CHEMICAL REACTIONS IN GEOTHERMAL CEMENTS

NB Milestone, CH Bigley, AT Durant, MDW Sharp and JRMC da Silva

Industrial Research Ltd, PO Box 31 3410, Lower Hutt, 5040

n.milestone@irl.cri.nz

Keywords: *hydrothermal cement, carbonation, durability, well completion, geothermal cement, slurry formulation.*

ABSTRACT

The Portland cements used for completion of geothermal wells undergo a series of chemical reactions as they cure in the increased temperatures of the wells. In hydrothermal conditions, the calcium silicate cements undergo transformations changing from the initial amorphous binder formed at room temperature into a crystalline one. On its own, Portland cement will slowly crystallise into a series of high Ca/Si ratio phases which have high porosity and low strength. The crystallisation of these phases causes a reaction known as ‘strength retrogression’, to occur with the actual phases formed depending on temperature. To avoid this phenomenon it is common practice to add ~40% silica flour (quartz) which allows the formation of low Ca/Si ratio phases such as tobermorite or xonotlite which have low porosity and high strength. These cements are placed in a formation that contains large amounts of reactive silica. Migration of silica and calcium during the curing reaction changes the phases that form and alters the durability.

In the New Zealand fields, the level of dissolved CO_2 in the geothermal fluids creates a further chemical reaction in the hardened cement, that of carbonation. This reaction occurs throughout the depth of the well with the rate dependent on CO_2 concentration and inversely proportional to the Ca/Si ratio of the binder, the stronger ones carbonating fastest. In many fields, an impermeable layer traps CO_2 so an acidic fluid forms which readily dissolves or corrodes the carbonated cement leaving the casing unprotected so the wells may corrode within a few years.

This rapid corrosion of calcium based cements means that new cementing systems are needed to fully exploit our geothermal resources, work now being conducted at IRL.

1.0 INTRODUCTION

To extract steam from geothermal fields wells are drilled into a formation which is usually weak and often porous. Drilling is carried out in stages with different diameter holes into which a series of steel casings are lowered and cemented in place by a cement slurry pumped through the casing to return to surface providing a cement sheath around the outside of the steel casing ensuring it is anchored to the formation. In a completed well there are usually three concentric casings, each with its own particular use and cement annulus. These are the surface casing for the first 20 metres or so to consolidate the formation and provide a base for further drilling; an anchor casing for the next 100 metres, which as its name implies ensures the well remains in the ground, and the production casing which typically runs the length of the well to prevent well collapse. The cement plays an important role in well completion by:

- providing a seal between the various layers of the formation
- ensuring high pressure steam reaches the surface and its release can be controlled
- Providing support for the steel casing and hopefully providing corrosion protection to the steel casing.

Portland cement is a calcium silicate cement made by firing limestone and clay to high temperatures. The two main phases are tricalcium silicate and dicalcium silicate which make up over 80% of the material. When Portland cement hydrates it forms two main compounds, crystalline calcium hydroxide and an amorphous binder known as calcium silicate hydrate gel, C-S-H[1]. The Ca/Si ratio of the binder varies with temperature, becoming silica rich with increasing temperature with increased $Ca(OH)_2$ formed. When heated in air the C-S-H decomposes above 105°C slowly losing water, while the $Ca(OH)_2$ decomposes at 440°C when all strength is lost. Under hydrothermal conditions this dehydration does not take place and a series of crystalline hydrates are formed, their composition depending on available Ca/Si ratio, the type and amount of any additional silica present, and the temperature. Around 150^oC α-C_2SH crystallises from pure Portland cement along with $Ca(OH)_2$, while at higher temperatures, a mixture of phases form; reihardbraunsite, C_5S_2H, jaffeite, $C_6S_2H_3$, and kilchoanite, C_3S_2. These high Ca/Si ratio phases are not good binders, with very low strength and high porosities and measures are taken to avoid their formation in high temperature well cementing. At elevated temperatures, the crystals of α-C_2SH continue to grow and strength continues to decrease – the phenomenon known as ‘strength retrogression’.

Kalousek (1949, 1954) found by adding >30% silica flour (fine quartz), strength retrogression could be avoided with formation of a further set of crystalline phases. At 150^oC quartz reacts to give 11Å tobermorite, $C_5S_6H_5$, while above 200^oC, tobermorite converts to yet another new phase, xonotlite, C_6S_6H. These low Ca/Si ratio phases make good binders and typically 40% silica flour additions form the basis of today’s oilwell cement formulations. Tobermorite is the binder phase in autoclaved cement/fibre products while xonotlite is used in insulation and as the porous support for acetone in acetylene cylinders.

1.1 Preliminary Downhole Exposures

Cementing for the wells drilled at Wairakei in the 1950’s was carried out using plain Portland cement with additions of a few percent Porongahau bentonite to provide a suitable slurry density. Generally, few problems have been encountered in the well cementing at Wairakei, although

---

[1] Cement oxide nomenclature: C = CaO, S =SiO_2, A = Al_2O_3, F = Fe_2O_3, H=H_2O

Kennerley (1961) showed that in samples of the cement recovered from wells there, many had skins of calcite and α-C_2SH was the phase present as expected.

Following the work by Kalousek (1954), when cementing was considered for the new wells to be drilled at Ohaaki in the 1980's, recommendations were to use a Portland /silica flour blend with the new American Petroleum Institute (API) class of cements as strength retrogression was uppermost in the minds of the drilling engineers. A series of formulations were prepared and exposed in well BR23. Results from the downhole exposures after 6 months were surprising. Extensive carbonation had occurred and many samples had suffered severe corrosion (Milestone et al. (1986)). While some samples showed a skin of calcite, the expected calcium carbonate phase, other samples had almost completely converted to aragonite and up to 60% of some samples had been lost by corrosion.

Workover on wells designated for production, which had been drilled several years before and kept shut in, showed that for several wells, the casing had corroded and perforated (Driver and Wilson (1984), Bixley and Wilson (1985)). This fact, coupled with the results from the cement exposure, prompted a re-evaluation of the field chemistry and resulted in a new picture of the geothermal fluids. Hedenquist and Stewart (1985) identified a low temperature aquifer in which CO_2, boiled off near the production zone, had percolated through the porous formation and become trapped beneath an impermeable capping layer, typically lying several hundred metres below surface. This trapping lead to high levels of dissolved CO_2 within this aquifer. Similar zones have since been identified in other fields where a cooler layer of water is heated by up risings from deeper fluids and corrosive gases are dissolved (Clearwater et al. (2012)).

2.0 CARBONATION AND CORROSION IN GEOTHERMAL WELLS

Milestone et al. (1986) showed that samples, which had been pre-cured in a laboratory autoclave at 150°C for 72 hours and then exposed down-hole in wells in the Ohaaki geothermal field in New Zealand, underwent both extensive carbonation and corrosion at 150°C. (Fig. 1) The outside layer of these samples was a slippery coating of silica gel from which all calcium had been leached. At 260°C, only carbonation occurred when they were exposed to high CO_2 containing fluids. (Fig. 2)

One of the key features of that work, and of subsequent laboratory work carried out at Brookhaven National Laboratory by Milestone et al. (1986, 1987a, b), was the revelation that the addition of around 40% silica flour, normally added to counter strength retrogression, created a matrix which was extremely rapidly carbonated. The expected low Ca/Si ratio phases of tobermorite and xonotlite, chosen to give low porosity and high strength at elevated temperatures, carbonated rapidly and became porous. In contrast, the high Ca/Si ratio phases α-C_2SH (at 150°C) and reinhardbrausite or kilchoanite (at 260°C) formed in association with $Ca(OH)_2$, gave low strength binders, but formed a dense, protective carbonation sheath with low permeability and high strength.

At 150°C, carbonation of $Ca(OH)_2$ gives rise to calcite while carbonation of calcium silicate hydrates gives metastable aragonite so that mixtures of aragonite and calcite were present in the carbonated layers which were thin. At 260°C both $Ca(OH)_2$ and the calcium silicate hydrates form calcite upon carbonation.

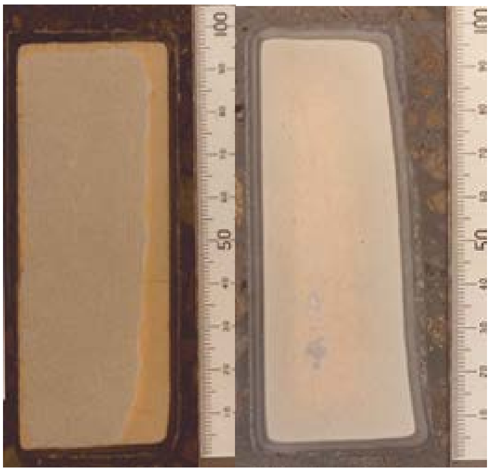
(a) (b)

Figure 1: Exposure of grout cylinders in BR23 Ohaaki (150°C, $[CO_2]$ 0.35moles/l, pH_T 4.59) for 6 months

(a) Pure cement: The centre core is α-C_2SH plus $Ca(OH)_2$, middle orange layer is calcite, with an inner layer of calcite and aragonite, outermost layer is silica gel. Minor corrosion has occurred.

(b) Cement plus 40% silica flour: Inner core is aragonite, middle layer is aragonite/calcite, outer layers corroded silica gel. Sample is extensively corroded.


(a) (b)

Figure 2: Exposure of grout cylinders in BR17, Ohaaki (260°C, $[CO_2]$ 0.064 moles/l, pH_T 6.49) for 6 months

(a) Pure cement: Inner core is high Ca/Si phases kilchoanite and reinhardbraunsite, outer rim is calcite. No corrosion.

(b) Cement plus 40% silica flour: Inner core is xonotlite and calcite, outer core is calcite and xonotlite, outside layer is calcite. No corrosion

Following his work at Brookhaven Laboratory, Milestone and co-workers in New Zealand (1990) undertook an extensive period of work downhole testing a wide variety of formulations based largely on additions to Portland cement in both the Ohaaki and Rotokawa fields. It became clear from these studies that in any Portland cement based system, the carbonation rate was very dependent on the volume of available Ca in any unit volume and particularly by any $Ca(OH)_2$ present. Carbonation resistance was enhanced by low addition rates of silica and low water/solids ratio mixes. Addition of bentonite, often added to control bleeding or segregation, proved detrimental as it stabilised any tobermorite that was formed, which rapidly carbonated and became porous (Milestone et al. (1987b)). It was aslo found that as the temperature was increased the bentonite stabilized slurry became unstable.

2.1 Mechanism of carbonation

Carbonation of cement grouts proceeds via a ‘through solution’ mechanism. This was initially described by Milestone et al. (1986) where Ca^{2+} ions migrate through a saturated matrix leaving a leached zone and then rapidly precipitate as $CaCO_3$ when they meet the dissolved CO_2 (‘carbonic acid’). This reaction can lead to a discontinuity as the precipitation reaction occurs faster than the rate at which the Ca^{2+}ions can migrate. The discontinuity is obvious in Fig. 3 where a sample of pure cement exposed in an Ohaaki well (BR17, $[CO_2]$ 0.064 moles/kg) at 260°C for 4 months shows the formation of a calcite skin which is only weakly attached and will readily separate, particularly if the sample is recovered from the well too quickly and dried out. The pH_T in this well is 6.49, above the neutral pH_T of 5.82, so there is no acid dissolution or corrosion. Carbonation of $Ca(OH)_2$ is an expansive reaction so the carbonated layer occupies more volume than that from where it has come and can separate. A petrographic thin section prepared from the same sample (Fig. 4) clearly shows the leached region along with the discontinuity. Ca^{2+} ions migrate from the sparingly soluble $Ca(OH)_2$ leaving a leached zone in which the loss of $Ca(OH)_2$ is clearly visible just inside the discontinuity. Ultimately, the skin of $CaCO_3$ will grow and penetrate to the centre with an increase in the volume of the cylinder but after 1 year of downhole exposure, the carbonated layer is only around 12mm thick.

Figure 3: Exposure of pure cement samples in BR17 at 260°C for 4 months

Figure 4: Photomicrograph of carbonated geothermal cement sample from Fig 3.

Scale bar is 1mm. Brown colour is calcite, white crystals αC_2SH, grey is Ca(OH)2. Discontinuity is ~0.7mm, leached zone ~1.2mm.

This has important issues if compressive strengths or permeabilities of cylinders are being used as measures of determining potential durability. The carbonate skin has high strength so what is measured for strength is due to a composite structure that may contain a discontinuity. The same applies in measuring permeability where water is likely to flow down the discontinuity rather than through the sample. Carbonation per se does not lead to decreased strengths, rather it enhances it.

The calcium silicate hydrates are much less soluble than $Ca(OH)_2$ meaning there are limited Ca^{2+} ions to migrate so the carbonation attack appears to occur directly on the matrix as seen in Figure 2b where a sample containing 40% silica flour exposed in the same well has no obvious leached zone. The carbonation of xonotlite, the stable low Ca/Si ratio phase at 260°C, results in a reduction of solid volume causing an increase in porosity so no distinct carbonation layer forms.

2.2 Mechanism of corrosion

As pointed out by Bruckdorfer (1986), the corrosion mechanism is one of dissolution of the $CaCO_3$ that forms by carbonation of the cement by ‘carbonic acid’ (Eq 1 and 2) to give soluble $Ca(HCO_3)_2$ which is lost (Eq 3). The samples in Figure 1 were exposed in a fluid where the dissolved CO_2 concentration (0.34 moles/litre) was sufficient to create a mildly acidic liquid environment of pH 4.59. Neutral pH at 150°C is estimated at 5.82 (Bandura and Lvova (2006)) so the pH is dictated by the amount of dissolved CO_2. Corrosion of the carbonates formed by carbonation follows in the high school reaction of limewater and CO_2 (Equations 1 and 3).

$$Ca(OH)_2 + CO_{2(aq)} \rightarrow CaCO_3\downarrow + H_2O \qquad (1)$$

$$C\text{-}S\text{-}H + CO_{2(aq)} + H_2O \rightarrow CaCO_3\downarrow + SiO_2.nH_2O \qquad (2)$$

$$CaCO_3 + CO_{2(aq)} + H_2O \rightarrow Ca^{2+}_{(aq)} + 2HCO_3{}^{-}_{(aq)} \qquad (3)$$

This corrosion reaction cannot occur in dry steam as there is no liquid for the ions to dissolve and be leached, although carbonation does occur. When the CO_2 concentration is such that the fluid is not acidic, as in BR17, then only carbonation occurs.

3.0 ADDITION OF SILICA

As described above, the addition of ~40% silica flour (fine quartz) is usually carried out to avoid the phenomenon of strength retrogression as crystals of α-C_2SH form and continue to grow. However, while quartz addition does form the high strength, low Ca/Si ratio phases of tobermorite and xonotlite, these phases are not carbonation resistant and will corrode readily under acidic conditions. Milestone and Aldridge (1990b) suggested the use of 15% silica flour as a compromise between carbonation resistance and strength retrogression. This removed the excess $Ca(OH)_2$ but the formation of a new high Ca/Si ratio phase, killalaite, C_6S_3H, still gave some degree of carbonation resistance.

Recent work being conducted at Industrial Research utilises a local natural resource, fine hydrothermal silica (Microsilica WG), which is predominantly amorphous with small amounts of crystalline quartz, cristobalite and trydimite present. Adding this at 20% by weight of cement (BWOC) provides a binder system which remains amorphous after 6 months at 150°C, does not undergo strength retrogression and offers good carbonation resistance. Compressive strength results are shown in **Table 1,** with those for silica flour shown for comparison.

Table 1: UCS values in MPa under curing with and without an overpressure of CO_2.

Mix Design	150˚C No CO_2	150° with CO_2	300°C no CO_2	300°C with CO_2	300° with CO_2
Class G 0.4 W/C	20	20.5	14	9	8
Class G plus 20% BWOC silica flour	44	38.5	15	25	25
Class G plus 20% BWOC Microsilica WG	30	28	9	51.5	22
Class G plus 20% BWOC Microsilica WG and 20% silica flour	53	28	39	48	47
Age at test	84 d	84d	150d	84d	2d

UC Strengths in MPa. Samples in columns 1-4 initially cured at 90°C for 2 days then heated in autoclave. Samples in column 5 set (6hrs) then placed in autoclaves and heated.

Class G cement loses strength with temperature when cured on its own. When 20% silica flour is used the strength reduction is not as marked. While using Microsilica WG does not provide as high compressive strengths, it is adequate to meet the API specification of 6.9MPa and does not regress further over time. Strengths at 300°C with 20% Microsilica WG or silica flour are less than those at 150°C and indicate a change in the chemistry of the binder phase, although with Microsilica WG the binder remains amorphous (Columns 1-4).

In column 5 the samples were allowed to set at ambient (4 hours) then placed directly in the 300°C autoclave and heated in the presence of CO_2. Only for the Class G and the Class G plus 20% Microsilica WG samples did a carbonation sheath form and the core remain uncarbonated, with the sheath being thicker with the Microsilica WG sample. Carbonation was extensive in the samples with silica flour and unreacted quartz remained in the core along with calcite.

This indicates that carbonation will occur during curing and can upset the expected curing reactions. The $Ca(OH)_2$ released during cement hydration carbonates rapidly, ‘fixing’ Ca which is not available for reaction with silica. So the quartz effectively is an inert diluent reducing the Ca concentration per unit volume so a protective impermeable sheath cannot be formed. Microsilica WG reacts sufficiently quickly that it competes for $Ca(OH)_2$ with the CO_2.

4.0 LIGHTWEIGHT CEMENT SLURRIES

One of the issues in cementing a geothermal well is that it is usually drilled through a weak formation, often with porous zones where lost circulation of the drilling fluid and cement is a problem as the formation collapses. As a consequence, slurries with low density are sought to ensure the weight of the column of cement slurry does not collapse the formation. This was originally addressed in New Zealand by using formulations with higher water/cement ratios with bentonite added to control segregation. However, Milestone et al. (1987b) showed that additions of bentonite enhanced and stabilised the formation of tobermorite which is not carbonation resistant.

The use of hollow ceramic cenospheres or microspheres to obtain lightweight slurries in well cementing is now wide-spread, along with foamed cement. The cenospheres are obtained from flyash and have the same overall glassy silicate composition so are pozzolanic, ie they will react with $Ca(OH)_2$. They allow slurry densities as low as 1.55g/cc (13.5 ppg) to be easily obtained without the high water content which can give rise to segregation. In a recent study we conducted, a slurry of Class G cement plus 25% hydrothermal silica BWOC and 15% of cenospheres BWOC (14lb/sack) was mixed at a water/solids ratio of 0.41 to give a slurry with density of 1.65g/cc (13.8 PPG) and cured at 165°C for 28 days in a geothermal brine[2] under 6 bars CO_2 pressure. While the compressive strength obtained was 25.7 MPa, a distinct carbonation rim of ~5mm formed which increased with time. A photo-micrograph of the core (Fig 5) shows distinct reaction rims around the cenospheres, many of which have reacted and are filled with aragonite and calcite.

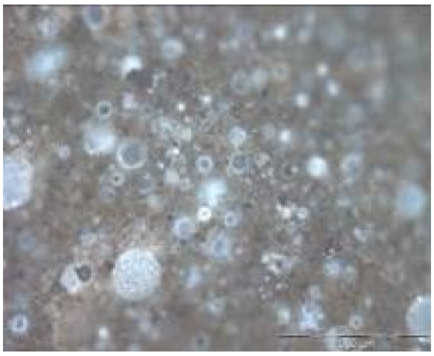

Figure 5: Photomicrograph of Class G cement plus 25% hydrothermal silica and 15% cenospheres mixed at w/s of 0.41 and cured for 28 days in CO_2 saturated brine at 160°C

The carbonation rim is fully carbonated to calcite whereas in the core, tobermorite and a trace of xonotlite were present along with large amounts of aragonite and calcite. The siliceous cenospheres readily react with $Ca(OH)_2$ from Portland cement hydration to give pockets of the low Ca/Si

---

[2] (15.8 g NaCl, 4.1g KCl, 0.2g Na_2SO_4, 0.05g $CaCl_2$, 15.6g CB8 colloidal silica (50% solids) dissolved in 20 litres distilled water)

ratio phases tobermorite/ xonotlite which carbonate readily. In a Class G plus 25% hydrothermal silica slurry without cenosphere addition, which has a density of 1.89g/cc (16.5 PPG) there is no carbonation beyond the first mm or so. As the carbonation rate is determined by the concentration of Ca per unit, volume addition of additives has a marked effect on the rate of carbonation. Thus in the lightened samples where the amount of Ca per unit volume is low, carbonation is rapid as no protective sheath is formed.

This is further highlighted in a recent study where we have controlled the slurry density of a Class G cement plus 25% BWOC Microsilica WG with water and proprietary additives, curing under the same conditions as above. (Fig 6) While the standard density slurry performed well, carbonation through to the core occurred for the lighter weight samples in Fig. 6 (b and c). Interestingly, the chemical additives used in these samples to ensure segregation did not occur, contained significant amounts of sulfate, which changed the expected range of products.

Figure 6: Grout formulations containing 25% Microsilica WG at different densities cured at 150°C

(a) 15.0 PPG, (b) 12.4 PPG, (c) 11 PPG

The major phase in the Class G plus 25% hydrothermal silica slurry with a density of 1.89g/cc (15 PPG) sample is amorphous C-S-H with small amounts of xonotlite and afwillite ($C_3S_2H_3$) and unhydrated cement present, along with traces of calcite after 28 days curing. As the density was decreased, the 12.4 PPG sample still contained a large amorphous component but with increased amounts of xonotlite and afwillite and a decreased amount of unhydrated cement but there was a small amount of the zeolite gismondine, CAS_2H_4, present in the core, while in the well-defined skin, aragonite and calcite were present. Finally, with the 11 PPG sample, carbonation had penetrated to the centre of the sample giving a mixture of calcite and aragonite along with xonotlite and anhydrite ($CaSO_4$). No silicates were present in the middle layer which was a mixture of aragonite and calcite with a small amount of anhydrite, while the skin was principally calcite along with some aragonite.

Normally, tobermorite (which usually only forms with quartz) or xonotlite will not readily form with the addition of only 20% silica as the Ca/Si ratio is not low enough. However, carbonation removes available Ca from the matrix and has allowed the formation of these lower Ca/Si ratio phases. The anhydrite found arises from the interaction of Ca^{2+} ions and sulfate from the additives needed to prevent settling in the higher w/s mixes.

5 0 INTERACTIONS WITH FORMATION

The porous formation through which the wells are drilled is often described as 'rhyolitic'. Rhyolite aggregates have been shown to be reactive with the alkalis present in Portland cement when used in concrete at ambient conditions, a phenomenon known as alkali silicate reaction (ASR). (C&CANZ, 2004). The rhyolite in geothermal fields has itself undergone a form of hydrothermal alteration which renders it silica rich. This hypogene alteration described by Grindley at al. (1965) and Steiner (1977) gives rise to minerals that are highly siliceous.

Using a rhyolite ignimbrite (Hinuera stone) as a porous mould, samples of several cement formulations (Table 3) were cast in holes drilled into blocks, set in brine at 90°C for 2 days and autoclaved at 150°C for 28 days. After curing the samples were cut axially and samples selected for XRD, TGA (powdered samples drilled from four zones across the sample), optical microscopy (thin section) and SEM. (polished sample).

Table 3: Mix design for cement/rock interactions

Sample Mix	Bentonite	Temp °C
Class G cement	no	150
Class G cement +	yes	150
Class G cement +20% silica flour	no	150
Class G cement +20% silica flour	yes	150
Class G cement + 40% silica flour	no	150
Class G cement + 40% silica flour	yes	150
Class G cement	no	300
Class G +20% silica flour	no	300
Class G + 40% silica flour	no	300

Details of the exposed samples have been recently been presented (da Silva et al. (2012)). In the cut samples three distinct zones were identified, the cement core labeled 'int', the inter-transitional zone (ITZ) split into 'cement' for the portion closet to the cement and 'rock' for the portion closest to the unaltered rock sample and the rock which was labeled 'centre'. The ITZ can be up to 2mm wide and both the cement and rock are altered within it. Using SEM element maps migration of Si and Ca can be followed. A typical SEM micrograph from a sample exposed at 150°C showing the location of calcium and silicon is given in Figure 7(a) and (b). A clear ITZ can be seen as Ca migrates into the rock. Typical petrographic thin sections at 150 and 300°C are shown in Figs. 8 and 9 where the ITZ is clearly seen.

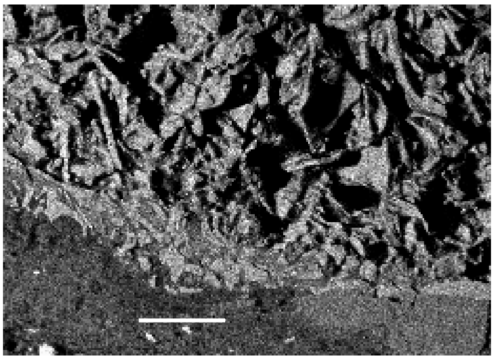

Figure 7(a): Si map of transition zone between G cement plus 20% silica flour 150°C

Ignimbrite is at top of picture with a clearly defined ITZ below it and cement matrix at bottom of picture. Bar is 1mm.

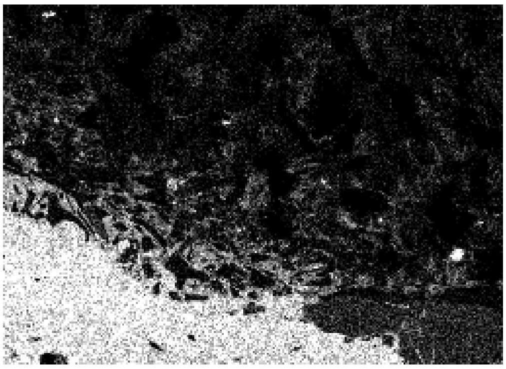

Figure 7(b): Ca map of transition zone between G cement plus 20% silica flour 150°C

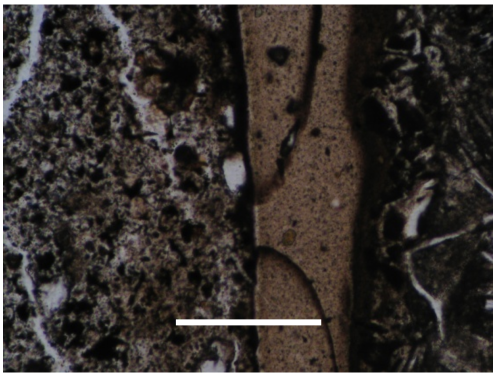

Figure 8: Typical optical micrograph of the transition zone between G plus 20% silica flour with a bentonite layer.

Cement is at left with bentonite layer in the middle and the ignimbrite on the right. Bar is 1mm

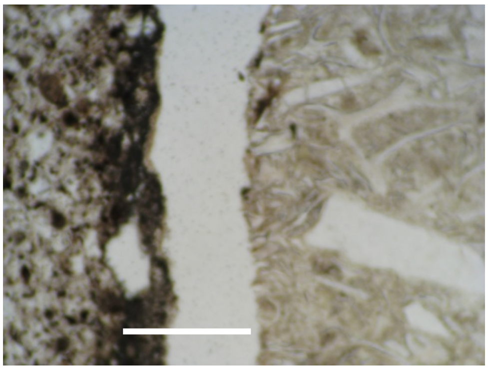

Figure 9: Typical optical micrograph of the transition zone between G plus 40% silica flour 300°C

Cement matrix is at left with rock at right. The discontinuity is in the middle. Bar is 1mm.

5.1 XRD results.

A summary of phases identified in the three zones where there is interaction of the cement is given in Table 4.

5.2 Discussion

From the current work, it is obvious that reactions occur between the rock and the cement as both Ca^{2+} and OH^- ions migrate into the rock forming an ITZ. The OH^- ions solublise Si so it can move into the cement layer (Fig 7(a). The extent of this reaction is dependent on temperature (increasing from 150°C to 300°C) and on the presence of a drilling mud such as bentonite. The migration reactions driven by Ca^{2+} ion migration would appear to occur faster than the expected reaction of $Ca(OH)_2$ with quartz since considerable quartz is left in the cement matrix of the G plus 20% silica flour and G plus 40% silica flour samples. The presence of bentonite from the drilling fluid exacerbates the reaction in the ITZ, generally giving a wider reaction rim and a discontinuity can sometimes be seen.

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 additional aluminium which allows 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 effect is enhanced with bentonite at 150°C where a discontinuity occurs which appears associated with the presence of gehlinite. This phase has little strength and leads 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 such as CO_2 exposure, hydrothermal alteration of the rock, rock type and curing time will be considered.

Table 4 – Compounds identified by XRD analysis

Specimen	Sample	Identified peaks and other relevant features
G150	G150int	Amorphous with $Ca(OH)_2$ and traces of calcite and unhydrated cement.
	G150cem	Reduced $Ca(OH)_2$ with traces of calcite and unhydrated cement.
	G150rock	Similar minerals to rock centre with reduced amounts of quartz.
G20SF150	G20SF150int	Amorphous with traces of calcite, quartz, tobermorite and αC_2SH.
	G20SF150cem	Similar to above but with slight increase in quartz.
	G20SF150rock	Similar to centre of rock.
G40SF150	G40SF150int	Large amorphous component with significant quartz and tobermorite.
	G40SF150cem	Similar to G20SF150cem.
	G40SF150rock	Similar to rock centre.
Gb150	Gb150int	Amorphous with $Ca(OH)_2$ and traces of calcite, kilchoanite and αC_2SH.
	Gb150cem	Amorphous with decreased $Ca(OH)_2$ from above**,** αC_2SH and kilchoanite not present. Aragonite and gehlenite present.
	Gb150rock	Similar to G150 but without the reduction in quartz. Gehlenite present.
G20SFb150	G20SFb 150int	Amorphous with quartz and trace amounts of αC_2SH, katoite and calcite.
	G20SFb150cem	Amorphous with decreased amounts of quartz, αC_2SH and calcite from G20SFb150int. No katoite. Gehlenite also present.
	G20SFb150rock	Albite and anorthite are present with no reduction in quartz from IGN150. Gehlenite also present.
G40SFb150	G40SFb 150int	Large quartz present with αC_2SH, tobermorite, calcite and gismondine.
	G40SFb150cem	Quartz and tobermorite present with traces of αC_2SH, gismondine and calcite which are unchanged from G40SFb150int. Slight traces of gehlenite.
	G40SFb150rock	Albite, anorthite and no reduction in quartz from IGN150. Traces of gehlenite.
G300	G300int	$Ca(OH)_2$, calcite and reinhardbraunsite with small amounts of killalite and αC_2SH. Perhaps some katoite present.
	G300cem	Portlandite decreased substantially from G300int but amount of katoite, killalite and αC_2SH appear to remain the same while the amount of reinhardbraunsite and calcite increase.
	G300rock	Albite, anorthite and quartz are present with small amounts of reinhardbraunsite and αC_2SH seem to be present as well, although the noisy results make it difficult to fully identify phases.
G20SF300	G20SF300int	Killalite, kilchoanite and quartz with traces of xonolite.
	G20SF300cem	Killalite, kilchoanite, xonotolite with increased quartz.
	G20SF300rock	Albite, anorthite, no reduction in quartz from IGN300.
G40SF300	G40SF300int	Quartz, xonolite and killalite.
	G40SF300cem	Increased quartz and xonolite from G40SFb300int.
	G40SF300rock	Albite, anorthite and no reduction in quartz from IGN300.

6.0. SUMMARY

Carbonation reactions of calcium silicate based geothermal cements override any other reactions occurring within the cements. Systems where silica flour is added to prevent strength retrogression due to elevated temperatures only serve to reduce the concentration of Ca per unit volume and lead to extensive carbonation. Carbonation of $Ca(OH)_2$ to calcite is expansive which tends to block pores, while carbonation of the calcium silicate hydrates gives rise to metastable aragonite around 150°C and calcite above 200°C. Whether this reaction is expansive or non-expansive depends very much on the Ca/Si ratio of the solid hydrate with the neutral point being compounds around Ca/Si = 1.5, below which carbonation leads increased porosity. Above this value an impermeable carbonation sheath is formed which offers some protection.

Laboratory experiments cannot readily study corrosion. In fields where CO_2 arising from depth can be trapped beneath an impermeable capping layer, the concentration of dissolved CO_2 can be sufficient for the fluids to become mildly acidic. This acidic fluid will initially carbonate then dissolve any calcium carbonate as bicarbonate leading to corrosion of the carbonated cement. The depth below surface of the ‘corrosive zone” is limited, and may only be several metres thick, but reactions occurring within the zone cause major problems with both cement and well casing integrity. Corrosion rates of cement can be high, depending on slurry density, concentration of Ca per unit volume and CO_2 concentration, but up to 60% of the volume of a 100 x 50 mm cylinder can be lost within 6 months.

While at least 40% BWOC addition of silica flour (quartz) is needed to form the high strength crystalline calcium silicate hydrates tobermorite and xonotlite, addition of a hydrothermal silica (Microsilica WG) gives rise to an amorphous calcium silicate hydrate binder which does not appear to undergo strength retrogression and yet offers good carbonation resistance.

There is considerable interaction of the well cement with acidic rocks from the formation. Calcium ions migrate into the surrounding rock which the hydroxide attacks the glassy fraction of the ignimbrite releasing silica which migrates into the outer layer of the cement initially forming a band of low Ca/Si ratio phases such as tobermorite which carbonates readily. Addition of a layer of bentonite drilling mud only accentuates the reaction and appears to create a break between the cement and the formation.

ACKNOWLEDGEMENTS

This work is funded by MSI through Programme C08X0902, Cements for Extreme Environments with co-funding from a consortium of Mighty River Power, Contact Energy, Halliburton and Baker Hughes.

REFERENCES

Bixley, P I and D M Wilson, "Rapid Casing Corrosion in High Temperature Liquid Dominated Geothermal Fields", *Proc. 10th Workshop on Geothermal Reservoir Engineering, Stanford University*, Stanford, California, January 22-24, 1985, SGP-TR-84

Cement and Concrete Association of New Zealand, (2004) "Alkali Aggregate Reaction – Guidelines on Minimising the Risk of Damage to Concrete" (TR3).

Clearwater, J., J Burnell and L Azwar, "Modelling the Ngatamariki geothermal system", Proc., 37th Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, Jan 30 - Feb 1, 2012 SGP-TR-194

Driver, PM, and PT Wilson, "*Geothermal Well Casing External Corrosion: a Case History"*, Proc. Aust. Corros. Soc. Conf., Rotorua NZ, Nov 1984 Paper 47

Grindley, W F Harris and A Steiner, "*Geology, structure, and exploitation of the Wairakei geothermal field, Taupo, New Zealand*", New Zealand Geological Survey. Bulletin, n.s. 75 (1965)

Hedenquist, J.W., and Stewart, M.K. "Natural CO_2-rich steam-heated waters in the Broadlands-Ohaaki geothermal system, New Zealand, their chemistry, distribution and corrosive nature", *Geotherm. Res. Coun. Trans*. 9(2). 245-250 (1985).

Hedenquist, JW, "The thermal and geochemical structure of the Broadlands-Ohaaki geothermal system, New Zealand", *Geothermics,* 19 (2), 151-185, (1990)

Kalousek, G.L. and M. Adams, "Hydration products formed in cement pastes at 25 to 175°C", *J Amer. Concr. Inst* 23, 77-90, (1952)

Kalousek, G.L., C.W. Davis Jr. and W.E. Schmertz, "An Investigation of Hydrating Cements and Related Hydrous Solids by Differential Thermal Analysis", *J Amer Concr. Inst.* 20 693-712 (1949)

Kennerley, R.A. "Products from hydrothermal alteration of cements from geothermal bores", *NZ J. Sci.* 4 453-468, (1961)

Milestone, N.B., T. Sugama, L.E. Kukacka and N. Carciello, "Carbonation of Geothermal Grouts - Part 2: CO_2 Attack at 250°C", *Cem. Concr. Res.* 17, 37-46 (1987)

Milestone, NB, DA St John, JH Abbott and LP Aldridge "CO_2 corrosion of geothermal cement grouts", *Proc. 8th Internat. Cong. Chem. Cements, Rio de Janeiro Sept 1986* V 141-144

Milestone, N.B., T. Sugama, L.E. Kukacka and N. Carciello, *"Carbonation of Geothermal Grouts - Part 1: CO_2 Attack at 150°C", Cement Concr. Res*. 16, 941-950 (1986)

Milestone, N.B., T. Sugama, L.E. Kukacka and N. Carciello, *"Carbonation of Geothermal Grouts - Part 3: Effect of Bentonite". Cem. Concr. Res*. 17 295-306 (1987).

Milestone, N.B., and L.P. Aldridge, "Corrosion of Cement Grouts in Aggressive Geothermal Fluids", *Trans. Geo. Resources Council* 14 (I) 423-429 (1990).

Milestone, N.B., and L.P. Aldridge, "Best Available Grout", Report to Gas and Geothermal Trading Group, NZ, 1990.

Steiner, A., "The Wairakei Geothermal area, North Island, New Zealand", *New Zealand Geological Survey. Bulletin,* n.s. 90 (1977)