The Effect of Drilling Fluid and Temperature on the Cement-Rock Interaction in Geothermal Wells

João R. M. C. Da Silva1, 2, Neil B. Milestone1, and James H. Johnston2

1Industrial Research Ltd, Lower Hutt, New Zealand
2Victoria University of Wellington
j.dasila@irl.cri.nz

Keywords
Cement-rock interaction, geothermal well cements, ignimbrite, bonding, drilling-fluid, bentonite

ABSTRACT

The current study has investigated the interactions between well cements and one of the most common types of rocks found in geothermal environments, under hydrothermal conditions.

Holes were drilled in blocks of ignimbrite rock and API class G cement with 0, 20 and 40% added silica flour, was poured into the cavities. The whole assemblage was autoclaved, under typical geothermal conditions at 150° and 300°C for 28 days.

The results show that chemical reactions occur in the inter-transition zone, which are dependent on both drilling fluid and temperature. The use of bentonite as a drilling fluid and the exposure to higher temperatures (300°C) when compared to 150°C, seem to exacerbate the reactions occurring in the ITZ. Consequently, there is formation of new crystalline products, which have worse performance when the physical bonding between the cement and the rock is considered.

The effect of other variables such as CO2 exposure, the hydrothermal alteration of the rock and the curing time are currently being investigated within this research project.

1.0 Introduction

Numerous investigations into geothermal well cements have been conducted in an attempt to develop a cement formulation that will handle the aggressive environments in geothermal wells and give increased durability. One of the issues to be considered is the interaction that can occur between the cement and the rock formation which can change the direction of reactions which occur within the cementing matrix. The work conducted in this field has been limited. Four factors need to be considered, the type of rock, the temperature, and the hydrothermal fluid along with the characteristics of the cement grout itself.

1.1 Geothermal Environments

Although there are considerable variations in conditions, even within the same geothermal field, several factors emerge which can influence the cement rock interactions. These are:

- The hydrothermal fluid, which Pirajno (2010) defines as a hot (ca. 50 to >500°C) aqueous solution, containing solutes that are commonly precipitated as the solution changes its properties. These fluids are subject to variations in temperature, pressure and density. Hydrothermal solutions are a mix of waters from several origins and can contain volatile gases, such as H2O, CO2, H2S, HCl, SO2 and CH4.

In NZ, the brines are often enriched with CO2 (up to >40,000 ppm CO2) arising from boiling at depth where gases are concentrated beneath a cap rock or sediment. Sometimes high concentrations of H2SO4 in the supergene zone near the surface render the waters acidic (pH <1.5). Ambient total pressure at the top of the basement is presumably in the range 100-250 bars (normal hydrostatic), depending on location, giving well head pressures commonly within the range 10-100 bars, with a CO2 overpressure of 6 bars (Wolery et al., 2010; Henneberger, 1983).

- The rock formation, with its own factors of stratigraphic distribution, mineral composition, permeability, porosity and hydrothermal alteration of the rock influence the reaction. The Ohaaki-Broadlands geothermal system near the eastern fault margin of the TVZ, is a good example of a common geothermal field in NZ, (Hedenquist, 1990; Browne and Ellis, 1970; Browne, 1973) which can be generally explained with the following layers:

  ◦ Near the surface, a mudstone cap overlies much of the field (Huka Falls Formation, a lava with high horizontal permeability and hydraulically connected to groundwater aquifers (Ohaaki Rhyolite), the main producing aquifer with heterogeneous uncompacted pumice and lapilli tuffs (Waiora Formation), the second important aquifer composed of coarse breccias (Rautawiri Breccia), rocks of poorly known material (Rangitaiki Ignimbrite, Ohakuri...
phases form, namely reihardbraunsite (C₅S₂H), jaffeite (C₆S₂H₃) as the crystals enlarge and densify leaving a rather porous matrix

or kilchoanite (C₃S·H₂O) over 120°C), Igimbrite is a fine grained igneous rock found in large exposed sheets in New Zealand and consists of crystalline rock fragments in a matrix of glass shards which are usually welded together in a matrix of volcanic ash (tephra) made up of shards and fragments of volcanic glass, pumice fragments, and anhedral crystals. The phenocrysts contain biotite, quartz, sanidine (or other alkali feldspar), and occasionally hornblende, but rarely rarely pyroxene. Chemically, the ignimbrite composition is generally over 65 wt% SiO₂, with varying contents of sodium, potassium, and calcium, and lesser amounts of iron and magnesium (Pellant, 2000; Henneberger, 1983). These rocks can, however, be altered due to the long-time exposure to the hydrothermal fluid.

- Drilling muds provide a barrier for well control, removing cuttings during drilling, transmitting hydraulic power to the drilling bit, maintaining formation pressure and stability and minimizing fluid losses to the formation (Culver, 1998; IPIECA and OGP, 2009). Currently, drilling muds are primarily mixtures of western bentonite (sodium montmorillonite) and water. While it is common practice to wash the annulus between the casing and formation before cementing, much of the mud still adheres to the formation, particularly if it is porous and so can interact with the cement, modifying its reaction with the formation.

1.2 Geothermal Well Cements

Well cementing grouts are formulations designed to be pumped downhole and when hardened, provide a seal between the steel casing and rock formation, protecting the steel against corrosion and supporting the casing against vibration (Nelson and Guillot, 2006).

Geothermal well cementing engineers have adopted the same nomenclature and standards as those used by the American Petroleum Institute (API). The most common API cement is Class G, a calcium silicate cement similar to Ordinary Portland Cement (OPC).

At elevated temperatures and pressures, the hydration reactions are different to those that occur at ambient temperature. The hydrates no longer lose water but form new compounds depending on temperature and overall Ca/Si ratio. Continuous exposure of high Ca/Si ratio cement to hydrothermal conditions induces a gradual and slow compressive strength loss in the hardened cement investigated by Kalousek and his co-workers (1951, 1954, 1955). They showed this to be caused by the formation and slow growth of new high Ca/Si ratio crystalline phases which are associated with an increased porosity and permeability (e.g.: α-C₅S·H₂O over 120°C), as the crystals enlarge and densely leaving a rather porous matrix that has little strength. Above 200°C, further high Ca/Si ratio phases form, namely reihardbraunsite (C₅S₂H), jaffeite (C₆S₂H₃) or kilchoanite (C₃S·H₂O) alongside Ca(OH)₂. These products do not act as binders, giving very low strength and high porosity to the grout (Milestone, 2011).

However, Kalousek (1954) found that by adding >30 wt% silica flour (pure quartz) the overall Ca/Si ratio in the binder was decreased, which avoided strength retrogression through the formation of yet further crystalline phases, tobermorite (Ca/Si ratio 0.8 - 1.0) between 150°C and 180°C and xonotlite (Ca/Si ratio 1.00), about above 200°C. Below 100°C quartz will not react readily with Portland cement (Iverson et al., 2010).

1.3 Cement-Rock Interaction

At ambient temperatures a chemical reaction can occur between certain concrete aggregates and alkalis from cement, the alkali-silicate reaction (ASR) which has been widely studied. The reaction between silica and alkalis from the pore solution is complex, and in some conditions, may be similar to the pozzolanic reaction (Hobbs, 1988). From several references it is likely similar reactions will occur at high temperatures, even though the reaction products will be modified (Poole, 1992; Criaud et al., 1994; Andrei et al., 1996).

Hodgkinson and Hughes (1999) examined the reaction at 85°C between a selection of rock-forming minerals and calcium hydroxide. After about 1 month they observed, as expected, carbonation but in samples containing quartz, albite, muscovite and anorthite, dissolution occurred, often along preferred crystallographic directions, to form etch pits visible by SEM. New calcium aluminosilicate phases were precipitated. The product from muscovite contained so much Al³⁺ that it lay close to the zeolite compositional field. From anorthite katoite was formed at 4 days with a poorly ordered fibrous C-A-S-H phase also forming after 8 days which became well-ordered after a month. For quartz and albite, only a very minor precipitation of new phases was observed.

Where Ca(OH)₂ was present in the reactant fluid, the precipitating phases were an amorphous or poorly crystalline CSH gels (though stoichiometrically related to the fully crystalline CSH forms of tobermorite and jennite) and other cement minerals (hydrogarnet, hydrocalumite, zeolites, feldspars,…) (Bateman et al., 1998; Rochelle et al., 1992; Savage and Rochelle, 1993; van Aardt and Visser 1977a, b; Hodgkinson and Hughes, 1999).

Hodgkinson and Hughes (1999) concluded that at low temperatures (<110°C) the main reactions were formation of calcium silicate hydrate (CSH) gels, while at higher temperatures (>110°C) the main products were zeolites and feldspars (especially, in the presence of NaOH or KOH). Andrei and Criaud (1996) showed that the products of reaction obtained at 150°C were similar in texture (amorphous and polymorphous gels) to those at normal conditions, with a broad range of chemical composition. Over 150°C, experimental work conducted with alkali hydroxides (NaOH and KOH) and clays, formed zeolites and sometimes feldspars rapidly, with a high pH causing the alteration of smectite to illite or illite/smectite interlayers (Chermak, 1992, 1993; Inoue, 1983; Komarneni and White, 1981, 1983; Johnston and Miller, 1984; Hodgkinson and Hughes, 1999).

Langton et al. (1980), aiming to understand the relationship between the chemical and physical properties of the interfacial region formed between cement paste and rock, undertook hydrothermal cement-rock interaction experiments at temperatures of 200°C and 250°C, at 51.7MPa pressure. They used an API class J cement (C₃S + quartz), with tuscarora quartzite (95% quartz with
a silica cement) and Valentine limestone (99.9% calcium carbonate), which they considered as unreactive.

From the shear strength measurements, they observed that the cement-quartzite bond seemed dependent on temperature for the first 7 days of curing, as the 200°C sample achieved much higher shear strength compared with that at 250°C, whereas the cement-limestone sample was more stable and not dependent on the temperature (200/250°C) or on the curing time, although it did not achieve as high shear strengths as the quartzite sample.

From chemical analysis across the cement-rock interface, after only one day of curing, they observed that the cement-quartzite sample had relatively sharp decrease in silicon up to 50μm into the cement and a sharp decrease in calcium over about the same range into the rock, whereas the cement-quartzite sample had a sharp gradational change for calcium and silicon, across the interfacial region.

They concluded that the both shear strength and hydration changes for both samples depended on the temperature and on curing time. Moreover, they reckoned that the degree of paste hydration (in normal cement pastes) or of belite (βC₂S)-quartz reaction (in hydrothermal cements) increased with time along the degree of crystallinity of calcium silicate hydrates in the interfacial region and the paste, which increased with time and temperature.

It was suggested that the shear bond strength that developed between 'unreactive' wall rock and cement reasonably approximated, within experimental error, the tensile strength of the hydrothermally cured cement itself and they felt that mechanical bonding was primarily responsible for the shear strength of the unreactive wall rock-cement contact, rather than any chemical bonding.

2.0 Methodology

2.1 Raw Materials

The raw materials ignimbrite (supplied from the Hinuera Stone quarry), silica flour (SSA-1) unhydrated bentonite (Western bentonite) and class G cement (Holcim) were analysed by X-ray fluorescence (XRF) and X-ray diffraction (XRD). A thin section of ignimbrite was prepared and analysed in optical microscope.

2.2 Hydrothermally cured cement-rock system

Three different cementing formulations were used to examine rock/cement interactions, with and without the presence of a layer of bentonite. These were API class G cement (G), API Class G + 20 %wt silica flour (G20SF) and Class G cement + 40%wt silica flour (pure quartz) (G40SF).

25 mm cavities were drilled in small ignimbrite blocks, which were immersed in geobrine solution at 90°C for 7 days. One set were filled with a 3% bentonite suspension and exposed at 90°C before being emptied, quickly washed and filled with cement. Cement slurries were prepared according to API RP10 at a w/s ratio of 0.45 and poured into different holes. The assemblages were then cured for 2 days in geobrine at 90°C and cured in autoclaves for 26 days (making a total of 28 days cure). Two curing temperatures were used, 150°C and 300°C.

After curing, each cement-rock system was cut in half, photographed and prepared for x-ray diffraction (XRD), optical microscopy, SEM/EDS and TG analysis.

2.3 Sample Identification

Four distinct zones were identified in each sample, namely: interior zone of the cement (int); cement side of the ITZ (cem); rock side of the ITZ (rock) and exterior side of the rock (IGN). This nomenclature (int, cem, rock and IGN) was combined with the type of cement mixture (G, G20SF and G40SF) and the previously explained bentonite/temperature combinations (150, 300°C).
3.0 Results

3.1 XRD Analysis

XRD results are presented in Table 1.

Table 1. Compounds identified by XRD analysis.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sample</th>
<th>Identified Peaks and Other Relevant Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>G150 (Figure 2)</td>
<td>G150int</td>
<td>Amorphous with portlandite and traces of calcite and unhydrated cement.</td>
</tr>
<tr>
<td>G150 (Figure 2)</td>
<td>G150cem</td>
<td>Reduced amount of portlandite with traces of calcite and unhydrated cement.</td>
</tr>
<tr>
<td>G150 (Figure 2)</td>
<td>G150rock</td>
<td>Similar minerals to the centre of rock with reduced amounts of quartz from IGN150.</td>
</tr>
<tr>
<td>G20SF150 (Figure 3)</td>
<td>G20SF150int</td>
<td>Amorphous with traces of calcite, quartz, tobermorite and αC₂SH.</td>
</tr>
<tr>
<td>G20SF150 (Figure 3)</td>
<td>G20SF150cem</td>
<td>Similar to above but with slight increase in quartz.</td>
</tr>
<tr>
<td>G20SF150 (Figure 3)</td>
<td>G20SF150rock</td>
<td>Similar to G150rock.</td>
</tr>
<tr>
<td>G40SF150 (Figure 4)</td>
<td>G40SF150int</td>
<td>Large amorphous component with significant quartz and tobermorite.</td>
</tr>
<tr>
<td>G40SF150 (Figure 4)</td>
<td>G40SF150cem</td>
<td>Similar to G20SF150cem.</td>
</tr>
<tr>
<td>G40SF150 (Figure 4)</td>
<td>G40SF150rock</td>
<td>Similar to G150int but without reduced quartz from IGN150.</td>
</tr>
<tr>
<td>Gb150 (Figure 5)</td>
<td>Gb150int</td>
<td>Amorphous with portlandite and traces of calcite, kilchoanite and αC₂SH.</td>
</tr>
<tr>
<td>Gb150 (Figure 5)</td>
<td>Gb150cem</td>
<td>Amorphous with decreased portlandite from Gb150int. αC₂SH and kilchoanite not present. Aragonite and gehlenite present.</td>
</tr>
<tr>
<td>Gb150 (Figure 5)</td>
<td>Gb150rock</td>
<td>Similar to G150int but without the reduction in quartz from IGN150. Gehlenite present.</td>
</tr>
<tr>
<td>G20SFb150 (Figure 6)</td>
<td>G20SFb150int</td>
<td>Amorphous with quartz and trace amounts of αC₂SH, katoite and calcite.</td>
</tr>
<tr>
<td>G20SFb150 (Figure 6)</td>
<td>G20SFb150cem</td>
<td>Amorphous with decreased amounts of quartz, αC₂SH and calcite from G20SFb150int. No katoite. Gehlenite also present.</td>
</tr>
<tr>
<td>G20SFb150 (Figure 6)</td>
<td>G20SFb150rock</td>
<td>Alumina, anorthite are present with no reduction in quartz from IGN150. Gehlenite also present.</td>
</tr>
<tr>
<td>G40SFb150 (Figure 7)</td>
<td>G40SFb150int</td>
<td>Large quartz present with αC₂SH, tobermorite, calcite and gismondine.</td>
</tr>
<tr>
<td>G40SFb150 (Figure 7)</td>
<td>G40SFb150cem</td>
<td>Quartz and tobermorite present with traces of αC₂SH, gismondine and calcite which are unchanged from G40SFb150int. Slight traces of gehlenite.</td>
</tr>
<tr>
<td>G40SFb150 (Figure 7)</td>
<td>G40SFb150rock</td>
<td>Alumina, anorthite and quartz and no reduction in quartz from IGN150. Traces of gehlenite.</td>
</tr>
<tr>
<td>G300 (Figure 8)</td>
<td>G300int</td>
<td>Portlandite, calcite and reinhardbraunsite with small amounts of killaite and αC₂SH. Perhaps some katoite present.</td>
</tr>
<tr>
<td>G300 (Figure 8)</td>
<td>G300cem</td>
<td>Portlandite decreased substantially from G300int but amount of katoite, killaite and αC₂SH appear to remain the same while the amount of reinhardbraunsite and calcite increase.</td>
</tr>
<tr>
<td>G300 (Figure 8)</td>
<td>G300rock</td>
<td>Alumina, anorthite and quartz are present with small amounts of reinhardbraunsite and αC₂SH seem to be present as well, although the noisy results make it difficult to fully identify phases.</td>
</tr>
<tr>
<td>G20SF300 (Figure 9)</td>
<td>G20SF300int</td>
<td>Killaite, kilchoanite and quartz are present with traces of xonolite.</td>
</tr>
<tr>
<td>G20SF300 (Figure 9)</td>
<td>G20SF300cem</td>
<td>Killaite, kilchoanite, xonotolite with increased quartz.</td>
</tr>
<tr>
<td>G20SF300 (Figure 9)</td>
<td>G20SF300rock</td>
<td>Alumina, anorthite, no reduction in quartz from IGN300.</td>
</tr>
<tr>
<td>G40SF300 (Figure 10)</td>
<td>G40SF300int</td>
<td>Quartz, xonolite and killaite are present.</td>
</tr>
<tr>
<td>G40SF300 (Figure 10)</td>
<td>G40SF300cem</td>
<td>Increased quartz and xonolite from G40SFb300int.</td>
</tr>
<tr>
<td>G40SF300 (Figure 10)</td>
<td>G40SF300rock</td>
<td>Alumina, anorthite and no reduction in quartz from IGN300.</td>
</tr>
</tbody>
</table>

3.2 Microscopy (Optical Microscopy and SEM/EDS)

**G150**

**Figure 10.** G150 ITZ in PPL (100X).

**Figure 11.** G150 ITZ in XPL (100X).

**Figure 12.** G150 ITZ in SEM (100X).

Under the optical microscope in plane polarized light (PPL), the unhydrated cement is seen as pleochroic grains and small sized crystals but in crossed-polarized light (XPL), most seems amorphous.

The interaction zone (ITZ) in PPL is a dark brown rim of about 100 µm, (150cem+A150rock), whereas both the rock and cement are mostly colourless. In XPL, this zone appears totally dark (except for a few quartz or feldspar crystals present). SEM/EDS analysis shows very high amounts of Ca in the cement, with significant amounts of Fe and Si. In the ITZ, Ca seems to penetrate up to about...
300 µm into the rock, and the Si concentration in the ITZ seems to be more uniform than in the rock or in the cement.

**G20SF150**

Compared to G150, the most noticeable difference by optical microscopy is the presence of quartz crystals, which are colourless in PPL, with a 90° extinction angle in XPL.

The ITZ is dark brown with more small and medium-sized grains (assumed to be non-hydrated cement particles and/or silica) than G20SF150cem than in the G20SF150int. There are less quartz crystals in G20SF150cem than in G20SF150int.

From SEM/EDS Ca migration from G20SF150cem to G20SF150rock has occurred. Within the ITZ the concentration of Ca and Si is higher and more uniform distribution than in the rock or in the cement.

**Gb150**

As this is a similar sample to G150 we would expect similar results. However, under the optical microscope, there is clearly a higher concentration of non-hydrated cement grains in the ITZ, and the bentonite barrier is easily distinguished.

Nevertheless, the ITZ seems to be about the same, 300 µm, although calcium has migrated to about 600 µm. The Si is more uniformly distributed in the interaction zone than anywhere else.

**G40SF150**

In optical microscopy, the most noticeable difference to G20SF150 is the large amount of unreacted quartz crystals in the cement matrix.

The ITZ is again a dark brown rim. There are less quartz crystals in G40SF150cem than in G40SF150int.

**Ca** has moved from G40SF150cem into G40SF150rock. There are high levels of both Ca and Si in the cement from the silica flour. The ITZ has the highest concentration and more uniform distribution of Ca, Si and O in the ITZ, rather than in the rock or in the cement.

**Gb150**

Similar results to G20SF150 were seen.

While the EDS data was not of acceptable quality, but from the optical microscope and SEM analysis, the bentonite barrier was very easily distinguished from the rest of the specimen.
**G40SFb150**

Figure 25. G40SFb150 ITZ in PPL (100X).

Figure 26. G40SFb150 ITZ in XPL (100X).

Figure 27. G40SFb150 ITZ in SEM (100X).

Little difference from G40SF150 is noted but with a noticeable bentonite barrier. The EDS data was not of acceptable quality.

**G300**

Figure 28. G300 ITZ in PPL (100X).

Figure 29. G300 ITZ in XPL (100X).

Figure 30. G300 ITZ (cement) in SEM (100X).

Figure 31. G300 ITZ (ignimbrite) in SEM (100X).

The first noticeable feature of this cement is its reddish colour although this is not obvious under the optical microscope. The cement seems to have penetrated into the rock but afterwards, it detached, as there is a distinct loss of bonding. The ITZ is about 700 μm (0.7mm) across.

Considerable calcium migration has occurred in this sample, from the cement to the rock.

**G20SF300**

Similar to G300, this cement also appears reddish which is not noticeable under the optical microscope. Unlike G20SF150, the quartz crystals in the cement are not present. In the ITZ, the cement has detached from the rock. There are some red coloured spots on the cement side of the border which may be the consequence of movement of iron from the rock to the cement.

The EDS data was not of acceptable quality.

**G40SF300**

Figure 32. G20SF300 ITZ in PPL (100X).

Figure 33. G20SF300 ITZ in XPL (100X).

Figure 34. G20SF300 ITZ in SEM (100X).

Figure 35. G40SF300 ITZ in PPL (100X).

Figure 36. G40SF300 ITZ in XPL (100X).

Figure 37. G40SF300 ITZ (ignimbrite) in SEM (100X).

Figure 38. G40SF300 ITZ (cement) in SEM (100X).

This sample is also reddish. Abundant quartz crystals are present (confirmed by XRD).

The ITZ is wide and brown with a dark rim. As noticed in the other 300°C samples, the Ca²⁺ cations seemed to have penetrated in the rock, which was probably followed by a detachment in the rock side.

From the SEM/EDS analysis, high amounts of Ca and Si were observed to be present in this cement. There are also considerable amounts of Fe, K, Mg and O. The iron is more homogeneous in the cement than in the rock.
4.0 Discussion

4.1 G150 and Gb150

Along with the amorphous component, portlandite was found in large amounts in the centre of the cement matrix in these samples, along with small quantities of calcite (possibly derived from handling) and unhydrated cement. The substantial decrease of portlandite from G150int to G150cem is due to migration of Ca\(^{2+}\) (and OH\(^{-}\)) ions from the cement into G150rock and ultimately the ignimbrite mould, confirmed by SEM/EDS results.

The very distinctive dark ITZ rim seen by optical microscopy supports the hypothesis of a reaction rim at the interface where new compounds may form. New compounds are not seen with G150int, although there is a marked decrease in the amount of portlandite in this zone. The highly uniform Si concentration across the whole ITZ, suggests this element also moves through this zone from the rock, solubilised by OH\(^{-}\) ions migrating from the cement into the rock, a reaction which is not readily detected.

The presence of the bentonite layer in Gb150 changes the reaction sequence which occurs in a wider ITZ with small amounts of several crystalline phases forming e.g. αC\(_2\)SH and kilchoanite (C\(_3\)S\(_2\)). Their formation seems due to interaction with bentonite as gehlenite also forms in Gb150rock. This suggests that the first two compounds may react with aluminium from the bentonite (likely to be more reactive than the ignimbrite as it is not seen by XRD) to form gehlenite or that compound may crystallise directly from the mixture of ions in an alkaline environment. Ca penetrates deeper into the rock (up to about 600 µm) which may be driven by cation exchange as more aluminium is substituted into a silicate network which requires a counter cation.

The addition of a bentonite layer also decreases the bonding between the cement and the rock, in other words the ITZ that forms, is a weak zone. This may be due to the formation of more phases that are more crystalline, probably due to the ready availability of aluminium as the bentonite reacts. Bensted and Hewlett (2008) examined hydrogarnet-type cements, where the predominantly gehlenite hydrate binder had high compressive strengths (ca. 110-136 MPa) and low porosities (1-10 %). However, it was instable at above 100°C, which may be the reason for the poor performance in the cement-rock bonding, as the specimens were submitted cured to 150°C.

4.2 G20SF150 and G20SFb150

The quartz present in this matrix would be expected to slow the migration of Ca\(^{2+}\) ions across the ITZ into the rock but the SEM/EDS results show it still occurs. The low intensity peaks in XRD indicate that the cement matrix still remains largely amorphous even though the added silica flour has restricted the formation of portlandite. In both G20SF150int and G20SF150cem, small amounts of tobermorite have formed, indicating the Ca/Si ratio in these zones has dropped low enough through Ca migration, and the availability of additional Si to allow tobermorite to form.

There appears more quartz in G20SF150int than G20SF150cem, suggesting Ca leaching into and through the ITZ is rapid, leaving less available Ca to react with the quartz in the interior of the binder matrix. As explained by Klimesch and Ray (1998), the ready availability of aluminium makes the formation of tobermorite easier. Aluminium can be supplied into solution as both bentonite and the glass in ignimbrite react with the migrating OH\(^{-}\) ions along with soluble SiO\(_2\). Tobermorite will then precipitate in the ITZ. There are also slightly lower amounts of quartz in the G20SF150rock than IGN150 indicating even in the ignimbrite, the quartz is able to react with the migrating OH\(^{-}\) and available Al. The complete lack of portlandite in the cement side of the interface is due to reaction with quartz and Ca\(^{2+}\) ion migration.

The addition of the bentonite layer in G20SFb150 again causes gehlenite to form, mostly on the rock side of the ITZ as a product of a reaction of Ca migrating from the cement with the Al and Si oxides present in the bentonite. Again there is a weakening of the cement/rock bond.

4.3 G40SF150 and G40SFb150

As expected, 40% silica flour addition has enhanced the formation of tobermorite with complete removal of portlandite, although the bulk of the binder still remains amorphous. The SEM/EDS analysis shows Ca migration from G40SF150cem into G40SF150rock still occurs indicating the reaction with quartz is slow and attack on the glass phases in the rock is preferential. There is also tobermorite formed on the rock side of the ITZ confirming the movement of Ca.

In a similar way to the Gb150 and G20SFb150 specimens, gehlenite seems to be present mostly in the rock side of the boarder (G40SF150rock).

4.4 G300

The most noticeable feature of this cement sample is the reddish colour noticed by the unaided eye in all 300°C samples which is likely due to the presence of iron. The ignimbrite when sold as a building stone is often heat treated around 600°C to obtain a brown colour which has been ascribed to the presence of oxidised Fe. Iron is known to leach in hydrothermal conditions so the red colour could be iron leaching from the ignimbire.

Chemically the increased temperature of curing leads to the formation of killalite and reinhardbrausnite, the high temperature high Ca/Si ratio phases not present in the 150°C specimens, portlandite and considerably less amorphous material. Deeper calcium migration occurs compared to the 150°C specimens and leads to more complex reaction increasing the width of the ITZ. No obvious alumina containing phases have crystallised but that may be because the reaction with ignimbrite has not released much compared to the samples with bentonite.

The fact that the cement has easily detached from the rock suggests that in crystallising, the cement has lost a lot of its cementing/bonding proprieties at 300°C although this may be due to differential expansion of the cement and ignimbrite.

4.5 G20SF300

For this matrix, the most noticeable change is the formation of kilchoanite and xonolite along with killalite (present also in the G300 specimen), whereas reinhardbrausnite has disappeared (un-
like in the G300). This will be due to the addition of silica flour which has completely reacted removing any portlandite. Nevertheless, xonotlite is unexpected at this Ca/Si ratio and probably results from extensive leaching of Ca\(^{2+}\) ions effectively lowering the Ca/Si ratio in the matrix.

The ITZ is wider and the cement and the rock have become completely detached from each other. On the cement side of the border are some red coloured spots, which may be the consequence of Fe moving from the rock into the cement and precipitating in the alkaline environment. The wider ITZ may, again, be attributed to a possible enhancement of Ca migration and further reaction during cooling to retrieve the samples has widened the discontinuity into a clear crack.

### 4.6 G40SF300

Similarly to the G20SF300 specimen, the large addition of silica flour will ensure complete reaction of portlandite and the Ca/Si ratio is low enough that xonotlite readily forms at the expense of other calcium silicates.

There is still a wide reaction zone when compared to the 150°C specimens (due to the higher temperature) where the cement separates from the rock, but it is smaller than G300, probably because there is less Ca overall in the cement matrix to migrate, it being consumed in the reaction with the large amount of added silica flour.

### 5.0 Conclusion

From the current work, it is obvious that reactions occur between the rock and the cement as Ca\(^{2+}\) and OH\(^{-}\) ions migrate. The extent of the reaction is dependent on temperature (increasing from 150°C to 300°C) and on the presence of a drilling mud such as bentonite.

These migration reactions driven by Ca\(^{2+}\) ion migration would appear to occur faster than the expected reaction of Ca(OH)\(_2\) with quartz. The presence of bentonite from the drilling fluid exacerbates the reaction in the ITZ, generally giving a wider reaction rim. The formation of the aluminosilicate gehlenite in the ITZ of the three specimens with a bentonite layer (unlike the other specimens) seems to be a consequence of the reaction between the cement and the bentonite and perhaps the rock, releasing Al and allowing this phase to form.

Despite a deeper penetration of Ca\(^{2+}\) ions into the rock, the specimens at 300°C seem to have lower cement-rock bonding (as they have detached easier than the other 150°C specimens), after being autoclaved. This discontinuity is enhanced with bentonite at 150°C and appears associated with the presence of gehlenite. The crystalline phases formed appear to have little strength and lead to a distinct break between the cement and formation which may be due to differences in molar volumes or shrinkage or differences in thermal expansion of the phases.

Further work on cement-rock interaction in a geothermal context is being conducted, where other important variables like such CO\(_2\) exposure, hydrothermal alteration of the rock, rock type and curing time will be considered.


---

1 Geobrine recipe: 0.19 g sodium sulphate (NaSO₄), 0.05 g calcium chloride dehydrate (CaCl₂·2H₂O), 15.6 g liquid precipitated silica (SiO₂), 4.1 g potassium chloride (KCl), 15.8 g sodium chloride (NaCl) are well mixed and filled with water to make up 20 litres.