

# DURABILITY OF THE CEMENT IN GEOTHERMAL WELLS

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## ABSTRACT

The cement surrounding the casing is an integral part of well design to exploit geothermal energy. It plays several roles including sealing in the high pressure steam and ensuring isolation of the various zones through which the well penetrates. Any degradation of cement may compromise the working life of the well where lifetimes in excess of 30 years are now being sought.

New Zealand's early wells were cemented with conventional construction cement after quenching to around 40°C and most of the wells associated with the Warakei development (the station came on stream in 1958) have lasted well with few problems. In later development at Ohaaki, where the wells were quenched to 60°C before cementing, significant corrosion problems due to acidic fluid interactions with the hardened cement were encountered.

Our recent research is showing that the conventional engineering approach of developing the strongest binder through use of silica flour, has not taken into account any chemical reactions that:

- (i) occur during the initial formation of the hydrothermal cementing phases as the cement hardens, and
- (ii) subsequently occur between the hardened cement phases and the down hole geothermal fluids.

These reactions can lead to issues with long term durability of the cement sheath. In recent well completions, the wells have been cooled by circulation of drilling fluid with cementing nominally undertaken around 90°C. The higher temperatures now encountered during cementing have changed the cement hydration mechanism so that some retarders will no longer function efficiently, and different hydration reactions can occur. The presence of CO<sub>2</sub> affects the way in which cement hydrates and the phases that are formed.

## 1.0 CEMENTS IN GEOTHERMAL WELLS.

The cement which surrounds and hopefully protects the steel casing in a geothermal well, plays a vital role in its lifetime. Apart from providing a seal to both contain the high pressure steam and isolate the various zones through which the well is drilled, the cement is expected to help support the casing from crushing and buckling due to geotechnical pressures and provide corrosion protection to the steel due to its alkaline nature, particularly in aggressive fluids. Thus any loss in the cement sheath is likely to lead to a shortened life of the well casing and can lead to abandonment of the well.

Most of the recent efforts into developing well cementing formulations, which have largely been conducted by

overseas cementing companies, have been on ensuring placement and initial strength development of the fresh cement, particularly at elevated temperatures. New admixtures have been formulated and the physical problems of setting or thickening time, issues of lost circulation, development of water pockets, and setting control due to rising temperatures, have been paramount to ensuring a 'good' cement placement. As most of the work has been conducted in house and is proprietary information, published results are few and far between, particularly related to long term testing and performance. While there has been extensive research into problems associated with CO<sub>2</sub> sequestration, issues of cement durability in geothermal situations have not been as extensively investigated.

The expected operating lifetime for any well has increased, particularly as the cost of well completion has continued to escalate (Hole (2013)) so operators are looking of lifetime in excess of thirty years. However, durability of the hardened cement grout sheath is very much a chemical property and with the overall success in well cementing operations has largely been ignored. As more aggressive conditions are being encountered in geothermal systems the search is on for a cement system which will give an enhanced performance and longer life times.

### 1.1 Cement formulations for geothermal wells

Work conducted by Menzel (1939) showed that when a concrete with pure Portland cement as the binder is hydrothermally cured, the concrete compressive strength continued to decrease with time, a phenomenon termed *strength retrogression*. This term strictly applies to a progressive loss in compressive strength with time, along with an increase in permeability although it is often used to simply denote lower initial strength.

Pure Portland cement upon hydrothermal treatment or autoclaving, crystallises, to give a crystalline calcium silicate hydrate binder known as alpha dicalcium silicate hydrate,  $\alpha\text{-C}_2\text{SH}^1$ , along with portlandite,  $\text{Ca(OH)}_2$ . *Strength retrogression* was shown by Kalousek (1951) to be due to the continued growth of increasingly larger crystals of  $\alpha\text{-C}_2\text{SH}$  which particularly occurred in the presence of  $\text{Ca(OH)}_2$  which maintains a very high pH (>13) within the water filled pores in the system. This reduction in strength is even more pronounced at higher temperatures (above 200°C) where new phases such as reinhardbraunsite,  $\text{C}_5\text{S}_2\text{H}$ , and jaffeite,  $\text{C}_6\text{S}_2\text{H}_3$ , are formed that have very low strength. Subsequently, Kalousek and his coworkers (1951, 1954) found that addition of >40% fine quartz sand by weight of cement (BWOC) alleviated this continued strength loss. Thus, the practice of adding around 40%

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<sup>1</sup> Cement nomenclature used: C = CaO, S = SiO<sub>2</sub>, H = H<sub>2</sub>O, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>

silica flour (finely ground quartz) to well cement formulations has become the norm for cementing wells where the downhole temperature is above 120°C. At this temperature, a new, crystalline, low Ca/Si ratio calcium silicate hydrate forms, 11Å-tobermorite,  $C_5S_6H_5$ , which offers a low permeability, high strength binder that does not reduce in strength with time. Above 200°C, tobermorite transforms to a second low Ca/Si ratio crystalline phase, xonotlite,  $C_6S_6H$ , which is slightly more permeable but moderately strong and stable to around 600°C. Adding still more quartz can give rise to further compounds like truscottite,  $C_7S_{12}H_3$ , and gyrolite,  $C_8S_{12}H_9$ , although we have not seen these often in our work in New Zealand geothermal wells as they need special conditions to form.

As oil and gas wells were drilled to ever increasing depths, thickening time of a pumped cement became important. Levels of  $H_2S$  were often high and so in 1952, the American Petroleum Institute (API) created its own class of cements and a standard by which the properties of that cement could be tested. Today, API Class G cement is most widely used in our geothermal well cementing. This cement has a coarser particle size than normal construction cements (Class A) and contains less alkalis and less of the fast hydrating phases. In addition, it has been designed as a sulfate resisting cement, so it contains large amounts of the iron containing phase  $C_4AF$  that is slow to hydrate. In fact we find a lot of this phase remaining even after autoclaving.

Thus it appeared that the solution for geothermal well cement formulations for high temperatures had been found, with the addition of large amounts of silica flour (typically 40% BWOC or 30% by weight of blend) giving a high strength, impermeable binder. API recommendations and standards are used to assess fresh slurry properties, although these tend to be for lower temperatures than apply in geothermal conditions.

The fine quartz in silica flour is slow to react and researchers have explored the possibility of using a more reactive silica or pozzolan. Work by researchers such as Luke (2004) and Grabowski and Gillott (1989a, b) showed that tobermorite would only form if most of the co-blended silica was in the form of fine quartz. The normal silica-rich pozzolans used in regular concrete for additional strength did not lead to the formation of crystalline tobermorite and so their use was dismissed. With American cementing companies now providing most of the well cementing operations, the high silica flour formulations were used extensively in New Zealand wells until recently. There is the suggestion that even 40% BWOC is not sufficient control strength in the long term (Iverson, (2006)).

But our New Zealand conditions are different to those in the USA and we have to ask the questions:

- Are these high silica flour formulations durable?
- Will they give well lifetimes of say 80 years?
- What chemical reactions occur with the geothermal fluids and will they be detrimental to lifetime?

The answers to these questions will very much depend on the chemistry of the fluids with which the cement interacts, as the cement binder, even when hard, is a reactive material and whether the expected curing reactions actually take place downhole. This paper highlights some of the issues

with cement durability in the hostile environment of geothermal wells.

## 2. CARBONATION IN GEOTHERMAL GROUTS

Kennerley (1961) was the first to examine geothermal grout samples that had been subjected to down-hole exposure in fluids at Wairakei, New Zealand. These samples had been recovered in 1959 from the upper parts of Wairakei production wells cemented around 1950. After the results of that analysis proved somewhat inconclusive, a set of laboratory prepared samples were exposed in well fluids in the same field at a depth of several hundred metres and a temperature of 210-255°C and examined after one year. The samples recovered from the production wells typically showed the presence of calcite with only small amounts of crystalline calcium silicate hydrates remaining, while the laboratory samples prepared without addition of quartz, showed  $\alpha$ - $C_2SH$  as the binder in the central core, a phase which is rather weak and porous, along with  $Ca(OH)_2$ . This core was surrounded by a very thin calcite layer present on the outside of the samples. In laboratory samples where moderate amounts of a diatomaceous pumicite had been added, traces of xonotlite,  $C_6S_6H$ , were found, but the predominant crystalline calcium silicate hydrate binder phase was still  $\alpha$ - $C_2SH$ , although there was no  $Ca(OH)_2$  present. It had all reacted with the reactive silica from the pozzolan.

Carbonation of Portland cement is well known and documented. In a well-designed and moist, well-cured concrete, carbonation rarely progresses beyond the first 5-10 mm. The carbonation of  $Ca(OH)_2$  to calcite (Eq 1) is an expansive reaction which seals the pores of the surface layers of concrete preventing further ingress of  $CO_2$ .



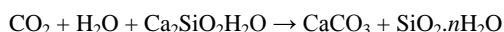
Carbonation reduces the pH of the pore solution by removing the buffer of solid  $Ca(OH)_2$  so that corrosion of the steel reinforcement may occur if the concrete is porous and carbonation goes deep enough. Steel corrosion is also an expansive reaction which results in cracking of the concrete, opening it to further attack and ongoing loss of strength.

Onan (1984) showed that  $CO_2$  would also attack the calcium silicate hydrate binder in oilwell cements as well as the  $Ca(OH)_2$ , although he was working with supercritical  $CO_2$  at low temperatures and not carbonated water at higher temperatures. The carbonation reaction is a through solution mechanism and relies on the pore water in the hydrated cement. It was Bruckdorfer (1986) who first showed that  $CO_2$  induced corrosion could occur with the cements used in enhanced recovery oil wells where  $CO_2$  was injected along with water, to flush residual oil. He suggested the use of pozzolans to slow carbonation as this would reduce the amount of  $Ca(OH)_2$  present and hopefully the carbonation overall.

In an extensive study at elevated temperatures, Milestone and co-workers at Brookhaven National Laboratory (Milestone et al., (1986a, b; 1987a, b) showed that removing the  $Ca(OH)_2$  by reaction with quartz to form the preferred crystalline phase tobermorite with its high strength, low permeability binding, did not give the expected durability against carbonation. They examined carbonation of a series of OPC/quartz blends over a range

of Ca/Si ratios from 2.5 to 0.6 at 150 and 250°C. While compressive strengths, the primary target of cementing engineers, improved with silica flour additions at both temperatures up to around 100% at 150°C and 40% at 250°C, the depth of carbonation, or carbonation resistance, was shown to correlate well with available Ca(OH)<sub>2</sub> content. In a paper presented at the 2013 workshop (Milestone et al. (2013)), we showed that any reduction of Ca concentration per unit volume gave rise to an increased rate of carbonation. It did not matter whether this reduction was due to additional water or aluminosilicate microspheres in an effort to decrease density, the rate of carbonation increased. Although we did not test foamed cement, the same reasoning would apply.

In well cement formulations where no added silica is used, carbonation of the sample is largely restricted to any Ca(OH)<sub>2</sub> present, giving rise to CaCO<sub>3</sub> (calcite) which forms as a skin of decreased permeability around the outside of the sample slowing any subsequent attack. If any calcium silicate hydrates are attacked, particularly if Ca(OH)<sub>2</sub> is not present, they carbonate to metastable CaCO<sub>3</sub> (aragonite) at 150°C. So it is easy to see which phases were being attacked. The reaction is shown in Eq 3.



The ready availability of soluble SiO<sub>2</sub> often gives rise to significant amounts of amorphous CaCO<sub>3</sub> in addition to the crystalline forms, and readily detected by thermogravimetry, (da Silva (2014)). In low Ca/Si ratio formulations where sufficient quartz has been added to form tobermorite (at 150°C) and xonotlite (at 250°C), rapid carbonation occurs to give aragonite and calcite respectively. With no Ca(OH)<sub>2</sub> present, there is a marked increase in permeability when this occurs at both temperatures. All this can largely be deduced by examining the changes in the solid molar volumes (Table 1).

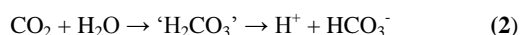
The interaction of CO<sub>2</sub> with well cements is proving an important issue in the efforts of sequestering CO<sub>2</sub> in abandoned oil wells. Research by Duguid and coworkers (2005, 2010, 2011), and Kutchko and coworkers (2007, 2008, 2009) have shown multiple reactions occur with carbonation a key influence, but that the C-S-H is attacked. Different results are obtained if scCO<sub>2</sub> or CO<sub>2</sub> saturated brine are used. Jacquemet et al. (2012) described the formation of a carbonated sheath that provides protection as the cements used do not usually have added silica so the Ca/Si ratio is high. Addition of a pozzolan to a Class H cement gave inferior results on carbonation (Kutchko et al. (2009)). These instances of damage by carbonation all take place at temperatures that are very much lower than those encountered in geothermal conditions and where the calcium silicate binder probably has not crystallised but they clearly illustrate that carbonation occurs rapidly, especially if water is present.

### 3.0 CEMENT CORROSION

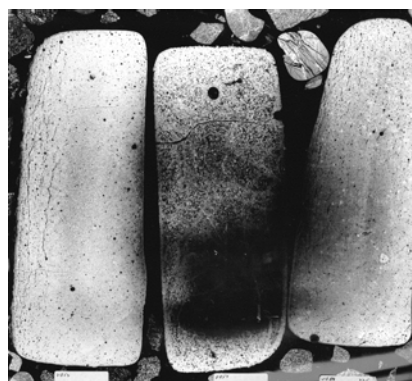
Initially, it was thought that carbonation only increased strength, something we have noted in our work. But what is it in our New Zealand fluids that limit durability of the cement in our wells? Perhaps the most important aspect is that our reservoirs contain “wet steam” as opposed to the “dry steam” found in the other parts of the world such as USA and Italy. This means that solubility of the various chemical species in the geothermal fluids is extremely

important along with the fluid composition itself which can lead to corrosion.

The first instance of issues linked with cement carbonation and corrosion were encountered with workover of the Okaaki wells prior to production testing for the new geothermal power station in the 1980's. Perforation of the casing due to metal corrosion in wells that had been shut in for some time was reported by Bixley and Wilson (1985). Issues with casing corrosion has been discussed more recently by Zarrouk (2004). This implied the cement was no longer providing the alkaline environment protecting the steel but the down hole chemistry was not well understood. It took some careful work by Hedenquist (1990) to isolate the problem as due to a CO<sub>2</sub>-rich zone some 400m below surface where fluid temperatures were around 150°C, well below the production fluid temperature of ~260°. The CO<sub>2</sub> concentration in this zone was high enough that the fluids were mildly acidic with ‘carbonic acid’ (Eq 2). Later work has shown similar zones occur in other fields.



In the early 1980's, initial downhole trials at Ohaaki of cement formulations containing a range of silica additions, as the effects of strength regression were well understood by then, showed unexpectedly that considerable corrosion of the cement had occurred, with up to 60% of the hardened cement volume lost in 6 months. In addition, the samples were almost fully carbonated with CaCO<sub>3</sub> (aragonite) the principal phase present. (Fig 1).



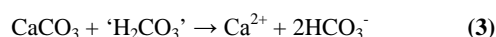
**Figure 1: Thin section of corroded samples from Ohaaki exposure**

Studying cement corrosion in the laboratory is difficult as saturation occurs rapidly. Large volumes of water flowing per sample are needed to ensure corrosion occurs within a sensible time. Finding a well where the acidic CO<sub>2</sub> rich zone can be tapped for downhole exposure or even surface exposure in a sealed vessel is not easy as this zone lies well above the production zone where the CO<sub>2</sub> concentrations are rarely high enough for the fluids to be acidic making it difficult to study cement corrosion. We have found generally, that cement formulations which carbonate rapidly due to increased permeability upon carbonation also corrode quickly. Corrosion of the carbonated cement is due to dissolution of CaCO<sub>3</sub> by carbonic acid (Eq 3)

**Table 1: Percentage Change in solid volume upon carbonation**

Compound	Ca/Si	MV	% change in solid MV of carbonated silicate*
CaCO <sub>3</sub> (calcite)	∞		0
CaCO <sub>3</sub> (aragonite)	∞		-8.2 going to calcite
Ca(OH) <sub>2</sub>	∞	74	+11.06
α-C <sub>2</sub> SH	2	68.84	+7.21
C <sub>6</sub> S <sub>5</sub> H <sub>5</sub> (tobermorite)	0.83	289.04	-36.17
C <sub>6</sub> S <sub>6</sub> H (xonotlite)	1.0	264.81	-16.39
C <sub>6</sub> S <sub>2</sub> H <sub>3</sub> (jaffeite)	3	458.61	-14.71
C <sub>5</sub> S <sub>2</sub> H (reinhardbraunsite)	2.5	419.57	+24.89
C <sub>6</sub> S <sub>4</sub> H (killalaite)	1.5	202.32	-0.77
C <sub>3</sub> S <sub>2</sub> (kilchoanite)	1.5	288.4	+14.77

\*Formation of calcite and assumes water is lost and hydrated SiO<sub>2</sub> does not contribute to the solid volume as it dissolves or is present as a gel which offers no solid contribution to a binder.



At the surface, oxidation of H<sub>2</sub>S will create H<sub>2</sub>SO<sub>4</sub> giving a pH typically around 2, so acid sulfate attack occurs. It is clear that lifetimes of Portland based cements will be shorter than required in zones where the fluids are acidic. Low pH fluids driven by sulfur acids will always attack any form of a calcium silicate binder and we see that at shallow depths in sewer lines in Rotorua and some of the early wells at Rotokawa (Milestone and Aldridge, 1990).

#### 4.0 ALTERNATIVE CEMENTING SYSTEMS WHICH MIGHT BE MORE CARBONATION/ACID RESISTANT

There are several cementing systems which have the potential to be more acid resistant, but getting them to the stage where they can be used for cementing a well is a challenge. In well cementing, the cement grout is pumped into place and so a controllable thickening time is essential, particularly at elevated temperatures. The wells at Wairakei were quenched before cementing to around 40°C while in the 1980's, cementing was undertaken at 60°C. This has often led to long recovery times of the wells so today, drilling fluid is circulated to cool the well to around 90°C. There is evidence that once circulation stops in preparation to cementing, the bottom hole temperature can rise again quickly (Kabinoff et al. (1992). At this temperature the cement hydration mechanism changes and many of the admixtures used lose their effectiveness above this temperature (Collier et al. (2015) so new tests are required over and above the standard API ones.

#### 4.1 Calcium aluminate cement

A phosphate modified calcium aluminate cement was developed by Sugama and Carciello (1991, 1992, 1993) and shown to be carbonation resistant. A modified form of that system has been commercialized by Halliburton as ThermoLock™. A number of wells both in New Zealand

and overseas where acidic fluids have been encountered have been cemented with it although no detailed test results have been reported. However, controlling the setting of this system is difficult, even at low temperatures (Swift, 2014), and problems have been encountered in using it New Zealand wells.

#### 4.2 Calcium aluminosilicate systems

Roy and coworkers (Roy et al. (1980), Langton et al. (1980)) were the first to examine this system for high temperature cementing as they felt that being similar to rock formations, it would provide greater stability at high temperatures and be resistant to carbonation. The phase they targeted was anorthite, (CAS<sub>2</sub>) using various cements and oxides as starting materials but problems obtaining suitable slurries and setting times were noted. This system has been further explored recently by Borglum et al. (2005) and Barlet-Gouedard and Goffe (2005) but starting from a calcium aluminate cement. We have tried a number of the Roy formulations but the only binder we have been able to form are the hydrogarnet phases katoite (C<sub>3</sub>ASH<sub>4</sub>) or hibschite (C<sub>3</sub>AS<sub>2</sub>H), both of which are very weak and anorthite did not form. It is a high temperature phase so that is perhaps not surprising.

A detailed investigation of the aluminosilicate phases formed under hydrothermal conditions was studied by the research group at Edinburgh. (Meller et al. (2005, 2009); Kyritsis et al. (2009a, b)) although these were often synthesised from pure compounds. When alumina is added to cement, the most common phase formed at 200°C is hydrogarnet, although other phases such as portlandite, jaffeite and α-C<sub>2</sub>SH can also form. While quartz additions of more than 20% BWOC gave good binders with xonotlite, gyrolite or truscottite forming, 20% Al<sub>2</sub>O<sub>3</sub> additions gave rise to hydrogarnets which exhibited very poor binder properties due to their permeable nature.

We have found addition of blast furnace slag also forms hydrogarnets with the predominant phase being the siliated katoite, ( $C_3ASH_4$ ), (Grant-Taylor et al (1996). While this phase offers good carbonation resistance, it forms a very poor binder with little strength. Recent work by Alp and Aitkin (2013) suggest that pure slags hydrated at elevated temperatures may give better results.

### 4.3 Inorganic polymer systems

Geopolymers or inorganic polymers based on the reaction of strong alkalis with reactive silicates would appear to have good potential. First described in detail by Davidovits (1991), they are claimed to have high acid resistance. There has been a suggestion these materials are suitable for use in  $CO_2$  sequestration wells (Nasvi et al. (2011, 2012) but no testing has been done. In many respects these are similar to the cement system developed by the South West Research Institute (SWRI) as part of the DOE investigation in the late 1970s (Curtis and Mallow (1979). In both systems, a strong sodium aluminosilicate binder can be prepared by reacting a concentrated alkaline solution with a reactive usually amorphous aluminosilicate and curing, usually at elevated temperatures. In the SWRI cement, the sodium silicate was added as a powder with activation occurring with alumina at hydrothermal conditions whereas with a geopolymer, a sodium silicate/hydroxide solution is used to activate a reactive aluminosilicate precursor which usually requires heating to cure.

Our trials with these systems show that when they have been cast in steel moulds before exposure to  $CO_2$  conditions set and cured, they do indeed show that they are carbonation resistant. However, when these systems are cast in porous moulds, such as hollowed out ignimbrite samples, and then allowed to “set” and cure in water in the autoclave, they either do not set or become porous and weak. Clearly the highly soluble sodium hydroxide or sodium silicate leaches to the surroundings so these systems will not function underwater, in other words they are not truly hydraulic cements.

We will continue to work with this system as it offers the best potential for an acid resistant cement but it requires a retarder system that will work reliably at temperatures above  $90^\circ C$  and preferably higher, to allow pumping as well as a gelling agent to try and retain the soluble reactants.

### 5.0 WHAT IS THE MOST DURABLE CEMENT FORMULATION BASED ON API CLASS G CEMENTS?

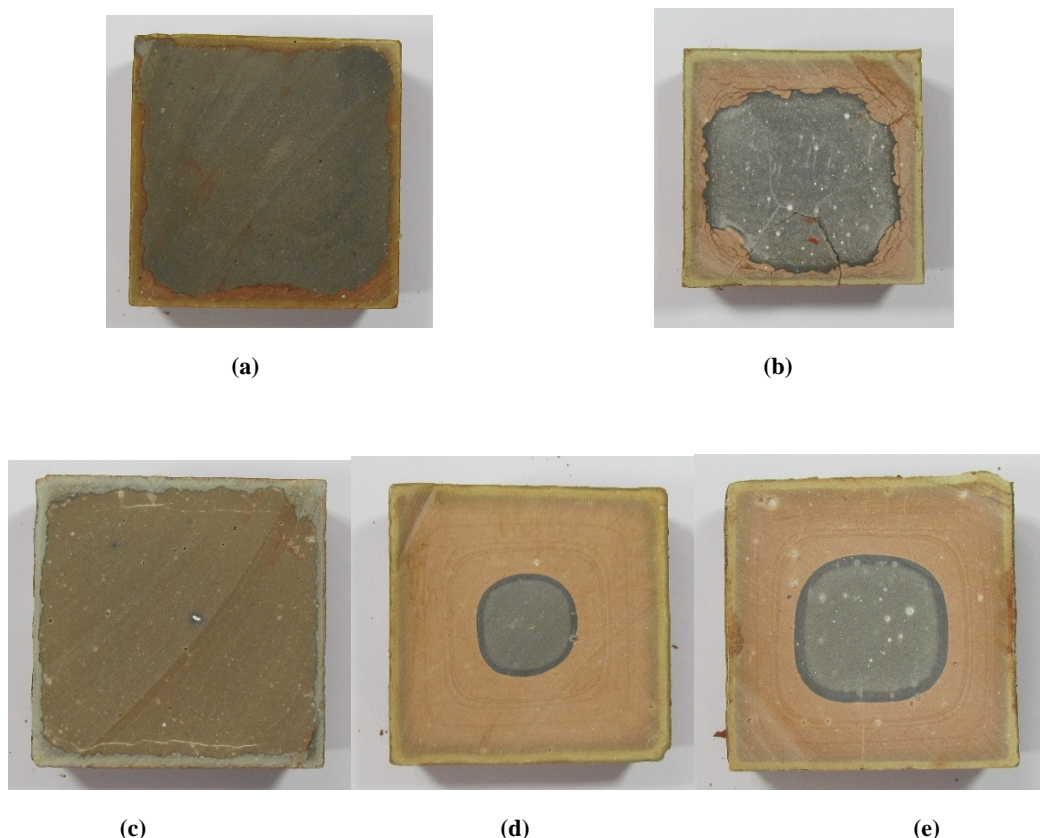
It is clear that a workable, non-Portland well cementing system that can be placed successfully in a geothermal situation and will cure to give a strong impermeable binder is still some distance away. This means we must look at extending the API Class G system where the reactants other than water are insoluble and seek a compromise between strength and durability in carbonated fluids.

If only 20% silica flour BWOB is added to a Class G cement, then all the  $Ca(OH)_2$  is removed by reaction with  $SiO_2$  and only  $\alpha-C_2SH$  crystallises. (Milestone and Aldridge, 1988). This formulation does give a reduced strength compared to that obtained with 40% silica flour when tobermorite forms, but the strength is largely retained with time as there is little tendency for crystal growth in the lower pH environment. As shown in Table 1, carbonation of  $\alpha-C_2SH$  is expansive so a protective sheath forms slowing any further reaction. As the temperature increases,  $\alpha-C_2SH$  will recrystallise to yet another calcium silicate hydrate phase, killalaite,  $C_6S_4H$ , which has moderate strength at higher temperatures and has been reported previously. This phase will carbonate but there is little loss in solid volume (Table 1) so the porosity/permeability does not increase.

A more exciting advance, is the addition of 20% Microsilica 600 as described in detail in the paper being presented by Matt Sharp. With addition of this material, reaction of the silica with  $Ca(OH)_2$  is rapid so  $Ca^{2+}$  ions are not removed by reaction with carbonated waters meaning more binder is formed. Crystallisation of the calcium silicate hydrate binder is limited as the pH has already fallen due to  $Ca(OH)_2$  removal so there is no ongoing crystal growth and consequently no *strength retrogression*. Good strength is obtained, which while lower than that obtained when tobermorite forms, decreases little with time, both at  $150^\circ$  and  $290^\circ C$ . Carbonation only forms an impermeable layer on the outside of samples so corrosion is slow as it is only the carbonated layer that corrodes.

In Figure 2, the effects of carbonation on the various forms and additions of silica are shown after 6 months exposure in a laboratory autoclave where 45 bars of  $CO_2$  pressure were applied in a flow through system. Figure 2a shows a pure Class G cement. Its strength is low but there is only a thin carbonation sheath. Fig 2b shows a sample with 20% silica flour. The strength is considerably higher but the carbonation sheath is greater than the pure cement. Fig 2c shows the addition of 20% Microsilica 600. Carbonation is less than with silica flour and comparable to pure cement but there is reasonable strength. Carbonation of the 40% quartz flour addition sample is extensive (Fig 2d), the extent depending on whether the sample was procured in a  $CO_2$  free environment or not. The strength measured is largely due to the calcium carbonate formed. Curing in a  $CO_2$  containing environment leads to increased overall carbonation as some of the  $Ca(OH)_2$  generated by cement hydration is immediately carbonated and unavailable to form a binding phase. Fig 2d is a sample cured for 14 days before being admitted to carbonated water. The extent of carbonation is considerably less.





**Figure 2: Carbonation rims in samples with varying amounts of added silica after 6 months exposure in carbonated water**

- (a) Pure Class G cement
- (b) Class G cement plus 20% silica flour
- (c) Class G cement plus 20% Microsilica 600
- (d) Class G cement plus 40% silica flour (carbonated water curing)
- (e) Class G cement plus 40% silica flour (precured without CO<sub>2</sub>)

## 6.0 CONCLUDING REMARKS

In New Zealand, waters trapped below impermeable zones can be so high in CO<sub>2</sub> concentration they become mildly acidic. Carbonation of the cement will occur followed by corrosion leading to shortened well lifetimes.

The conventional geothermal well formulation, API Class G cement plus 40% quartz flour BWOC designed to counter *strength retrogression*, is not carbonation resistant, rapidly carbonating and becoming more porous. The carbonated layer readily corrodes in mildly acidic conditions created by high concentrations of CO<sub>2</sub>.

Conditions under which the cement cures are important. Above 90°C many admixtures do not function well. Exposure to carbonated water decreases the amount of binder that can form as CO<sub>2</sub> precipitates any available Ca<sup>2+</sup> ions as CaCO<sub>3</sub>.

While any Portland cement system will not ultimately be stable in mildly acidic environments, the best compromise is a formulation where additions of ~20% BWOB of Microsilica 600 is used. While this does not provide the highest strength, it provides the greatest carbonation resistance, forming an impermeable carbonation sheath.

The aluminosilicate system appears carbonation resistant but work is still needed to develop a non-Portland cement system that be placed and reliably pumped.

## 7.0 ACKNOWLEDGEMENTS

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