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Material Testing and Challanges for Casing Materials for Superhot Geothermal Wells

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ABSTRACT

There are numerous challenges in the design, drilling and construction of superhot and deep geothermal wells, many of these are connected to the materials used. Higher temperature, pressure and more corrosive conditions in the drilling and construction of deep superhot geothermal are likely to facilitate problems if traditional design and materials for high temperature geothermal wells is used. In this paper, these main material challenges are introduced and identified as: i) difficulties in cementing and degradation of cement casing materials due to high temperatures and corrosive conditions; ii) the potential failure/rupture of carbon steel casings due to high plastic strains generated due large temperature difference during heating and cooling of the well and strength reduction at temperatures above 200°C; and iii) corrosion of casing materials due to high temperatures (>300°C) and corrosiveness of the geothermal fluid. The potential application of corrosion resistant alloys instead of standard API carbon steel casing material is discussed and the state of the art of cement casing materials and the potential usage of novel thermal schock resistant cement casings. Following this the experimental setup and design for high temperature testing of promising CRAs and cement casing materials in a custom made high temperature and high pressure autoclave laboratory with incorporation of corrosive gases at temperatures >300°C is described. The results from the test will give information on the durability and corrosion resistance of the chosen CRA and cement casing materials and thus hopefully aid in the design and material selection for future superhot geothermal wells.

1. MATERIAL CHALLENGES IN SUPERHOT GEOTHERMAL WELLS

Interest has increased around the world in utilizing geothermal energy from superhot or supercritical geothermal resources which has led to the initiation of several projects in this field. These include for example the Newberry Deep Drilling Project (NDDP) in the USA, the GeoMex project in Mexico, the Japan Beyond Brittle Project (JBBP) in Japan and the Iceland Deep Drilling project (IDDP) in Iceland (Reinsch et al., 2017). The focus of many of these projects is to drill deeper than for conventional high temperature geothermal wells (>3 km) to obtain superhot or supercritical geothermal fluid with temperatures exceeding 300°C and pressure above 100 bar. This consequentially gives rise to increased likelihood of encountering highly corrosive fluids. The goal of these projects is in general to obtain higher power output per well, higher than traditional high temperature wells.

In drilling and construction of deeper geothermal wells to obtain higher enthalpy geothermal fluids and produce more energy per well, the strength and integrity of the cement and steel casings becomes one of the limiting factors due to the high temperatures and pressure involved and corrosive conditions. In some cases, high pressures can be enough to cause casing failures but most casing failures are driven by large temperature changes. When commonly used carbon steel casing materials are used in high-temperature geothermal wells, permanent plastic strains form as the wells are warming up to production temperatures following the drilling phase where drilling fluids have cool down the well. The increase in temperature causes thermal expansion and large plastic stresses are generated in the carbon steel casings as they are constrained by cement (Kaldal et. Al. 2017). The same applies when hot wells need to be quenched with cooling water, where instead of thermal expansion the cooling results in thermal contraction of the steel casings (Kaldal et. Al. 2015).

The elevated temperatures also cause material strength reduction, which further increases the risk of failures. The New Zealand standard NZS 2403:2015 “Code of practice for deep geothermal wells”, including its 1991 edition, has been used for the last two decades for well design in geothermal conditions (NZS 2403:2015 et. Al. 2015). To account for strength reduction of casing materials at elevated temperatures the standard includes design curves up to 350°C. Strength reduction above 350°C lacks standardized definition. At 350°C both the yield strength of standard API casing materials (such as J55/K55 and L80/C90/T95) has decreased to 70 and 81%, respectively compared to yield strength at ambient temperature, the tensile strength of all grades has decreased to 84%, and the Young’s modulus (E) to 88% for all grades (NZS 2403:2015 et. al. 2015) .

The effect of temperature on casing properties can be evaluated by the thermal stress constant ($E \cdot \alpha$ (thermal expansion coefficient)) for casing steel held against movement. The thermal stress constant is around 2.5 MPa/°C for standard carbon steel casing materials, which means that an API K55 steel casing reaches its yield point (f_{ym} = 379 MPa) at a temperature change of approximately 150°C (Kaldal et. al. 2015). The K55 casing steel is very ductile and can therefore generate large plastic strain before problems occur. If the temperature rise while the well is initially discharged leads to compressive stresses reaching the yield strength and resulting permanent plastic strains, then if the well cools down again the plastic strains lead to tensile forces in the casing due to thermal contraction. These tensile forces can lead to tearing of the casing body or coupling rupture where the pin is teared out of the box, either by the threads of the coupling or near the first threads of the casing (Kaldal et.al. 2016).

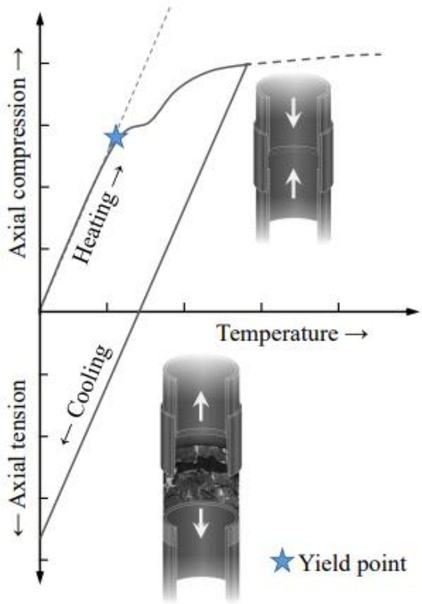

Figure 1. Concept diagram by Kaldal et al. showing how previously formed axial compressive stain can cause axial tension when a hot well is cooled down (Kaldal et. al. 2017).

This failure mode has occurred in several high-temperature geothermal wells in Iceland, including in the superhot IDDP-1 well, the first finished well of the IDDP project. A malfunction of the two master valves on the IDDP-1 wellhead led to quenching of the well with cooling water, which caused rupture of the production casing at several locations down to 600m depth (Holmgeirsson et. al. 2018). Computational results from FEM models, analyzing structural integrity of casings, have also shown collapse of casings due to the combination of external formation pressure and thermal cycling. The results show that the capability of casings to withstand external pressures decreases as the number of thermal cycles increase and that casings may fail under external pressure below its specified collapse strength (Kaldal et. al. 2017). Each thermal cycle can add to the buildup of plastic strain during multiple thermal cycles (warm-up, discharge, quenching). To mitigate buildup of plastic strain it is favorable that all the casings in a well warm up or cool down as uniformly as possible where slow wellbore temperature changes are required, which can however be difficult to control (Kaldal et. al. 2015).

Additionally, due to high temperatures (>300°C) and the increased likelihood of the geothermal fluid to have highly corrosive chemical composition, increased corrosion and erosion-corrosion can be expected in deep superhot geothermal wells. In vapor dominated geothermal systems (T>300°C) hydrogen chloride (HCl) is often present in wells with superheated geothermal steam in addition to other highly corrosive gases such H_2S and CO_2 that are commonly found in geothermal wells. Examples of this are at the Larderello in Italy, in Krafla in Iceland (KG-12 and IDDP-1) and Tiwi in the Philippines. The presence of HCl in superheated geothermal steam has caused severe corrosion problems which have led to major operating difficulties. Carbon-steel casings corrode at accelerated rates upon the condensation of the super-heated steam with H_2S, CO_2 and HCl gasses.

In the IDDP-1 well in Krafla the presence of HCl in the superheated steam was encountered which caused difficulties in utilizing the superheated steam for production (Karlsdottir et al. 2014, 2015). Material testing on-site was done in early 2012 in the IDDP-1 well geothermal steam before the well had to be quenched due to failure in the well and wellhead (Karlsdottir et al. 2014, 2015). During this time the IDDP-1 well was discharging dry superheated steam from the wellhead wich had high temperature (450°C) and pressure (140 bar). For all the material testing units the temperature and pressure had decreased to about 350°C and 12-13 bars, except for in the heat exchanger experiment the pressure was decreased to 52-60 bar and temperature to around 260-270°C for steam saturation. The steam was supersaturated with silica and when the temperature and pressure was dropped it caused silica deposition from the steam. The test results showed that all samples tested, including the carbon steels (S235JR, K02100, K55, TN95), austenitic stainless steels (S30403, S31603, S31254), Ni-based alloys (N06255 and N06625) and titanium alloys (R50400 and R52400) had very low corrosion rates (< 0.01 mm/year) but all the samples were prone to localized corrosion damages, i.e. cracking, pitting or both (Karlsdottir et al., 2014, 2015). Further testing could not be done on-site due corrosion and failure of valves in the wellhead equipment and casings after several months of discharging.

For the cement casing, effect of high temperature speeds up the degradation process of cement causing geochemical changes of the cement. This highlights the shortcomings if geothermal well design is based solely on compressive strength of well cement. Chemical reactions deteriorating the materials can occur in the presence of acidic fluids and restrict further utilization of the deeper sections inside the geothermal system. Acid attack, hydrolysis, is a typical reaction when condensed steam has low pH. The water is reacting with Cl and forms H^+. The most common geothermal gas, $H_2S(g)$ and $CO_2(g)$, contribute too according to the following reactions:

$$HCl_{(aq)} + H_2O \leftrightarrow H^+ + H_2O + Cl^-$$

$$H_2S_{(aq)} + H_2O \leftrightarrow H^+ + H_2O + HS^-$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{-2}$$

If the hardened well cement is in contact with the steam it leads to portlandite leaching and CSH (calcium silicate hydrate) decalcification (Duguid and Scherer 2010, Jacquemet et al. 2007, 2012). The pH changes inside the hardened well cement control oxidation–reduction, sulfidation, and carbonation reactions throughout the hardened cement exposed to the acidic gas mixtures (Kutchko et al. 2011). Sulfate attack was observed on 19 year old field samples where original cement casings reacted with the downhole formation brine. This resulted in abundant porosity and mineralogical changes withtin the cementitious matrix (Scherer et al. 2011). Concerns on well cement integrity also exist in fields with abundant CO_2 and also in CO_2 geological storage (Zhang and Bachu, 2011; Hernández-Rodríguez et al. 2017) due to carbonic acid leaching. Krilov et al. (2000) reveal well production failure from cement carbonation only after only 15 years. Studies on geochemical reactions of cement are typically not combined with the corrosion of steel. Material characterization of cements employed for the design of geothermal wells is a key parameter together with interface and boundary conditions, nonlinear response and transient behaviour (Philippacopoulos and Berndt 2002). Investigations have mostly been focused on studying geological CO_2 sequestration and experimental or modelled cement behaviour at lower temperatures and pressures (e.g. Garcia-Gonzalez et al. 2007: Gherardi et al. 2012; Milestone et al. 2012; William Carey 2013; Won et al. 2015). This leads, together with problematic cement sample extraction, to limited knowledge of well cement durability at close to or at supercritical conditions in geothermal wells.

Thus it is important to be able to test promising corrosion resistant alloys (CRAs) and cement casing materials in high temperatures and high pressure environments, with corrosive gasses that are expected to be encountered in superhot geothermal wells to be able to aid in the design and material selection for future superhot geothermal wells.

2. GEOTHERMAL CEMENTOUS CASING MATERIALS

2.1 Cement blends

In Table 1, a number of geothermal well cement mix designs are described. The "Icelandic well cement mix design" and small variations thereof has been used in geothermal wells in Iceland for decades. The mix originally used cement manufactured in Iceland, which contained microsilica. The production of Icelandic cement was halted in 2012 and as a reaction to this, a new mix was designed containing Portland cement and microsilica, which has been used ever since. The mix contains expanded perlite to decrease the density of the mix, although this light weight aggregate is not used for all cementing. Two mixes labeled IDDP are also included in the table, where the "IDDP mix design" is the recipe used for cementing for both the IDDP1 and IDDP2 wells. The "IDDP mix with additional microsilica" is a modification of that mix, where microsilica is also included to improve the properties of the mix, especially decrease the permeability of the hardened mix.

In addition to the traditional mix designs the thermal shock resistant cement (TSRC) is included based on development and experimental testing by Pyatina and Sugama (Pyatina and Sugama 2020). The novel TSRC well cement blend, a calcium-aluminate cement with alkali activated FAF (fly ash class F) showed promising self-healing ability. This is vital parameter as it preserves the required strength of the material and therefore integrity of the whole well. The TSRC demonstrated the best thermal shock resistance in the study by Pyatina and Sugama losing only about 20 % of the original strength in five 350 °C heat → 25 °C water thermal cycles. The addition of microglass fibres (MGF) in this mix improved the adhesion of the material with carbon steel, the most common material for geothermal well casing. The alkali-activated TSRC/MGF revealed the best wetting and adhesive behaviors with carbon steel, while these propertis of OPC/SiO_2 were relatively poor (Sugama and Pyatina 2021).

Based on this, these well cement blends will be tested in custom made high temperature and high pressure (HTHP) autoclave laboratory in simulated superhot geothermal well environment as will be descriped in following sections.

Table 1: The composition of different well cement blends that have been used in high temperature geothermal wells in Iceland, in the Iceland Deep Drilling Project, and a novel thermal shock resistant cement (TSRC) (Pyatina and Sugama 2020).

Mix name	Substance	Density (g/cm^3)	Mass fraction (%)
TSRC	Calcium-aluminate cement Secar 80	0.98	33.62
	Fly ash class F	0.90	22.41
	Sodium-meta-silicate	2.60	3.58
	Carbon micro fibres	1.81	3.31
	Micro-glass fibres	0.98	3.31
	Water	1.00	33.77
Icelandic well cement mix design	Anlegg cement	3.14	42.07
	Microsilica	2.20	2.10
	Sibelco M300	2.65	17.67
	Expanded perlite 2%	0.35	0.88
	Bentonite 2,5%	2.38	1.10
	Retarder (CRHT1)	1.00	0.09
	Fluid loss additive (Polytrol FL 32)	1.00	0.18
	Water	1.00	35.90
IDDP mix with additional microsilica	Dyckerhoff HT	3.00	67.09
	Water	1.00	29.14
	Microsilica	2.20	3.53
	Retarder (CRHT1)	-	0.24
IDDP mix design	Dyckerhoff HT	3.00	70.62
	Water	1.00	29.13
	Retarder (CRHT1)	-	0.25

3. GEOTHERMAL WELL CASING MATERIALS

The choice of casing material for geothermal wells is greatly influenced by the loads and subsurface fluid conditions that the material must withstand in well. Corrosion resistant alloys (e.g., highly alloyed austenitic and duplex stainless steel, titanium and nickel alloys) have shown resistance to general corrosion when tested in different high-temperature geothermal fluids (Thorbjornsson et al. 2014; Karlsdottir et al. 2014). CRA casing materials are generally used in oil and gas industry when there is a combination of the following factors: presence of CO_2 and H_2S, low pH, chlorides and high temperature as previously mentioned. But they are not as common in geothermal wells. Results from on-site testing of various materials in superheated geothermal steam from the first well drilled in the Iceland Deep Drilling Project (Karlsdottir et al. 2014) showed that nickel alloy Inconel 625 and Ti-alloy (Ti gr. 7) were the most corrosion-resistant materials tested.

To offset large axial stresses present in high temperature geothermal environments during warm-up and cooling of the well corrosion resistant materials with low elastic Young's moduli and lower thermal expansion coefficient than for carbon steel casing materials could be used. Titanium is less dense than nickel alloys, having a density of 4.516g/cm^3 (at 20 °C), a difference of more than 50%. In comparison to frequently used steels, it also has a 67% lower thermal expansion and a 50% lower Young's modulus (Gruben et al. 2021). Table 2 compares the mechanical properties of different CRAs and commonly used carbon steel casing for geoethermal wells. According to a study by Jackie et al., titanium alloy tubing can reduce the hook load of the drilling rig by 30% and the torque by 30%–40% in addition to resisting downhole corrosion up to 260 °C (Smith et al. 2001). This is significant since titanium demonstrated better corrosion performance of over the austenitic stainless steel 028 and the nickel-based alloys Incoloy 825 and 728 since for 90% yield strength load of the body it did not experience stress corrosion cracking or collapse. In a study published by Thomas it was concluded that Ti grade 29 might be the only useful tubular material that is corrosion resistant enough to provide an economic justification for the development of high-temperature (330 °C), highly acidic (pH > 2.3), and sour geothermal brine fields for power generation (Thomas, 2003). Furthermore, it has been reported that specific medium-to-high strength α-β titanium alloys and chromium-molybdenum-nickel based alloys can address the trend toward energy exploration at deeper depths, material and economic challenges (Schutz and Watkins, 1998). Thorhallson et al. (Thorhallsson and Karlsdottir, 2021) reported that Ti-0.4Ni-3.6Mo-0.75Zr demonstrated good corrosion resistance in a low pH (pH=3, 180 and 350 °C) simulated geothermal environment containing HCl, H_2S, and CO_2 gases in a custom designed Flow-Through Reactor (FTR) corrosion testing equipment. The author also reported that in superheated fluid conditions (at 350°C, pH=3 and 10-11 bar), carbon steel and Cu added high entropy alloys (HEAs) were prone to corrosion damage while negligible damages were observed in the corrosion-resistant alloys tested including the newly developed titanium alloy Ti-745 (Ti-0.4Ni-3.6Mo-0.75Zr), and the nickel alloys SM2245 and SM2550 (UNS N06255). When corrosion tested in the FTR in boiling and condensing conditions the carbon steel was prone to more severe corrosion damage in comparison with the superheated test fluid. Hence, the corrosion behaviour of carbon steel was associated with the physical condition and temperature of the corrosive fluid (Thorhallsson et al., 2020, 2021a, 2021b).

Table 2. Specified mechanical properties of casing pipe materials for geothermal energy extraction applications (Gruben et al. 2021; Schutz and Watkins, 1998; Thorhallsson and Karlsdottir, 2021).

Material	Grade/UNS Number	Yield strength (min) MPa	Yield strength (max) MPa	Tensile strength MPa	Hardness (HRC)
Carbon Steel	L80-type1	522	655	655	23
Martensitic SS	L80 - 13Cr	552	655	655	23
Stainless steel	UNS3040	-	1206	1310	41
Stainless steel	SM2245	-	951	1061	34
Stainless steel	SM2550	-	944	1013	32
Austenitic SS (Alloy 028)	N08028	500	750	620	30
Austenitic Ni-base (Incoloy 825)	N08825	758	965	792	35
Duplex SS (22Cr/ 25Cr/ SUP25Cr)	S31803/ S31260/ S32760	758	965	861	36
Ni-based alloy 600	N06600	478	480	712	
Ni-based alloy 625	N06625	444	451	905	24
Ni-based alloy 800	N08810	256	276	546	-
Ni-based alloy C276	N10276	343	353	783	50
Ni-based alloy 2550	N06255	758	925	792	-
Ti-Grade 12 –0.3Mo 0.8Ni	R53400	345	380	483	11
Ti-0.4Ni-3.6Mo-0.75Zr	Modified	552	786	965	-
Ti-Grade 23 –6Al –4V ELI	R56401	759	840	860	32
Ti-Grade 29 –6Al 4V 0.1Ru	R56404	759	825	917	32

3. HIGH TEMPERATURE AND PRESSURE MATERIAL TESTING

3.1 Experimental Design

To explore the potential of several corrosion resistant alloys and cement blends as casing materials for superhot geothermal wells the materials will be tested in high temperature and high pressure (HTHP) autoclave laboratory in simulated superhot geothermal well environment at University of Iceland. The HTHP autoclave laboratory is equipped to conduct high-temperature and high-pressure experiments with geothermal fluids containing H_2S and CO_2 gas with gas detectors and alarm systems insuring safe operation during experiments (Figure 2(a)). The laboratory was designed, constructed, and installed at the University of Iceland recently by Cormet Oy, Finland. A 3 L autoclave made of C276 Hastelloy and rated for temperatures up to 500 °C and pressures up to 300 bar is the central equipment of this laboratory (Figure 2(b)). A custom-made impeller is installed in the lid and connected to the stirrer motor with a magnetic drive installed on top of the autoclave lid. During the experiment, the test samples are installed between the vertical sample holder supports in the specimen holder, also installed in the lid. When samples have been installed and the water is filled in the autoclave, the lid is lowered by an electrical lifting mechanism and the 9 bolts connecting the lid to the autoclave vessel are fastened with 250 Nm torque. Water can be drained through a valve in the bottom of the autoclave. The pressure is measured with a Keller pressure transmitter and the temperature is measured with a Pt100 temperature in the vessel. Vessel temperature is adjusted by heating elements around the autoclave vessel connected to a temperature regulator and insulation of the lid ensure low heat loss to the surroundings during experiments (Figure 2(c)). After the autoclave lid is closed, it can be pressurized from the bottom gas inlet line with N_2, H_2S and CO_2. The amount of each gas component filled is measured and controlled by Brooks mass flow controllers installed in the gas filling panel (Figure 2(c), right part of the photo) with flowrates set in the logging program for the autoclave. Pressure, temperature, stirrer rpm., and the flow of the gas flow meters during filling are all recorded in the logging program. The gas/vapor phase can be depressurized from the autoclave through a gas draining line in the top. To avoid emission of H_2S gas during depressurization, the gas is drained through gas draining line in the top and flows through three 20 L plastic containers (Figure 2(c), left part of the photo), filled with alkaline water solution containing dissolved zinc acetate and NaOH with pH =13.5. H_2S gas from the autoclave reacts with the zinc acetate and form solid ZnS that precipitates out of the solution and sinks to the bottom of the plastic containers.

(a) (b) (c)

Figure 2. The corrosion laboratory constructed in a 40-foot high-cube container by Cormet Oy, Finland, shipped to Iceland, and installed at the campus of the University of Iceland (a). The autoclave with the lid opened before installation of test samples (b). Experimental setup with filling panel (right) and H_2S capture system (left).

Table 2. Test conditions planned for HTHP autoclave tests.

Test no.	Temperature [°C]	Pressure [bar]	Duration	Environment
1	350	200	1 week	Vapor and water with 500 ppm H_2S and 2000 ppm CO_2
2	400	200	1 week	Supercritical steam with 500 ppm H_2S and 2000 ppm CO_2
3	450	200	1 week	Supercritical steam with 500 ppm H_2S and 2000 ppm CO_2

3.1 Evaluation of materials performance

The measured corrosion rate (CR) of the test materials in mm/year is calculated via the weight loss method and according to standard:

$$CR = \frac{KW}{At\rho}$$

Where K is the corrosion rate constant equal to $8.76 \cdot 10^4$ mm/year, W is the mass loss in grams of the test material, A is the exposed surface area in cm^2 of a test sample, t is the exposure time in hours, and ρ is the material density in g/cm^3. Cleaning of the samples and weight measurements before and after testing are caried out according to ASTM[+] G1-03 (Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens) to measure the corrosion rate for the two testing periods. The chemical composition and microstructure of the corrosion scales that formed on the samples during testing were analyzed with Scanning Electron Microscopy (SEM) equipped with X-ray Energy Dispersive Spectroscopy (XEDS)

For cement blends high temperature and high-pressure tests are performed at the autoclave laboratory located at the University of Iceland. Geochemical modelling is managed with the aid of PHREEQC software version 3 and the phreeqc.dat database with the Peng-Robinson equation of state in order to develop optimal autoclave protocol and to reconstruct field conditions. Powder X-ray diffraction (XRD), X-ray Fluorescence Spectrometer (XRF) and Raman spectrometer are used to identify amorphous and crystalline phase compositions and transitions responsible for improving bond durability. The results of XRD are analyzed using PDF-4/Minerals 2015 database of International Center for Diffraction Data (ICDD). Microstructural, microtextural changes and chemical composition are evaluated with SEM/XEDS. The samples are tested in a Tinius Olsen Super L 602 60,000Kgf hydraulic universal testing machine, using a load rate as described in the EN-196 standard [British Standard Institution, 2005]. Both three point bending and compressive strength measurements are performed. The two halves of each sample from the three point bending test are used in the subsequent compressive strength testing.

4. SUMMARY

The main material challenges for casing materials of superhot geothermal wells were identified as: i) difficulties in cementing and potential degradation of cement casing materials due to high temperatures and corrosive conditions; ii) the potential failure/rupture of carbon steel casings due to high plastic strains generated due large temperature difference during heating and cooling of the well and strength reduction at temperatures above 200°C; and iii) corrosion of casing materials due to high temperatures (>300°C) and corrosiveness of the geothermal fluid. The application of corrosion resistant alloys instead of standard API carbon steel casing material is considered necessary in the design of future superhot geothermal wells to decrease the likelihood of corrosion problems and increase the structural integrity and lifetime of these wells. Also the need for an appropriate cement blend that is durable in extremely high temperature and pressure conditions in corrosive environment was highlighted. High temperature and pressure testing of promising CRAs and cement casing materials in a custom made HTHP autoclave laboratory with incorporation of corrosive gases at temperatures between 350-450°C is planned. The materials chosen for the test are the newly developed titanium alloy Ti-745 (Ti-0.4Ni-3.6Mo-0.75Zr), the nickel alloys SM2245 and SM2550 and self-healing and heat-and acid resistant cement blends, and IDDP well cement based blends. The results from the HTHP test will give information on the durability and corrosion resistance of the chosen CRA and cement casing materials and thus hopefully aid in the design and material selection for future superhot geothermal wells.

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