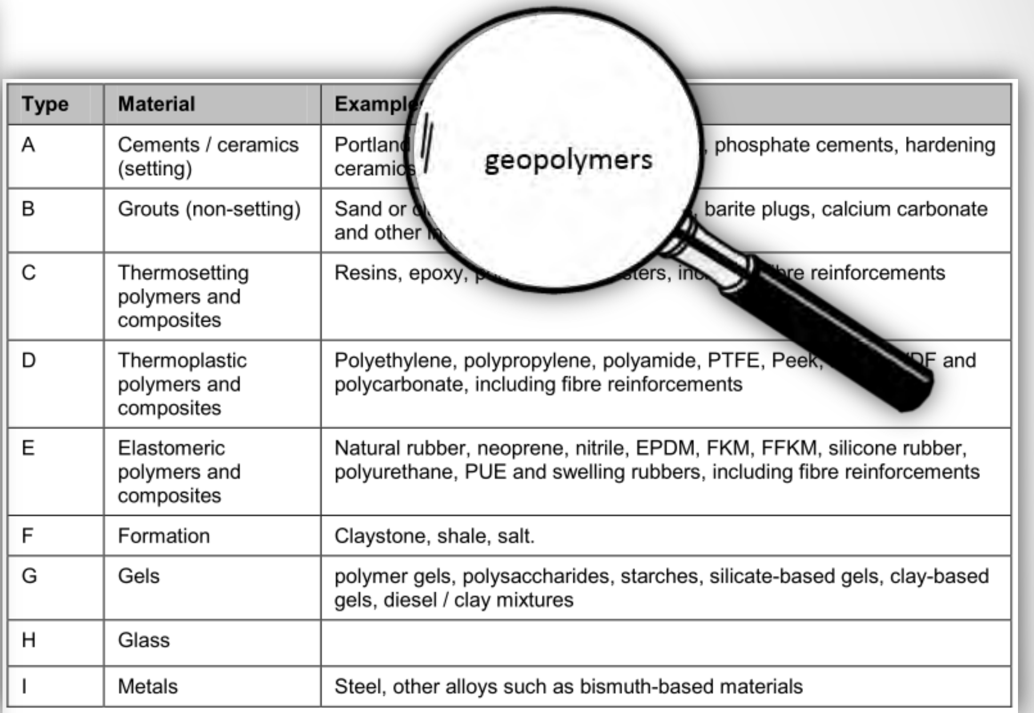
Alternative Plugging Materials





Type	Material	Exampl…
A	Cements / ceramics (setting)	Portlan… ceramic… …, phosphate cements, hardening
B	Grouts (non-setting)	Sand or … and other … … barite plugs, calcium carbonate
C	Thermosetting polymers and composites	Resins, epoxy, p… …sters, inc… …re reinforcements
D	Thermoplastic polymers and composites	Polyethylene, polypropylene, polyamide, PTFE, Peek, …DF and polycarbonate, including fibre reinforcements
E	Elastomeric polymers and composites	Natural rubber, neoprene, nitrile, EPDM, FKM, FFKM, silicone rubber, polyurethane, PUE and swelling rubbers, including fibre reinforcements
F	Formation	Claystone, shale, salt.
G	Gels	polymer gels, polysaccharides, starches, silicate-based gels, clay-based gels, diesel / clay mixtures
H	Glass	
I	Metals	Steel, other alloys such as bismuth-based materials

Geopolymers

- How do I produce the geopolymers?

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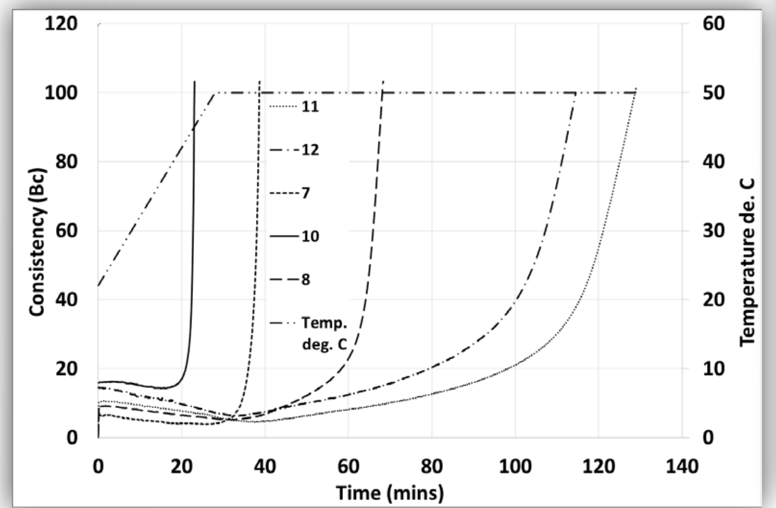
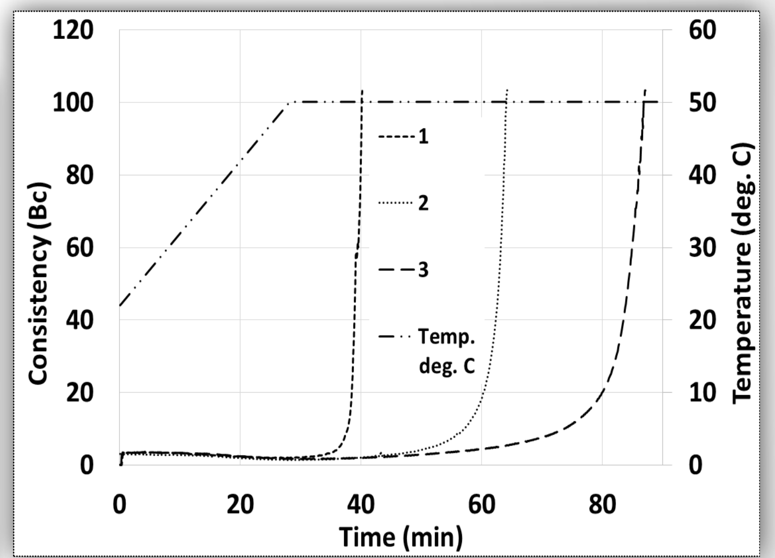
Placeability - Consistency

- 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.

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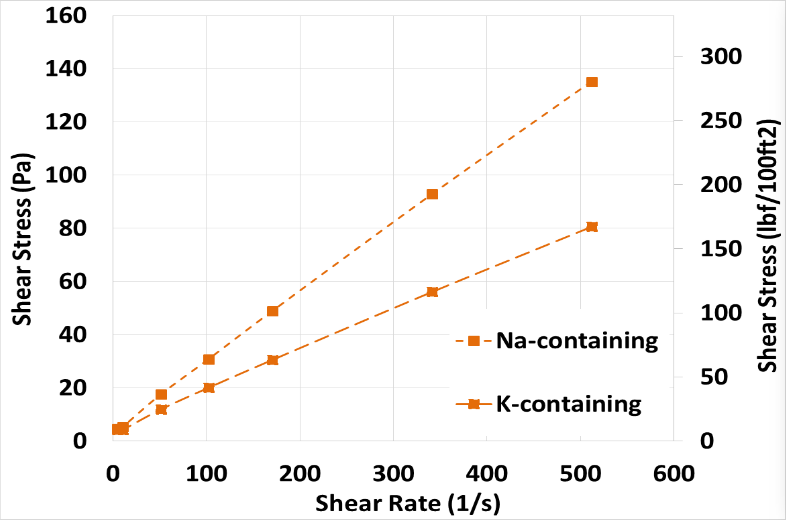
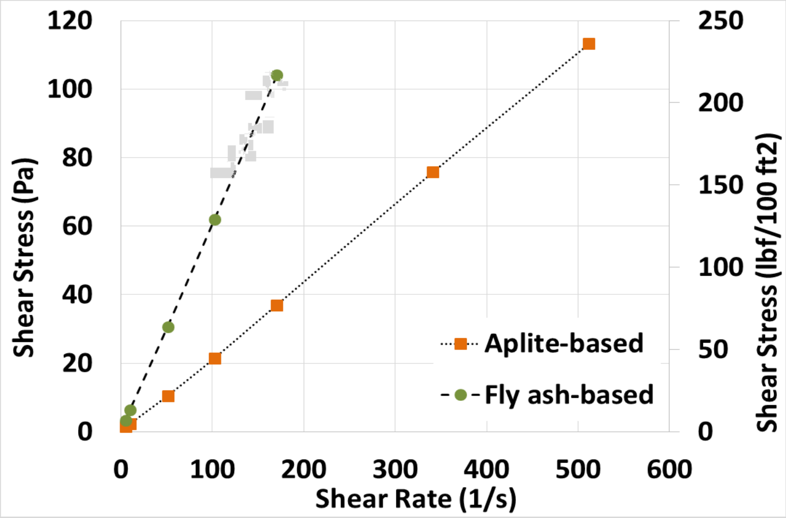
Placeability - Viscosity

- Non-Newtonian
  - Yield stress
- Shear Stress
  - Na-containing
  - K-containing
- Fly ash-based
  - Higher shear stress



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.

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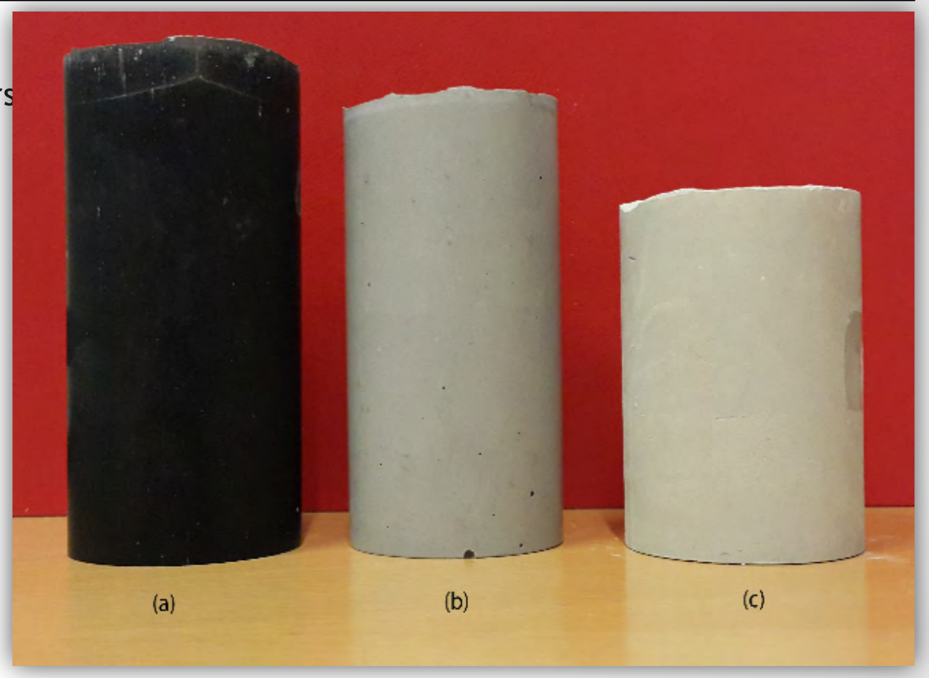
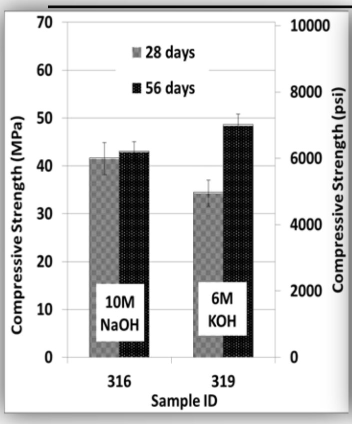
Physical Observations

- Color changes
  - Chemical indicator of the geopolymers
- Cracks
  - Water evaporation

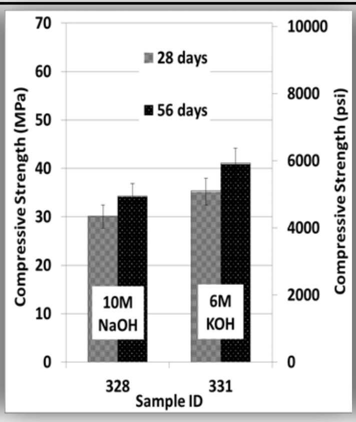


(a) cured at ambient pressure and temperature for 7 days,
(b) cured at 87°C and ambient pressure for 7 days, and
(c) cured at 87°C and ambient pressure for 365 days.

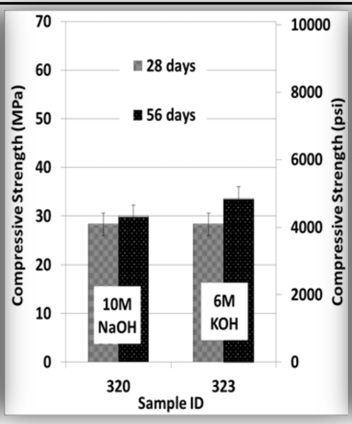
Properties of the Geopolymers - UCS



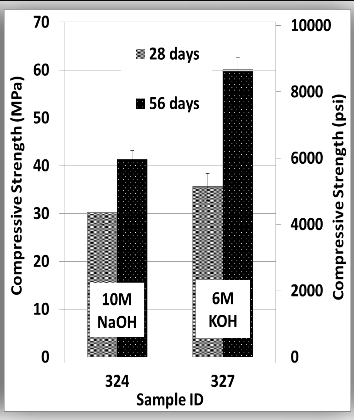
Na-silicate solution to alkali solution ratio of 1.



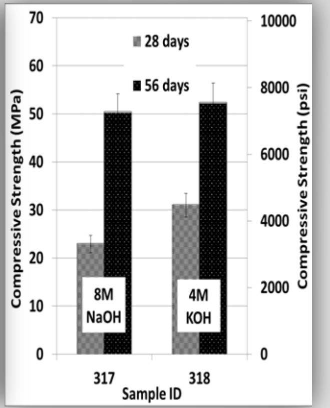
Na-silicate solution to alkali solution ratio of 3:1.



K-silicate solution to alkali solution ratio of 1.



K-silicate solution to alkali solution ratio of 3:1.



Na-silicate solution to alkali solution ratio of 1.

- The aplite-based geopolymers cured at ambient pressure and 87°C.
  - 6M KOH
  - K-silicate solution to alkali solution ratio of 3:1.

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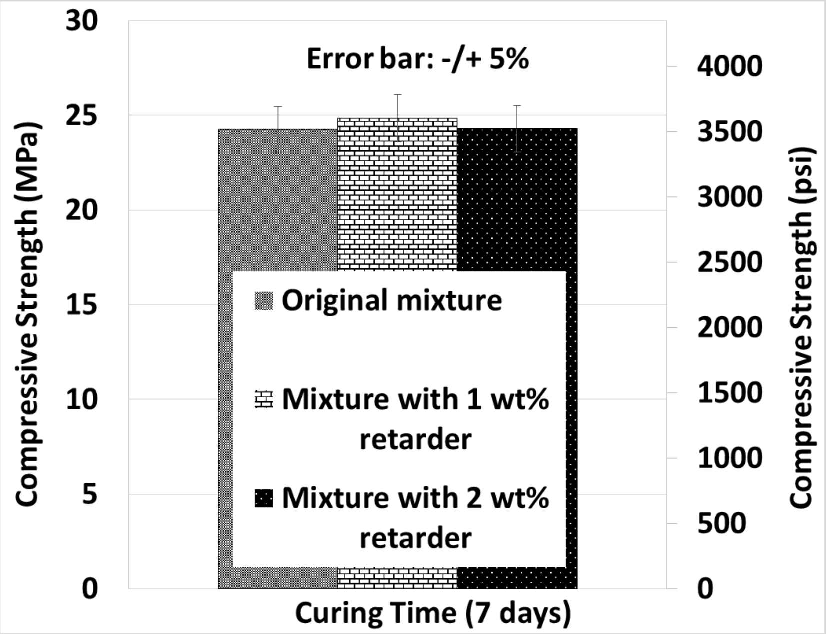
Properties of the Geopolymers - UCS

- Retarder Effect
  - Similar compressive strength
  - Dissolution



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

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Properties of the Geopolymers - CCM

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

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

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

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

*Average values from two tests.

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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

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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

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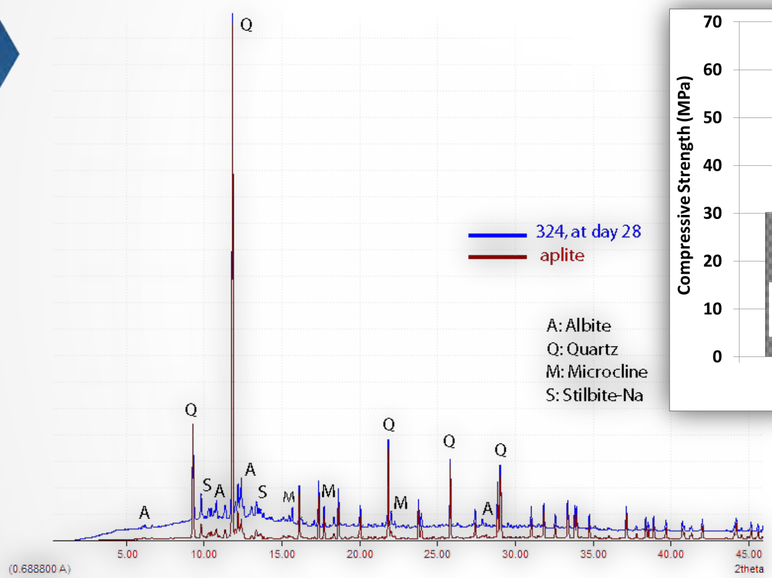
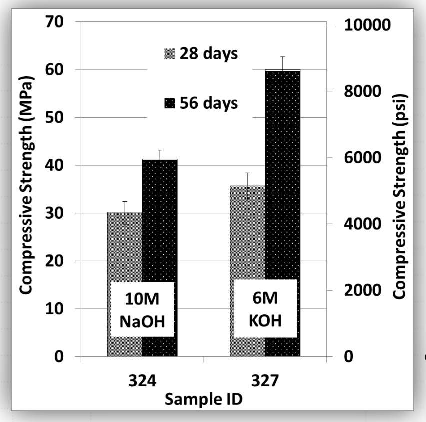
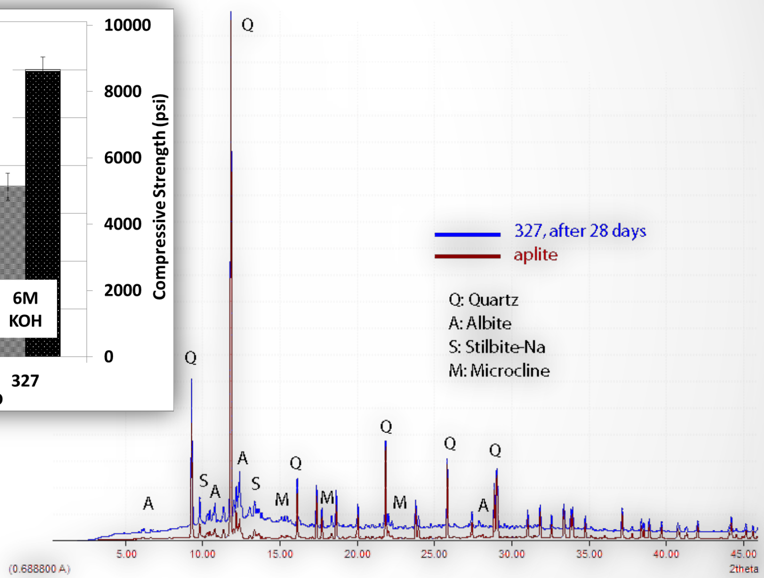
X-ray Crystallography of the Geopolymers

- 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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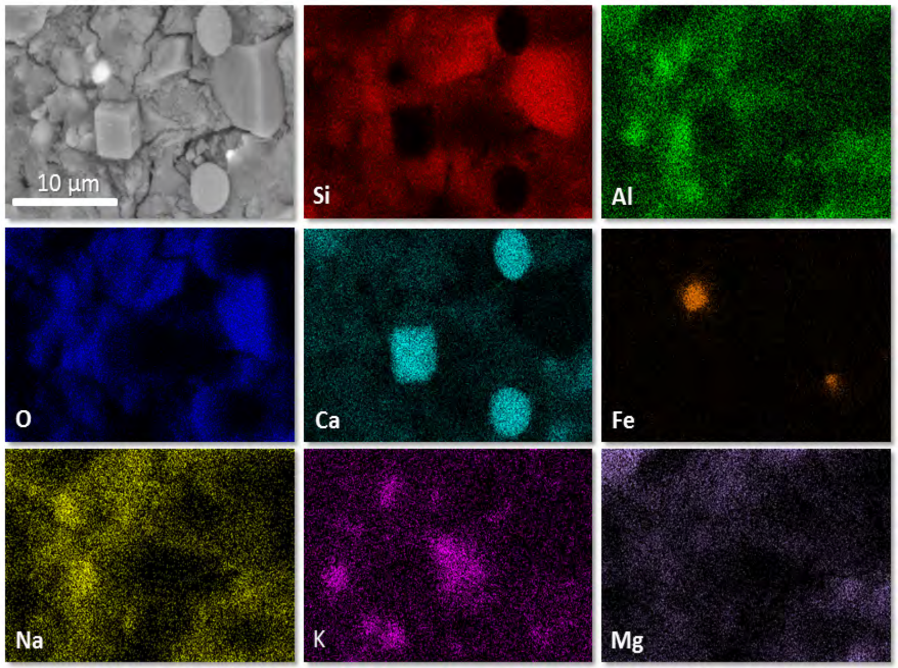
Microstructure Analysis of the Geopolymers

- 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.



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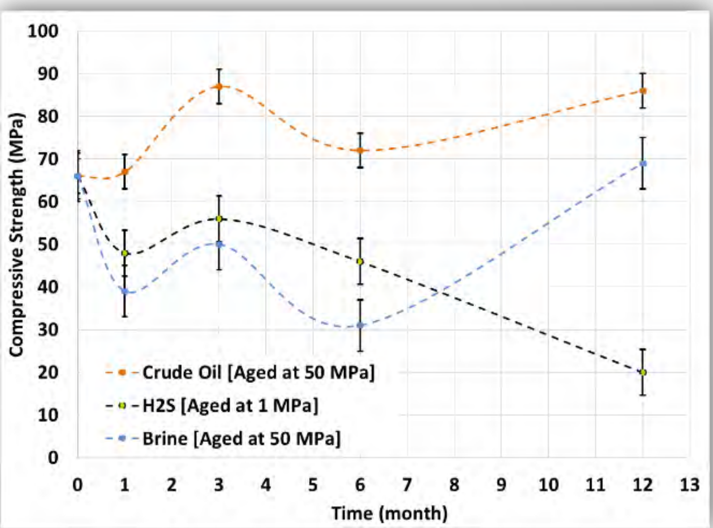
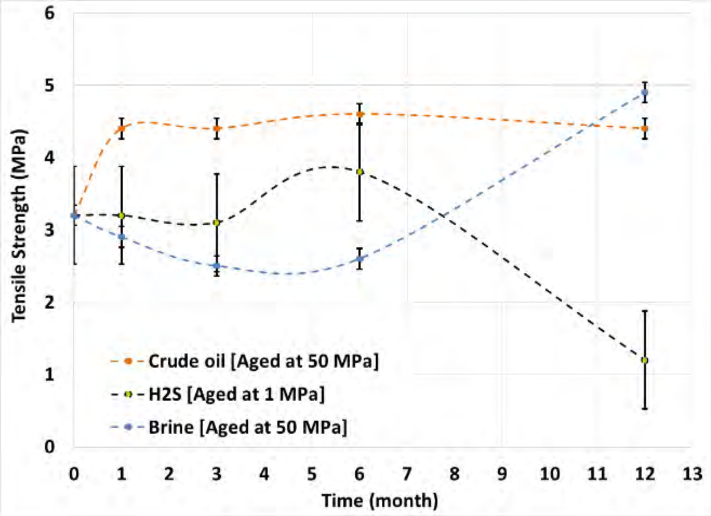
Long-Term Durability of the Geopolymers

- Aplite rock-based geopolymers
  - Ageing temperature: 100°C
  - Ageing pressure:
    - brine and crude oil: 7250 psi
    - H_2S: 145 psi



Compressive strength



Tensile strength

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

	Ageing Pressure (MPa)	1-month	3-months	6-months	12-months
Crude oil	50	-0.4±0.2	0.0±0.3	-0.9±0.1	-0.3±0.1
Brine	50	4.3±0.2	3.9±0.4	3.6±0.2	3.0±0.7
H_2S	1	3.1±2.0	1.1±1.0	-7.0±2.0	-10.5±3.0

Measured weight changes (%) of the geopolymers.

	Ageing Pressure (MPa)	1-month	3-months	6-months	12-months
Crude oil	50	-0.1±0.6	-0.4±0.7	*	-1.0±1.5
Brine	50	7.0±1.0	5.0±2.0	6.5±1.5	3.5±1.5
H_2S	1	5.4±1.0	11.0±4.0	4.0±2.0	0.9±0.6

Measured volume changes (%) of the geopolymers.

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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.

Summary

- 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.

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Summary

- The long-term exposure of geopolymers to H_2S 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_2S.
- 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.

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List of Publications

- Khalifeh, M., Hodne, H., Saasen, A., and Vrålstad, T. 2013. *Techniques and materials for North Sea plug and abandonment operations*. Paper OTC-23915 presented at the Offshore Technology Conference, 6-9 May, Houston, Texas, USA.

- Khalifeh, M., Saasen, A., Vrålstad, T., and Hodne, H. 2014. *Potential utilization of geopolymers in plug and abandonment operations*. Paper SPE-169231 presented at the SPE Bergen One Day Seminar held in Grieghallen, Bergen, Norway, 2 April 2014.

- Khalifeh, M., Saasen, A., Vrålstad, T., and Hodne, H. 2014. *Potential utilization of class C fly ash-based geopolymer in oil well cementing operations*. Journal of Cement and Concrete Composites 53 (2014) 10-17.

- Khalifeh, M., Saasen A., Vrålstad, T., Larsen, H.B., and Hodne, H. 2015. *Experimental study on the synthesis and characterization of aplite rock-based geopolymers*. Journal of Sustainable Cement-Based Materials.

- Khalifeh, M., Saasen, A., Vrålstad, T., Larsen, H.B., Hodne, H. 2015. *Cap rock restoration in plug and abandonment operations; possible utilization of aplite-based geopolymers for permanent zonal isolation and well plugging*. Paper SPE-17547-MS presented at the SPE Offshore Europe and Conference and Exhibition held in Aberdeen, Scotland, UK, 8-11 September 2015.

- Khalifeh, M., Saasen, A., Korsnes, R.I., and Hodne, H. 2015. *Cap rock restoration in plug and abandonment operations; possible utilization of rock-based geopolymers for permanent zonal isolation and well plugging*. Paper IPTC-18454-MS presented at the International Petroleum Technology Conference held in Doha, Qatar, 7-9 December 2015.

- Khalifeh, M., Saasen, A., Larsen, H.B., and Hodne, H. Submitted. *Experimental study on the formation (development) and characterization of norite-based geopolymer produced from an ilmenite mine waste stream, polymerized with NaOH and KOH solutions*. Submitted to a scientific journal in June 2015.

- Khalifeh, M., Todorovic, J., Vrålstad, T., Saasen, A., and Hodne, H. Submitted. *Long-term durability of rock-based geopolymers aged at downhole conditions for oil well cementing operations*. Journal of Sustainable Cement-Based Materials, 2016.

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Q&A

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