

PROPERTIES OF WELL CEMENTS FOR HIGH TEMPERATURE GEOTHERMAL WELLS

Jan ter Heege¹, Marcel Naumann², Penny Pipilikaki³, Frank Vercauteren⁴, Jens Wollenweber¹

¹ TNO Applied Geosciences, Princetonlaan 6, Utrecht, the Netherlands

² Equinor ASA, Sandsliveien 90, Sandsli, Norway

³ TNO Structural reliability, Stieltjesweg 1, Delft, the Netherlands

⁴ TNO Material Solutions, High Tech Campus 25, Eindhoven, the Netherlands

jan.terheege@tno.nl

Keywords: high temperature wells, well cement, experimental data, mineralogy, mechanical data.

ABSTRACT

Maintaining long term wellbore stability in high temperature environments one of the key challenges determining the success of geothermal wells. Changes in cement mineralogy and associated mechanical properties critically affect the integrity of high temperature wells. In this study, the relation between changes in mineralogy, microstructure and mechanical properties of cement samples was investigated. Laboratory-made synthetic cement samples consisting of API class G cement with 40% silica flour were exposed to temperatures of 60°C (curing only) up to 420°C (curing and exposure) for exposure times of 3 days (curing time) to 4 weeks (HT exposure). The effect of mineralogical changes on mechanical properties was investigated using a combination of (1) chemical analysis using X-ray diffraction (XRD), (2) microstructural analysis using scanning electron microscopy (SEM) and optical microscopy, and (3) mechanical properties (failure stress, Young's modulus) using triaxial strength tests at confining pressures of 2-15 MPa. The mineralogy was compared with cement samples from the excavated top section of the IDDP-1 well that were exposed to in-situ conditions for a prolonged time. It was found that the relation between mineralogy, microstructure and mechanical behavior of synthetic cement samples is complex and due to the combined effect of changing porosity, microstructure and strength of mineral phases. The most important mineralogical changes are the formation of stronger xonotlite and wollastonite phases with higher density. The cement is more brittle deformation at low confining pressures and more ductile deformation at high confining pressures with a considerable residual strength that may be able to carry large differential loads even after cement failure. Geothermal wells targeting super-hot reservoirs containing supercritical fluids may be critically affected by changing mechanical properties of well cement between 120 and 250°C during thermal recovery after drilling, while cement sheaths close to

the production casing may regain stiffness and strength after exposure at temperatures above ~400°C. Promising options for improved cement formulations with reduced water content use a combination of high shear mixing, and addition of superplasticisers and nano-particles.

1. INTRODUCTION

Geothermal drilling environments are often hostile to well materials, especially in magmatic settings where properties of well casing and cements may rapidly change as a result of high temperatures and chemically reactive formation fluids. Maintaining long term wellbore stability in high temperature environments is one of the key challenges for the commercial success of high enthalpy geothermal projects (Kaldal et al 2016). Recent wells target super-hot reservoirs containing supercritical fluids, such as the IDDP-1 and IDDP-2 well (Iceland Deep Drilling Project) with envisaged reservoir temperatures and pressures reaching up to above 400°C and 300 bars (Friðleifsson et al 2015). Long term wellbore integrity at these conditions is critically affected by changing mechanical properties of well materials that may ultimately lead to casing rupture or collapse (Kaldal et al 2016). Moreover, properties of interfaces between different casing components, cement sheaths and rock formation play a crucial role. To withstand such conditions, tailored high-temperature cements need to be developed and tested that ensure the plugging of loss zones during drilling, proper anchoring, corrosion protection of casing strings, zonal isolation and well integrity at these elevated temperatures and pressures (HPHT conditions).

The integrity of wellbore cement is particularly important in high temperature geothermal wells as cement damage promotes migration of reactive fluids along and through the cement sheath, and reduces thermal isolation of the casing by the cement sheath. The resulting reduction in zonal isolation, enhanced casing corrosion, and elevated thermo-mechanical stresses may significantly reduce the lifetime of geothermal wells.

In this study, the relation between changes in mineralogy, microstructure and mechanical properties of cement samples was investigated. Laboratory-made synthetic cement samples were compared with samples from the excavated top section of the IDDP-1 well that were exposed to in-situ conditions for a prolonged time. Synthetic samples consist of API class G cement with 40% silica flour. The synthetic samples were exposed to temperatures of 60°C (curing only) up to 420°C (curing and exposure) for exposure times of 3 days (curing time) to 4 weeks (HT exposure). The effect of mineralogical changes on mechanical properties was investigated using a combination of (1) chemical analysis using X-ray diffraction (XRD), (2) microstructural analysis using scanning electron microscopy (SEM) and optical microscopy, and (3) mechanical properties (failure stress, Young's modulus) using triaxial strength tests at confining pressures of 2-15 MPa.

Results show that the formation of high temperature mineral phases in the cement such as tobermorite, xonotlite and wollastonite is associated with marked changes in elastic properties and failure behaviour. Critical conditions for the changes in mineralogy and mechanical behaviour are determined, and compared to IDDP-1 conditions. The implications for well integrity and design of new cement formulations are discussed. To counter embrittlement of the cement due to mineralogical changes at high temperature, cement formulations need to be modified. Enhanced cement flexibility is required to account for extreme mechanical loads caused by casing deformation during temperature cycles. In addition, the residual water, required for cement placement rather than for hydration, in the hydrated cement or in pockets needs to be reduced as this can result in (over)pressures that eventually trigger casing collapse during the warm-up period(s). The main challenge remains to optimize cement properties for prolonging the integrity of cement at high temperatures while maintaining low viscosity of cement slurry during well cementation.

2. BACKGROUND

Standard cement formulations have been reported to reach their mechanical and chemical (stability) limits due to the harsh conditions and extreme cyclic temperature loads in geothermal wells (Kaldal et al 2016). For standard curing conditions, hydration of ordinary Portland cement (OPC, e.g., class G well cement) with a calcium oxide to silicon dioxide (C/S) ratio close to 3.1 produces the amorphous C-S-H and the crystalline $\text{Ca}(\text{OH})_2$. The product is a mixture of ordered and disordered phases with C-S-H present as a highly disorder version of the crystalline phases tobermorite and jennite (Taylor 1990). Tobermorite preserves high compressive strength and low permeability. Mineralogical and mechanical changes are expected to occur in OPC above ~110°C (Thorvaldson et al 1938; Patchen 1960; Taylor 1990; Kyritsis et al 2009). Reactions result in different hydration products, i.e. crystallization of alpha dicalcium silicate hydrate ($\alpha\text{-C}_2\text{SH}$ or $\text{Ca}_2\text{SiO}_3(\text{OH})_2$) is

favoured. The lime-rich alpha-dicalcium silicate hydrate ($\alpha\text{-C}_2\text{SH}$) is denser than the usual calcium silicate hydrate (C-S-H gel) product. Bulk volume decrease, and cement shrinkage or porosity increase is associated with this reaction, which results in a decrease in cement strength and increase in permeability (Patchen 1960; Pernites and Santra 2016). All types of OPC and other types of well cements with similar composition show lower strengths when cured above 110°C, compared to curing at 93°C.

Elevated curing temperatures are commonly reached by geothermal wells in areas with moderate to high geothermal gradients. Changes in cement properties need to be accounted in the design of cement formulations as well as cementation of these wells to ensure the plugging of loss zones during drilling, proper anchoring, corrosion protection of casing strings, zonal isolation and well integrity at elevated temperatures and pressures (HPHT conditions). Common practice is to use Portland-type cements with added silica (such as fly ash, silica fume or quartz flour) to stabilize cement to higher temperature. Reactions of $\text{Ca}(\text{OH})_2$ with added silica at elevated temperatures result in a C-S-H with a lower C/S ratio. Addition of 35 to 40% by weight of cement is enough to prevent the reaction forming $\alpha\text{-C}_2\text{SH}$. Instead, cement phases such as tobermorite or xonotlite are formed (Patchen 1960). Moreover, for a water to solids ratio of 0.4, a formulation with added silica results in 91% of the water being chemically bound against only 39 % of the available water in the OPC. Addition of ~40% silica flour thereby favours formation of high strength and low permeability mineral phases.

Despite the importance for well integrity of high temperature wells, data on mineralogical and mechanical changes during exposure of well cements to HPHT conditions is limited. Some relevant laboratory studies are available (Taylor 1990; Gabrovšek et al 1993; Meller et al 2009; Pernites and Santra 2016), but investigations of the relation between mineralogical and mechanical changes at different exposure times and temperatures are sparse.

3. EXPERIMENTAL APPROACH

Synthetic cement samples, Dyckerhoff HT Basic Blend of cement clinker (API class G cement) with 40 % silica flour was used as a starting material (Papaioannou, 2018). Specimens are prepared using the Dyckerhoff blend and demineralized water with a water to solid (cement + silica flour) ratio of 0.371 (m/m). For the mixing process, the EN 196-3 protocol was followed. For mineralogical and microstructural analysis, samples were exposed for 4 weeks to 60°C at atmospheric pressure, 120°C at 2 bar pressure, 250°C at 40 bars pressure, and 420°C at 350 bars pressure. For the triaxial experiments, samples of ~50 mm length and ~25 mm diameter were produced from cured only samples (curing for 3 days at 60°C) and from samples exposed for 1 week to 120°C at 2 bars, 4 weeks to 250°C at 40 bars, and 2 weeks to 420°C at 350 bars, respectively.

IDDP-1 samples were obtained from the excavated top section of the IDDP-1 well that experienced temperatures up to 450°C for several months. The upper section of the well, next to the surface consisted of 3 casings, and four annuli respectively. In the four different annuli of the well different types of cement were used: Cement sheath 1 & 2: Dyckerhoff high temperature basic blend (40% silica sand powder), cement sheath 3: Dyckerhoff Class G cement, cement sheath 4: Dyckerhoff Class G cement and mica flour. During plugging and abandonment of the well, a top segment of 6 m of the entire well was dug out.

Analysis of mineral phases in the samples with 4 weeks exposure and in the IDDP-1 samples was performed using X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). Microstructural analysis was performed using optical microscopy and scanning electron microscopy (SEM).

The triaxial experiments were conducted at confining pressures of 2-15 MPa, room temperature and pore pressures at ambient conditions. Samples were tested at initially fully saturated pore fluid conditions. Slow axial strain rate on the order of 5.10^{-6} s^{-1} were used to remain in drained conditions such that no excessive pore pressure is built-up internally. The setup and procedure follow largely the suggested method for determining the strength of rock materials in triaxial compression (Kovari et al., 1983), although axial strains were measured indirectly by means of an external linear variable differential transformer (LVDT) only and radial strains were not measured. Axial stress was measured by two load cells, located both inside and outside the pressure vessel.

Triaxial tests were conducted by hydrostatic loading of samples to predefined confinement, and subsequent triaxial compression at constant displacement rate until reaching an approximately constant plateau of post-failure (residual) stress. The triaxial experiments were used to determine mechanical parameters (static Young's modulus, failure and residual strength) as a function of confinement, specimen exposure temperature and duration.

4. RESULTS

4.1 Mineralogy & microstructure

Synthetic cement samples cured for 4 weeks at 60°C mainly consist of hydration products ettringite, portlandite and katoite, amorphous hydrate phase and clinker phases C_3S and brownmillerite that have not completely reacted (Table 1). Samples exposed for 4 weeks to 120°C mainly consist of hydration phases tobermorite, $\alpha\text{-C}_2\text{S}$ hydrate and afwillite. The clinker phase C_3S as well as the hydration products ettringite and portlandite have disappeared completely at these conditions, while brownmillerite and katoite are detected in smaller amounts. Dissolution of quartz occurs, but reactions involving quartz are limited. The amount of metastable high Ca/Si ratio amorphous phases increases. Xonotlite is the main mineral phase

that appears in samples exposed for 4 weeks to 250°C, accompanied by small amount of calcite. All other phases including cement hydrates, quartz and non-hydrated cement have disappeared. Samples exposed for 4 weeks to 420°C still mainly consist of xonotlite, but wollastonite, calcite and gypsum are also formed. The amorphous content decreased again compared to the samples exposed for 4 weeks at lower temperatures (Table 1). Both darker areas with dense C-S-H cement grains and lower capillary porosity, and lighter areas with higher capillary porosity are present indicating local separation of water and microbleeding. Samples exposed for 4 weeks to 120°C mainly consist of hydration phases tobermorite, $\alpha\text{-C}_2\text{S}$ hydrate and afwillite. The clinker phase C_3S as well as the hydration products ettringite and portlandite have disappeared completely at these conditions, while brownmillerite and katoite are detected in smaller amounts. Dissolution of quartz occurs, but reactions involving quartz are limited. The amount of metastable high Ca/Si ratio amorphous phases increases (Table 1). The microstructure and distribution of capillary porosity is more homogeneous than in the samples exposed to 60°C with similar porosity throughout the sample. A reaction front is observed between the C-S-H gel and the surrounding amorphous silica, and well-formed tobermorite crystals appear to grow inside the C-S-H gel.

Samples from the 4 different cement sheaths of the excavated top section of well IDDP-1 show different mineralogical changes for the different cement types in the sheaths. The cement in cement sheath 4 is class G cement with added mica. Formation of tobermorite indicates exposure temperatures which is normally formed between 100 and 150°C. Compared to the original cement composition, some mica and reaction products could be detected (Fig. 2).

Table 1: Mineralogical composition of samples exposed for 4 weeks at different temperatures determined by XRD analysis.

Mineral phase	60°C	120°C	420°C*
Ettringite	1.4	-	-
Portlandite	8.5	-	-
Katoite	3.5	2.6	-
C_3S	3.8	-	-
Brownmillerite	7.7	5.0	-
Tobermorite	-	10.4	-
Afwillite	-	0.6	-
$\alpha\text{-C}_2\text{S}$ hydrate	-	1.2	-
Quartz	26.2	13.1	-
Xonotlite	-	-	33.8-35.3
Wollastonite	-	-	14.8-15.9
Gypsum	-	-	1.1-2.4
Calcite	-	-	0.3
Amorphous content	48.9	67.1	46.1-49.9

*Range from measurement of two different samples.

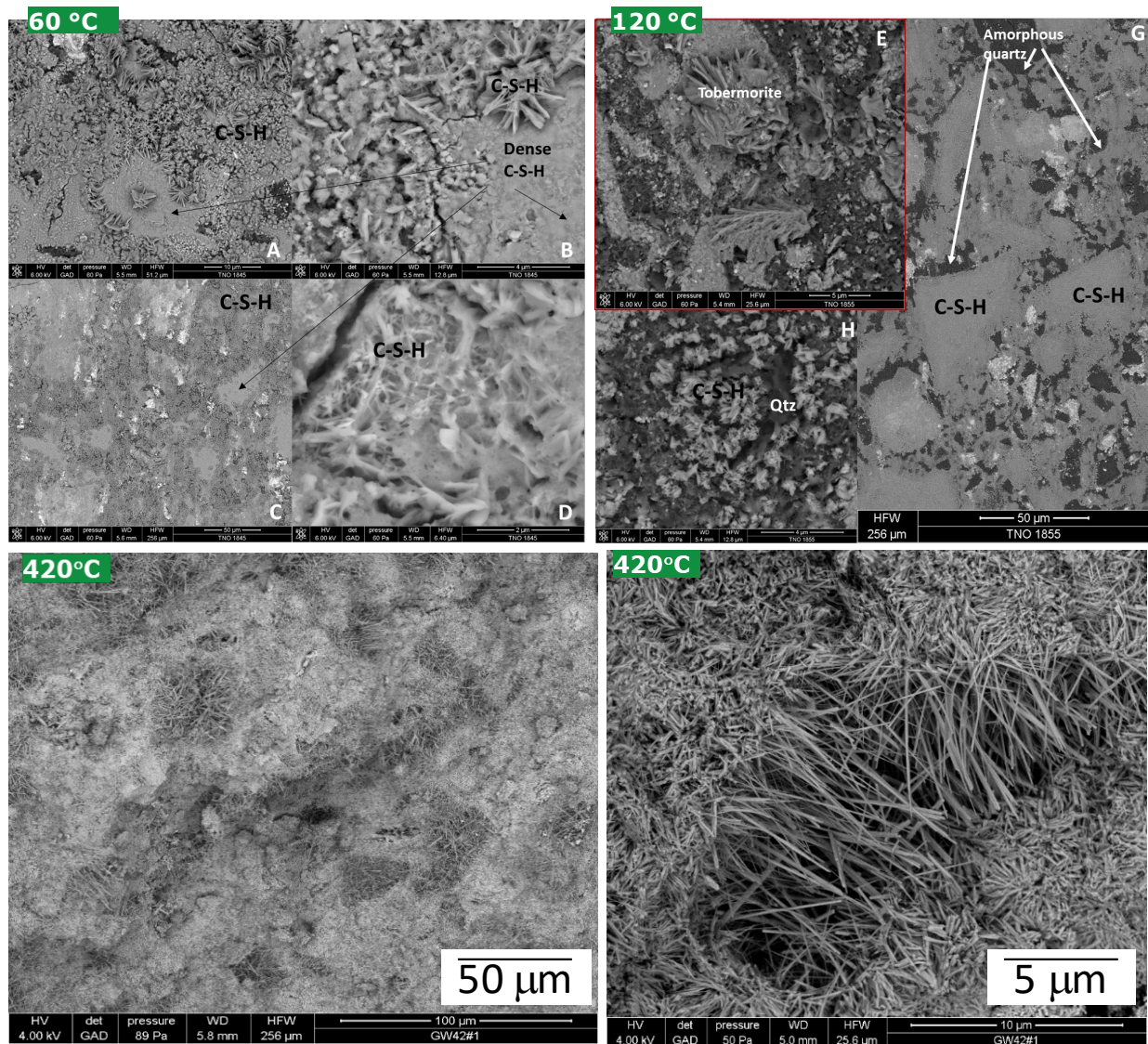


Figure 1: Scanning electron microscopy images showing microstructures of samples exposed for 4 weeks to 60-420°C. Upper figures from Papaioannou (2018). See text for description of phases.

Zoned quartz crystals with reaction rims consisting of calcium silica oxides enriched in silica oxide indicate partial dissolution of quartz at temperatures above 100°C and below those required to fully dissolve quartz. Crystals with leached cores containing hydrates with MgO, Fe₂O₃ and Al₂O₃ composition. Exposure temperatures are likely more than 100°C but less than 300°C as quartz particles have not completely reacted. The cement in sheath 3 Portland type G cement. Beside tobermorite, unreacted phases such as brownmillerite, C₂S and fine-grained (~0.02 mm) quartz are present, suggesting exposure temperatures below 220°C. Inhomogeneous distribution of porosity and water content supported by structures indicating micro-bleeding are also observed. Microcracking is also present, and cubical crystals with a Ca/Si ratio corresponding to that of CSH (1.6). The cement in cement sheath 2 is Dyckerhoff high temperature basic blend. The main crystalline phase is xonotlite (formation temperatures from 150°C up to 400°C), and small amounts of tobermorite. Absence of crystalline silica flour indicates reactions involving quartz. Needle-

shaped crystals developed inside bleeding channels. There is some indication that fine-grained crystals of truscottite (Ca/Si ratio of 0.58) has formed at the expense of xonotlite, which suggests temperatures above 200°C and local areas that are poor in Ca. The presence of xonotlite suggest exposure temperatures of 220°C to 400°C. Comparison of cement mineralogy between cement in sheath 2 and synthetic cement samples (i.e. presence of tobermorite) indicate that sheath 2 was exposed to temperatures lower than 250°C. Together, mineralogy suggest that exposure temperatures were between 200-250°C during operation of the well. Similar to cement in sheath 2 the cement in sheath 1 is Dyckerhoff high temperature basic blend. The composition in sheath 1 mainly differs from sheath 2 in that wollastonite is present (formation temperatures above 400°C) together with decomposition product silicon oxide. In both sheaths 1 and 2 porosity distribution is inhomogeneous. Fewer bleeding structures are present compared to cement sheath 2. Crystal morphology is different in sheath 1 with star-shaped crystals of xonotlite or wollastonite

composition that develop inside preexisting voids. Truettite may also be present that may be formed by decomposition of silica and wollastonite for parts with higher silica content while only wollastonite is formed in areas with dominant xonotlite composition.

Comparison of cement mineralogy between cement in sheath 1 and synthetic cement samples (i.e. presence of xonotlite and wollastonite) indicate that sheath 1 was exposed to temperatures above 400°C during operation of the well.

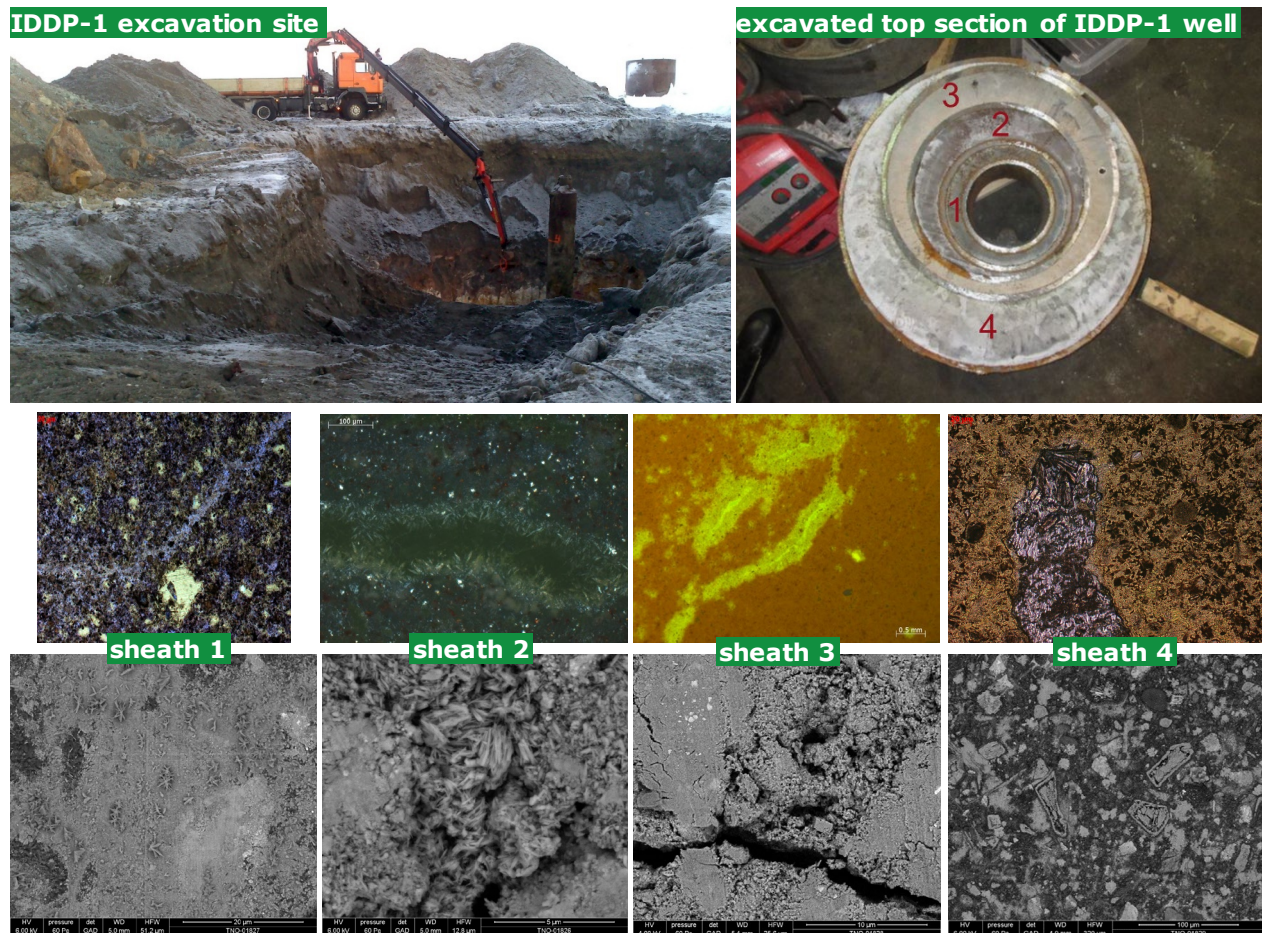


Figure 2: Optical microscopy and SEM images of samples from different cement sheaths in the excavated top section of the IDDP-1 well showing (1) xonotlite/wollastonite crystals grown in microbleeding channels, (2) bleeding structures overgrown by xonotlite crystals, (3) bleeding structures in dense cement matrix indicating inhomogeneous water separation and distribution, and (4) zones with fine crystals and reaction rims indicating reacted quartz (inner sheath 1 to outer sheath 4, left to right in bottom figures, Pipilikaki et al. 2017; Vercauteren et al. 2018). IDDP-1 samples, images (top row) and information courtesy of ISOR.

4.2 Mechanical behaviour

Cured only samples have a Young's modulus (E) that increases from 4.9 GPa at 2 MPa confining pressure (P_c) to 9.5 MPa at $P_c = 15$ MPa (Table 2, Figure 2). A similar increasing trend of Young's modulus with confining pressure is observed for samples exposed for 1 week to 120°C ($E = 6.4$ GPa for $P_c = 2$ MPa to $E = 7.5$ GPa for $P_c = 10$ MPa). Compared to cured only samples, Young's modulus is increasing for $P_c = 2$ and 5 MPa, and decreasing for $P_c = 10$ MPa. The trend of increasing Young's modulus with increasing confining pressure is reversed for samples exposed for 4 weeks to 250°C and for 2 weeks to 420°C. Young's modulus is increasing if samples are exposed for 1 week to 120°C, at least for low confining pressures. For longer exposures or higher exposure temperatures Young's modulus is mostly decreasing with increasing exposure

time and exposure temperature. One exception is a sample exposed for 2 weeks to 420°C tested at $P_c = 2$ MPa, which show slightly higher Young's modulus compared to cured only samples or samples exposed to 120°C.

The maximum (peak) differential stress (σ_p or failure strength) and (residual) differential stress after failure (σ_r or residual strength) increases with confining pressure in almost all samples (Table 2, Fig. 3). Failure strengths of the cured only samples are 49.3-58.1 MPa at $P_c = 2$ MPa to 80.1 MPa at $P_c = 15$ MPa. One sample exposed for 2 weeks to 420°C has similar failure strength for $P_c = 2$ MPa and 10 MPa, but its residual strength shows the general trend of increasing strength with increasing confining pressure.

Table 2: Mechanical data from triaxial experiments.

Sample	Exposure	P_c	σ_p	σ_r	E
		MPa	MPa	MPa	GPa
GWL003	Cured only	2	49.3	19.3	4.9
GWL005	Cured only	2	57.4	33.1	8.2
GWL011	Cured only	2	58.1	28.2	7.2
GWL004	Cured only	5	61.4	38.5	5.8
GWL002	Cured only	10	69.1	54.5	7.8
GWL009	Cured only	10	61.5	17.6	6.5
GWL006	Cured only	15	80.1	75.1	9.5
GWL012	1 week, 120°C	2	52.3	32.9	6.4
GWL013	1 week, 120°C	5	54.9	38.7	7.0
GWL007	1 week, 120°C	10	75.1	56.3	7.5
GWL018	4 weeks, 250°C	2	29.5	18.3	4.8
GWL014	4 weeks, 250°C	5	31.3	26.4	3.9
GWL019	4 weeks, 250°C	5	34.5	31.2	4.6
GWL016	2 weeks, 420°C	2	57.6	29.3	6.7
GWL015	2 weeks, 420°C	5	48.2	31.5	5.6
GWL017	2 weeks, 420°C	10	58.0	47.1	5.8

P_c - confining pressure, σ_p - peak differential stress, σ_r - residual differential stress, E- static Young's modulus.

Trends of failure and residual strength with exposure time and temperature are comparable as the trends observed for Young's modulus, i.e. overall failure and

residual stresses decrease with increasing exposure time and exposure temperature. Samples exposed for 1 week to 120°C have strengths that are comparable to the cured only samples. The relation between principal stresses (σ_1, σ_3) at failure (Fig. 4) suggest (1) a similar friction coefficient for samples exposed up to 250°C, (2) a change in friction coefficient with increasing exposure temperature between 250 and 420°C, and (3) a drop in uniaxial compressive strength (UCS) with exposure temperatures increasing from 120 to 250°C, followed by an increasing UCS between 250 and 420°C. Note that $\sigma_1 = C_0 + q\sigma_3$, with C_0 the uniaxial compressive strength and q related to the friction coefficient for a Mohr-Coulomb failure criterion (Al-Ajm and Zimmerman, 2005). The difference between failure and residual strength (Fig. 5) suggest a change from more brittle deformation at low confining pressures (i.e. a large stress drop after failure or large difference in strength) to more ductile deformation at high confining pressures (i.e. a small stress drop after failure that is spread out over larger axial strain).

The relative effect of exposure time and temperature on mechanical behaviour is unclear. Further experiments on samples need to be performed to systematically explore these effects (for examples samples exposed for 2 weeks to 250°C or for 4 weeks to 420°C).

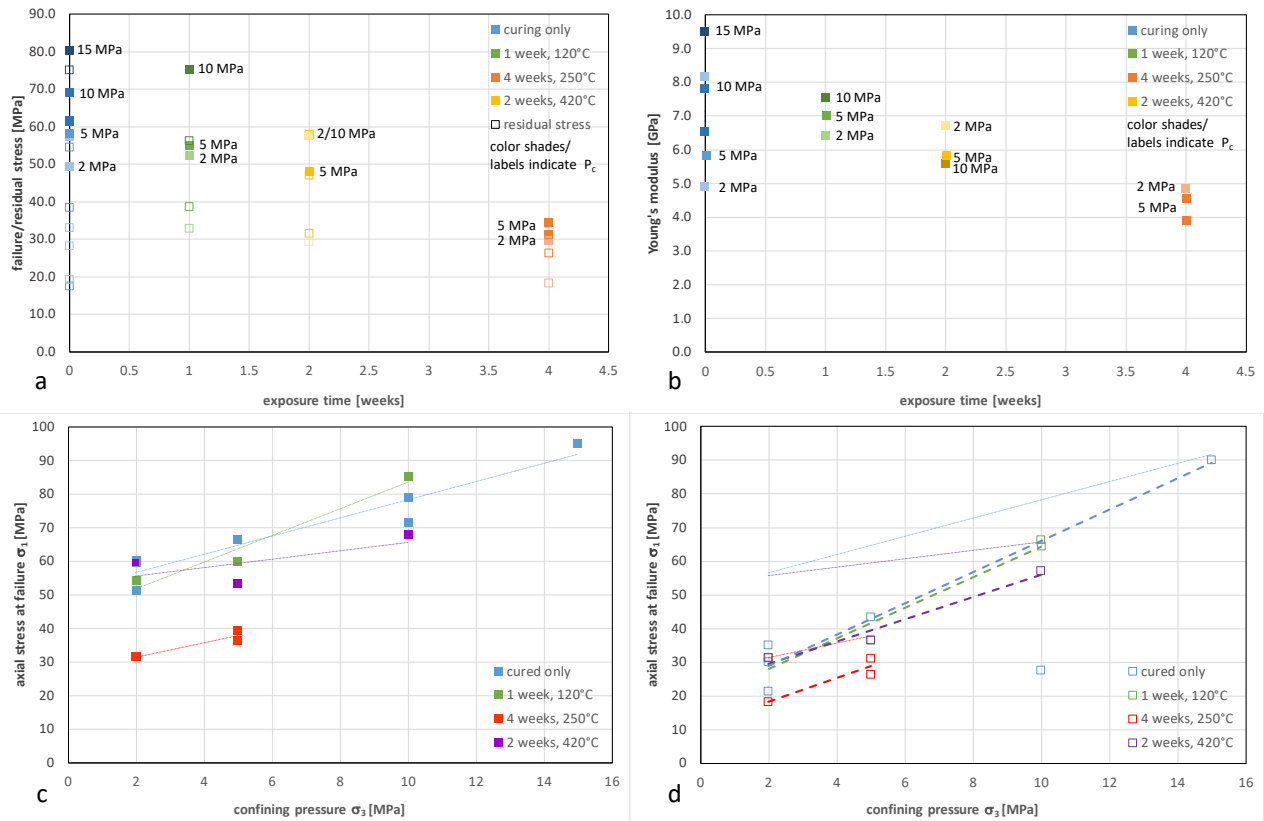


Figure 3: Experimental data of the mechanical behaviour of “cured only” synthetic cement samples and synthetic cement samples exposed for 1-4 weeks to 120–420°C. (a) Young’s modulus. (b) Failure and residual strength, (c) Relation between the maximum principal stress (σ_1) at failure and minimum principal stress ($\sigma_3 = P_c$) with best fit linear trends (dashed lines). (d) Relation between the maximum principal stress (σ_1) at post failure residual strength and minimum principal stress ($\sigma_3 = P_c$) with best fit linear trends (dashed lines).

4. DISCUSSION

Previous studies showed that addition of 35 to 40% by weight of cement is enough to prevent the reaction forming α -C₂SH, and favor formation of stronger mineral phases such as tobermorite or xonotlite (Patchen, 1960). Addition of ~40% silica flour is therefore expected to favor formation of high strength and low permeability mineral phases at high temperatures, thereby improving cement stability and well integrity in high temperature wells. The results of this study provide additional insight on the relation between mineralogy, microstructure and mechanical behavior was investigated for cement samples consisting of Dyckerhoff HT Basic Blend of cement clinker (API class G cement) with 40% added silica flour. It shows that deformation of the cement is more brittle deformation at low confining pressures and more ductile deformation at high confining pressures. The relation between mineralogy, microstructure and mechanical behaviour is complex. Mineralogical changes occurring between curing at 60 and 120°C mostly result in slightly stiffer (i.e. higher Young's modulus) and stronger (i.e. higher failure and residual strength) cement. Cement becomes less stiff and weaker if temperatures are raised to 250°C. It becomes and stiffer and stronger again if temperatures are further increased to 420°C. The observed changes may also be affected by exposure times, which have not been systematically varied. Comparison with other studies (Papaioannou 2018) and mineralogical observations (i.e. formation of stronger mineral phases) suggest that (1) samples may become stiffer and stronger for longer exposures at 120°C, and (2) stiffness and strength will further increase for longer exposure to 420°C. The change in mechanical behaviour is likely due to the combined effect of changing porosity, microstructure and strength of mineral phases, i.e. (1) formation of stronger xonotlite and wollastonite phases with higher density at the expense of tobermorite, α -C₂S hydrate, afwillite, brownmillerite and katoite (absent after exposure for 4 weeks at 420°C) and change in amorphous content (Table 1), (2) change in porosity due the different volume of reaction products, and (3) different microstructure (i.e. voids filled with needle-shaped crystals).

The most important issue with this complex relation between mineralogical, microstructural and mechanical changes in this high temperature cement is with the reduction in stiffness and strength around ~250°C. Young's modulus can drop by 25-44% between 120°C and 250°C within weeks of high temperature exposure, depending on confining pressure and exposure times (Table 2). This drop in stiffness can be accompanied by a drop in failure strength of ~40%. In this temperature interval, support and protection of the casing by cement sheath can be significantly reduced, and well integrity can be jeopardized.

Geothermal wells that target super-hot reservoirs containing supercritical fluids, such as the IDDP-1 and IDDP-2 well (Iceland Deep Drilling Project) can reach

bottomhole temperatures and pressures above 400°C and 300 bars (Friðleifsson et al., 2015). Analysis of mineralogy and microstructures of cement samples from the excavated top section of well IDDP-1 shows that during operation the top section of the inner cement sheath 1 was likely exposed to temperatures above 400°C, the top section of cement sheath 2 was likely exposed to temperatures of 200-250°C, the top section of cement sheath 3 was likely exposed to temperatures below 220°C, and the top section of the outer cement sheath 4 was likely exposed to temperatures was likely exposed to temperatures of 100-150°C. Exposure temperatures of deeper sections of the cement sheaths are likely higher as produced fluids cool down and formation temperatures are lower at shallower depth. Casings are generally cemented all the way to the surface in these wells. Long term exposure of well cement surrounding the production casing to temperatures above 400°C is expected for geothermal wells targeting supercritical fluids. Accordingly, the integrity of cement sheaths in these wells may be critically affected by changing mechanical properties of well cement between 120 and 250°C during thermal recovery after drilling. The inner cement sheath (and possibly sheath 2) may regain stiffness and strength after exposure at temperatures above ~400°C due to formation of stronger mineral phases (e.g., xonotlite, wollastonite). Exposure temperatures may not be high enough in the other cement sheaths, leading to differences in stiffness and failure strength between different sheaths.

Important issues with loss of well integrity in high temperature wells are that cement damage leads to (1) fluid migration along the wells (i.e. casing-cement-rock interfaces) and through the cement sheath to the casing, and (2) reduced support of the casing to sustain mechanical loads. Fluid migration reduces thermal isolation of the casing by the cement sheath and enhances thermal stresses and corrosion. Higher mechanical loads on the casing will increase the risks of casing buckling and collapse. For the high temperature cement investigated in this study, a change in the mechanical behaviour of the cement is observed from more brittle deformation at low confining pressures to more ductile deformation at high confining pressures with a considerable residual strength after exceeding the failure strength. It suggests that the cement may still support relatively large differential loads even after exceeding its failure strength. Accordingly, the experimental data in this study aid in the development new cement formulations with improved mechanical properties and in the design of operations for high temperature wells to mitigate cement damage.

The main challenge in designing improved cement is to mitigate problematic changes in mechanical properties during exposure at high temperatures while maintaining low viscosity of cement slurry during well cementation. Low viscosity of the cement slurry is generally achieved by adding excess water, i.e. water not consumed by reactions during cement curing but

required for proper flow behaviour of cement slurry during cementation of well casings. The pressure generated by excess water in the cement sheath both in water pockets (because of incomplete placement) and in the cement itself can generate high (supplementary) pressures that can cause indentations or buckling of the casing. Accordingly, reduction of water and supplementary pressure is beneficial for well integrity. It is estimated that almost 80% of water that is present in a Portland cement with w/c ratio of 0.4 and 40% of silica flosser needs to be replaced to get rid of water that is not required for curing. Promising options for water reduction use a combination of high shear mixing, and addition of superplasticisers and nano-particles.

5. CONCLUSIONS

- The relation between mineralogy, microstructure and mechanical behavior of synthetic cement samples is complex. Mineralogical changes occurring between curing at 60 and 120°C result in slightly stiffer and stronger cement. Cement becomes less stiff and weaker if temperatures are raised to 250°C, and stiffer and stronger if temperatures increase to 420°C.
- The change in mechanical behavior is likely due to the combined effect of changing porosity, microstructure and strength of mineral phases. The most important mineralogical changes are the formation of stronger xonotlite and wollastonite phases with higher density at the expense of tobermorite, α -C₂S hydrate, afwillite, brownmillerite and katoite, and changes in amorphous content. These mineralogical changes are accompanied by a change in porosity due the different volume of reaction products, and by changes in microstructure (e.g., voids filled with needle-shaped crystals).
- For all exposure times and temperatures, deformation of the cement is more brittle deformation at low confining pressures and more ductile deformation at high confining pressures. A considerable residual strength remains after exceeding the peak differential stress, and the cement may still carry large differential loads even after exceeding its failure strength.
- Analysis of mineralogy and microstructures of cement samples from the excavated top section of well IDDP-1 shows that cemented casings of geothermal wells targeting super-hot reservoirs containing supercritical fluids may be critically affected by changing mechanical properties of well cement between 120 and 250°C during thermal recovery after drilling. Cement sheaths close to the production casing may regain stiffness and strength after exposure at temperatures above ~400°C due to formation of

stronger mineral phases (e.g., xonotlite, wollastonite).

- The main challenge in designing improved cement is to mitigate problematic changes in mechanical properties during exposure at high temperatures while maintaining low viscosity of cement slurry during well cementation. Reduction of excess water not used for curing reactions is critical beneficial to lower supplementary pressure that affects casing integrity. Promising options for water reduction in cement formulations use a combination of high shear mixing, and addition of superplasticisers and nano-particles.

REFERENCES

- Al-Ajmi, A.M. and Zimmerman, R.W.: Relation between the Mogi and the Coulomb failure criteria, *Int. J. Rock Mech. & Min. Sc.*, **42**, (2005), 431-439.
- Gabrovšek, R., Kurbus, B., Mueller, D. and Wieker, W.: Tobermorite formation in the system CaO, C₃SSiO₂Al₂O₃NaOHH₂O under hydrothermal conditions, *Cement and Concrete Research*, **23**, (1993), 321–328.
- Friðleifsson, G.Ó., Pálsson, B., Albertsson, A.L., Stefánsson, B., Gunnlaugsson, E., Ketilsson, J. and Gíslason, Þ.: IDDP-1 Drilled Into Magma – World’s First Magma-EGS System Created, *Proceedings World Geothermal Congress 2015*, Melbourne, Australia, (2015).
- Kaldal, G.S., Jonsson, M.T., Pálsson, H. and Karlsdóttir, S.N.: Structural modeling of the casings in the IDDP-1 well: Load history analysis, *Geothermics*, **62**, (2016), 1-11.
- Kovari, K., Tisa, A., Einstein, H.H. and Franklin, J.A.: Suggested methods for determining the strength of rock materials in triaxial compression: Revised version, *Int. J. Rock Mech. Min. Sci. & Geomech. Abstr.*, **20**, (1983), 283–290.
- Kyritsis, K., Hall, C., Bentz, D.P., Meller, N. and Wilson, M.A.: Relationship between engineering properties, mineralogy, and microstructure in cement-based hydroceramic materials cured at 200 - 350 C, *Journal of the American Ceramic Society*, **92**, (2009), 694–701.
- Meller, N., Hall, C. and Phipps, J.S.: A new phase diagram for the CaO–Al₂O₃–SiO₂–H₂O hydroceramic system at 200°C, *Materials Research Bulletin*, **40**, (2005), 715–723.
- Papaioannou, A.: *Impact of in-situ ageing on the mineralogy and mechanical properties of Portland-based cement in geothermal applications*, M.Sc. thesis Utrecht University, (2018).
- Pipilikaki, P., Vercauteren, F., and Wollenweber, J.: Chemical and microstructural alterations of

annular cements of a high-temperature geothermal well, *Celle Drilling 2017*, (2017).

Patchen, F.D.: Reaction and Properties of Silica-Portland Cement Mixtures Cured at Elevated Temperatures, *Journal of the Society of Petroleum Engineers*, **219**, (1960), 281–287.

Pernites, R.B., and Santra, A.K.: Portland cement solutions for ultra-high temperature wellbore applications, *Cement and Concrete Composites*, **72**, (2016), 89-103.

Stiles, D.: Effects of Long-Term Exposure to Ultrahigh Temperature on the Mechanical Parameters of Cement, SPE-98896, (2006).

Taylor, H.F.W.: *Cement chemistry*. Academic Press, (1990).

Thorvaldson, T.: Portland Cement and Hydrothermal Re-actions, *Symposium of the Chemistry of Cement, Stockholm*, (1938).

Vercauteren, F., Naumann, M., Pipilikaki, P., Ter Heege, J., Wollenweber, J., and Kampfer, G.: Testing and development of cements for high-temperature geothermal wells, *AAPG "Geothermal Cross Over Technologies Workshop"*, Utrecht, Netherlands (2018).

Acknowledgements

The work has been published as part of the GEOWELL project, funded by the European Union's Horizon 2020 research and innovation program under grant agreement number 654497. Discussions with partners of the GEOWELL research consortium are gratefully acknowledged.