Cementitious materials for HT geothermal wells – recent advances and future challenges

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Specifics of Geothermal Wells

- **Oil-field cement formulations have limitations in geothermal-well applications**

- Significantly larger thermal-mechanical stresses than in oil-field
- Fragile formations – common lost-circulation problems (formation damage, placement T is difficult to estimate)
- Durability under geothermal-well conditions (acidic, highly corrosive, high dissolved solids, frequent shocks, high temperatures)
- Expected service life and criteria of a successful cementing job are very different
- Limited additives that can be used for modification of cement properties

Cement from Icelandic IDDP well

- Increased class H/SiO$_2$ cement porosity after organic additives degradation at 300$^\circ$C
- Melted/degraded organic inclusions in the cement matrix
Geothermal Wellbore Cementing Objectives

- **Zonal isolation** – prevention of fluids and gas migrations between different well zones and ground water contamination

- **Support of casing and well structure** – significantly more severe conditions than in oil and gas wells, normally all the length of the well is cemented

- **Corrosion prevention** – aggressive environments at very high temperatures

- **Insulation for preventing heat losses** – efficient heat recovery up to the surface

- **Heat conductive materials for heat recoveries** – heat recovery in hot zones

CS corrosion for **OPC/SiO$_2$-protected** casing after repeated TS tests

CS corrosion for **advanced CAC-based composite protected** casing after repeated TS tests
Advantages of proper designed cement sheath in geothermal wells

- **Materials cost:** If the cost-effective CS can be used when properly protected by cement sheath, the cost of casing and tubing can be reduced by nearly 3- and 20-fold compared with that of SS and NiCr alloy, respectively.

- **Corrosion protection:** The brine-caused corrosion rate of CS debonded from OPC sheath after TS cycling was nearly 4 times that of CS protected by advanced CAC-based cement. The use of advanced cement could extend casing life by nearly 4 times, reducing well operation and maintenance.

- **Decreasing heat losses:** Insulating cement sheath can minimize heat losses to cooler rock formations with high thermal conductivity (TC). E.g., in the case of 3.2 km-deep well, the working fluid of 93°C at the bottom of the well may undergo temperature decrease of 64.5% to 33°C when it reaches the wellhead. In contrast, if insulated material with low TC of 0.45 W/mK is deployed between casing and formation the heat loss rate to the rock formation is only 16.1% (4 times less).

- **Increasing heat recovery:** Heat recoveries can be increased by increasing cement conductivity and improving the bond with the formation in the hot regions of a well. Increasing conductivity to 8 W/mK may increase the temperature of the fluid at the surface by 40%.
Cement needs to be designed so that it can withstand the loadings in the target geothermal wells
- The loadings should be controlled if possible
- Very high pore pressures may be created at HT resulting in formation and propagation of micro annulus similar to fracturing

From: Axel Boise, Curistec
General advantages and concerns of Portland cement-based formulations

- Known additives and logistics, long experience, availability and low cost
- Poor resistance to strong acids and carbonate (poor corrosion protection)
- Poor thermal-shock resistance
- Poor cement-steel bonding (zonal isolation and corrosion protection)
- Not stable under very high temperatures

![Graph showing compressive strength and bond strength reduction over acid exposure and thermal shock](image)

**OPC/SiO2**

- Before acid exposure
- 14 days acid exposure
- Another 14 days acid exposure for 1st crack samples

**Compressive strength, psi**

- 0
- 2000
- 4000
- 6000
- 8000

**pH 0.2 H₂SO₄**

**TSRC**

**FAC/FAF**

**GBFS/SiO2**

**Shear-shear bond strength, psi**

**Bond strength reduction after 6 cycles, %**

**TS: 350°C → 25°C**
Alternative Geothermal Well Cement Compositions

- **Calcium phosphate system** \( \text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O} \)
  - Developed for carbonation resistance, commercialized and used in Japan, Indonesia, Italy for high-temperature geothermal wells;
  - Composition: calcium-aluminate cement, fly ash, type F and sodium polyphosphate

- **Calcium-aluminosilicate systems**
  - Cements that resemble the composition of the formation in geothermal wells (Roy et al., 1979, 1980). Of particular interest there was CaO-Al\(_2\)O\(_3\)-SiO\(_2\) system (desirable product anorthite).
  - Anorthite cement from calcinated kaolinite as an aluminum source in combination with class G and silica flour (SLB). Placement problems.
  - Thermal Shock Resistant Cement (TSRC) – calcium-aluminate cement, fly ash F and sodium-meta-silicate: \( \text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O} \)

- Various “synthetic cements” (organically-modified, e.g. epoxy-based polymer systems) are not applicable for high temperatures
Thermal Shock-Resistant Cement - TSRC

60% CAC – 40% FAF; Sodium Metasilicate activator at 6% by weight of blend

Hydrothermal synthesis of new cement consisting of hydro-garnet, feldspar, zeolite and aluminum-containing phases.

Reactants:
- Calcium-aluminate cement: CaO·Al₂O₃ and CaO·2Al₂O₃
- Fly Ash F: 3Al₂O₃·2SiO₂ + SiO₂
- Sodium-meta-Silicate: Na₂O·nSiO₂

Products:
- Ca₃Al₂Si₂O₈(OH)₄ hydrogrossulars
- Ca₃AlFe(Si₃O₁₁)(OH)
- Ca₂Al₂(OH)₁₂ katoite
- Na₄Al₃Si₃O₁₂(OH)- hydroxsodalite
- Ca₃Al₂(SiO₄)₃ - garronite
- NaCa₂Al₅Si₄O₂₀·6H₂O - thomsonite
- Na₈Al₈Si₁₆O₄₈(H₂O)₈ - analcime

Hydrothermal synthesis (H₂O) at 200°C-300°C
TSRC multifunctional performance – summary

**Thermal shock**
**Resistance and Bond Strength**

- Crystalline phases:
  - Zeolites – Sodalite
  - Cancrinite
  - Analcime
  - Thomsonite

- Amorphous phase:
  - NaO-Al$_2$O$_3$-SiO$_2$-H$_2$O

**Carbon fibers reinforcement**

*Binding phases: CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O, analcime*

**Corrosion protection**

*Amorphous phase: NaO-Al$_2$O$_3$-SiO$_2$-H$_2$O*

**Carbonation resistance**

*Stable Crystalline phase: Carbonated sodalite, Sodium Cancrinite*

$H_{0.88}Na_8Al_6(SiO_4)_6(CO_3)_{1.44}(H_2O)_2$

**Acid resistance**

*Stable Crystalline phase: Alunite*

*Amorphous phase: Aluminum silicate*

**CS bond strength**

*Crystalline phase of cement-CS interactions: Brownmillerite; Hedenbergite, Andradite Ca-andradite*

**Calcium phosphate (CaP)**

*OPC/SiO$_2$, TSRC, G/SiO$_2$*
Energy storage wells – thermally insulating cements

Step 1.
- Using polymethylhydrosiloxane (PMHS) to make light-weight super-hydrophobic cement
- Thermal conductivity under water-saturated condition ~0.4 W/mK (TC of water is 0.6 W/mK)
Insulating TS - resistant cement – energy storage wells

Low TC

Contact angle (°)

Before TS test

After TS test

PMHS content

Thermal conductivity (TC), W/mK

Water TC Criteria

PMHS content

Pre-TS test sample
Shear bond strength: 88.8 psi
Adhesive strain extension: 2.6%

Post-TS test sample
Shear bond strength: 52.3 psi
Adhesive strain extension: 3.7%
Although sheath developed hair cracking, cement well adhered to casing, promising corrosion protection

Corrosion rate, mm/year

OPC/SiO₂

Pre-TS test
Post-TS test

Rust

CS 0 1 3 5

PMHS (%)
Some research and development needs for geothermal wells

- Materials for super-critical conditions – cements and formation/cement/casing system
- Thermally conductive cement for efficient heat recovery at high temperatures
- Placement technologies for HT wells

Super-critical cement

1) Fundamental understanding of super-heat resistant cement (SHRC) chemistry and physicochemical behaviors in possible supercritical environments (A, B, and C in Figure);
2) Technology modifications to optimize SHRC performance;
3) Placement technology for the optimized formulation, including effect of pumping schedule on cement hydration
4) Assessment and optimization of SHRC stability under different thermochemical environments including brine, HCl_{(gas)}, H_2S_{(gas)}, and CO_2_{(gas)}
5) Investigation of bonding and bond durability of SHRC to high-temperature metal alloy casings and formation;
6) Evaluation of the corrosion/oxidation protections of casings by SHRC
THANK YOU!