THE ROLE OF SILICA IN GEOTHERMAL CEMENTING

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ABSTRACT

When pure Portland oil well cements are heated hydrothermally, the calcium silicate hydrate binder crystallises. The phases formed depend on several factors which include temperature and Ca/Si ratio. Without added silica, alpha di-calcium silicate hydrate, αC_2SH, forms along with $Ca(OH)_2$ between 120 and 200°C, while above 200°C, phases such as reinhardbraunsite, C_5S_2H, and jaffeite, $C_4S_3H_3$, form together with $Ca(OH)_2$. These high Ca/Si ratio phases are weak, porous binders which undergo "strength retrogression" where strength decreases with time.

In the 1950's, Kalousek showed that by adding ~40% silica flour (quartz) by weight of cement (BWOC), high strength, low Ca/Si ratio phases formed, tobermorite around 150°C and xonotlite above 200°C. These phases avoid strength retrogression and high additions of silica flour to oil well cements have formed the basis of all geothermal cement formulations used in recent years. Research into using other forms of silica to replace quartz has not been successful in forming tobermorite.

However, both tobermorite and xonotlite carbonate very readily in the CO_2 rich fluids of New Zealand geothermal fields and become porous. The carbonated layer readily dissolves if the concentrations of CO_2 in the surrounding fluid make it mildly acidic so the steel casing is no longer protected and will corrode. In contrast, carbonation of the weak high Ca/Si ratio phases forms an impermeable carbonation sheath around the samples slowing the rate of carbonation. By adding only 20% silica flour, the $Ca(OH)_2$ is removed and although the final strength of the αC_2SH binder formed is lower than that of tobermorite, the on-going loss in strength is reduced, and the binder has reasonable carbonation resistance.

Recently, a natural hydrothermal amorphous silica from New Zealand, Microsilica 600 (MS600), has been used in cement formulations that have shown marked advantages in carbonation resistance. Unlike with crystalline quartz, we have found that additions of MS600 of around 20% BWOC, give an amorphous calcium silicate hydrate which does not crystallise at hydrothermal temperatures. This binder has good strength that does not decrease over 6 months, even when heated to 300°C. Laboratory autoclave experiments in CO_2 saturated water (6 bar) show carbonation is limited to a thin sheath which increases slowly with time. The formation of this sheath can be improved by addition of a small amount of $Ca(OH)_2$ to the formulation. It appears that MS600 reacts rapidly with $Ca(OH)_2$ before the hydrating cement can carbonate and the resulting product does not crystallise, so strength retrogression does not occur.

1.0 INTRODUCTION

1.1 Role of cement

To obtain and control steam from a geothermal well requires that the well casing be firmly anchored to the formation. This is usually achieved by pumping a carefully formulated cement slurry down through the steel well casing and up through the annulus between the casing and the edge of the drilled hole before the cement sets. Once hardened the cement plays several important roles:

- It must provide a seal between the production fluids and the casing to ensure the steam can be delivered to the surface in a controlled way.
- It ensures the different zones within the well continue to remain isolated from each other
- It provides support to the casing
- It provides corrosion protection for the steel casing.

Traditionally, the cement formulations used for wells have been based on calcium silicate cements typified by Portland cement. While construction Portland cements have been used in the past, the requirements of well cements are different to those of construction and a series of Portland based oil well cements have been specified by the American Petroleum Institute (API), classes A to H depending on requirements. Within these classes, they are further subdivided by chemistry differences in sulphate resistance by reducing the tricalcium aluminate, C_3A^*, content.

1.2 Effects of Temperature on hydration

It is well known in construction that 'steam curing' above 60°C at atmospheric pressure can lead to a reduction in strength. Paul and Glasser (2000) attributed this to a denser hydration product which formed quickly preventing on-going hydration of the cement particles. Menzel (1934) found that when a cementitious composite was autoclaved, there was a notable reduction in strength over a conventionally cured composite. But it was work by Kalousek (1951) who showed that this was due to crystallization of the calcium silicate hydrate to giving a well defined product known as alpha dicalcium silicate hydrate (αC_2SH) along with calcium hydroxide ($Ca(OH)_2$). The crystals of αC_2SH are dense and contain little water so the matrix becomes permeable and is weak. In the highly alkaline matrix dictated by the presence of $Ca(OH)_2$, the αC_2SH crystals continue to grow giving rise to the phenomenon known as ***strength retrogression***.

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*Cement nomenclature C=CaO; A=Al_2O_3; S=SiO_2; H=H_2O

Later Kalousek and Adams (1954, 1955) established the reactions that occur upon autoclaving and showed that if around 40% fine quartz sand was added, strength could be maintained. They found this was due to the formation of a new crystalline phase with a low Ca/Si ratio, tobermorite ($C_5S_6H_5$). This crystallises in a fibre-like form which includes water in the structure so is a lot less dense than αC_2SH. The fine needle-like crystals lock together well so tobermorite functions as a very good binder. The $Ca(OH)_2$ formed from hydrating cement reacts with the quartz forming additional binder so the composites are strong and impermeable. Additions of around 40% quartz flour have become the norm in wells where down hole temperatures exceed ~120°C and this avoids the problems associated with strength retrogression.

Above 200°C, tobermorite converts to another low Ca/Si ratio phase, xonotlite (C_6S_6H), while the high Ca/Si ratio phase αC_2SH slowly converts to kilchoanite (C_3S_2) and reinhardbraunsite ($C_5S_2H_2$). While xonotlite retains much of the strength of tobermorite, it contains less water and is slightly more permeable although the strength remains comparable. However, the high Ca/Si ratio phases made from pure Portland cement continue to lose strength and become even more permeable and are avoided in wells. In recent work Iverson et al. (2010) have shown that even adding 40% silica flour may not ensure that strength is maintained and they have recommended that up to 60% be added.

The reaction of $Ca(OH)_2$ with fine quartz is slow below 150°C. Klimesch in her PhD study (2000) found that additions of aluminium containing kaolinite or metakaolinite greatly improved the rate at which quartz reacted. She showed the reaction usually proceeded via αC_2SH. The tobermorite product formed contained aluminium and had some advantageous properties.

Tobermorite is also the binder in commercial autoclaved fibre cement products. These are manufactured from a slurry of ~40-60% quartz flour, cement and ~8% cellulose fibre via the Hatscheck process. The green products are allowed to hydrate, often with steam curing, for several hours before undergoing autoclaving at 175°C for up to 16 hours. However, in this short time, only the finer fraction of quartz reacts, forming a layer of tobermorite around the quartz grains which act as a form of fine reinforcement.

The quartz/ $Ca(OH)_2$ reaction is rather slow and the use of other forms of silica has been examined. But addition of other forms of silica tends not to give rise to tobermorite and so their use has not been actively pursued. Why only quartz gives rise to tobermorite is not well understood, but is believed to be associated with the rate of solubility of the quartz.

2.0 EFFECT OF QUARTZ ADDITIONS ON DURABILITY

Binders based on tobermorite and xonotlite function well in alkaline highly saline conditions, but do not perform well in New Zealand fields where down-hole fluids are acidic due to high concentrations of dissolved CO_2. While carbonation had previously been encountered overseas, the formation of calcium carbonate was not considered a problem as strength was little affected. However, in the wet steam environment in New Zealand fields the carbonated material can readily dissolve as the bicarbonate in the acid fluids. In many fields, this acidic layer lies well above the production fluid, forming a corrosive zone where the cement is readily dissolved and attack on the steel casing occurs. Studies by Milestone and Aldridge (2000) showed that up to 60% of a volume could be lost in 6 months. Surprisingly, it was the low strength, high Ca/Si ratio phases that proved more resistant to carbonation and corrosion.

The reason for this is associated with the molar volumes of the phases. When tobermorite carbonates the solid volume of the resulting carbonated phase is only 60% of the original volume of tobermorite giving increased porosity and permeability, while for αC_2SH, the solid volume increases, reducing porosity and permeability resulting in the formation of an impermeable carbonation sheath which only slowly dissolves. The same is also true at higher temperatures although corrosion is normally not a problem in production fluids.

Following an extensive study involving down-hole testing, Milestone and Aldridge (2000) recommended a grout where only 20% silica flour was added. Under hydrothermal conditions, the fine quartz reacted with $Ca(OH)_2$ leaving αC_2SH as the binding phase. While this phase does not provide the high strength given by tobermorite, because there is no $Ca(OH)_2$ present controlling the internal pH, the expected strength retrogression does not occur. At higher temperatures, the αC_2SH (without the presence of $Ca(OH)_2$) converts to yet another phase, killalaite (C_6S_4H), which is weaker but proves carbonation resistant (Milestone et al. (1987b)

The potential for using forms of silica other than quartz, such as supplementary cementing materials (SCMs) pulverised fuel ash (PFA), blast furnace slag (BFS) or amorphous silica, has advantages in hydrothermal curing. These reactive silica additives could react quickly with the $Ca(OH)_2$ formed during initial hydration and reduce the internal pH. This rapid reaction competes with carbonation during hydration and ensures most of the calcium becomes a calcium silicate hydrate rather than calcium carbonate (Milestone et al. (2012). This could slow the growth of large crystals of αC_2SH in geothermal wells (as seen with 20% quartz addition). The cellulose degradation shown to occur during the ambient precuring of autoclaved fibre cement products (Milestone and Suckling (2004)) is also caused by a combination of high pH and available Ca^{2+} ions due to slow reaction of quartz so use of a reactive amorphous silica would also prevent attack on cellulose fibres.

In recent work, Bigley et al. (2010) described additions of naturally occurring amorphous silica (MS600), readily available in New Zealand, to geothermal well cements. The use of this material as a pozzolan for concrete was described by Chisholm (1997). It reacts quickly with $Ca(OH)_2$, unlike quartz which requires hydrothermal conditions. With 20% addition and hydrothermal treatment, the binder formed is amorphous, slow to carbonate and performs well up to 300°C.

This paper describes addition of several types of siliceous additives and their effect on tobermorite formation and likely use for geothermal cement formulations.

3.0 EXPERIMENTAL

3.1 Additions of slag and PFA

Powders used were OPC (CEM1 Castle cement UK), PFA and BFS supplied by NNL UK, with compositions given in Table 1. The BFS was coarser than the slag normally used for construction ($260m^2g^{-1}$ instead of $450m^2g^{-1}$). Natural crystalline quartz of purity 99% was ball milled to a median particle size of 18µm and used. XRD analysis of the PFA showed it to contain ~3-5% quartz and a small amount of hematite, while the BFS contained 3-5 % gehlenite.

Table 1: Chemical analysis of raw materials

Oxide	OPC	BFS	PFA
CaO	64.6	42.1	1.44
SiO_2	21.0	34.5	48.64
Al_2O_3	5.2	13.7	25.88
Fe_2O_3	2.6	1.0	7.57
MgO	2.1	7.3	1.42
SO_3	2.5	-	1.20
K_2O	0.6	0.5	2.83
Na_2O	0.3	0.2	1.91
LOI	0.7	-1.1	4.16

Mixtures of OPC, PFA and quartz covering the range from pure OPC to a 1:1:1 cement:PFA:quartz tri-blend were prepared with a w/s ratio of 0.4, poured into cut down polycarbonate tubes and heated in sealed vessels at 160°C for up to 90 days. Similar mixtures of cement plus BFS were also prepared and subjected to the same autoclaving regime.

pH of the liquid in the mix was measured before initial set using a pH electrode.

Samples were removed from reaction vessels, dried with acetone and examined by XRD and SEM.

3.2 Addition of Microsilica 600

Microsilica 600 is amorphous hydrothermal silica supplied by Golden Bay Microsilica. It has a typical particle size of 1-10µm. Blends of Class G cement and 10, 15 and 20% additions MS600 were prepared, cast as 100x100x100 mm cubes and cured at 90°C before autoclaving at 150°C and 300°C for periods up to 6 months with an overpressure of CO_2 of 6 bars. Samples were tested for compressive strength and composition as well as carbonation depth.

4.0 RESULTS

4.1 BFS and PFA

4.1.1 pH during precuring

Table 2 shows that the pH of the initial liquid in the samples with a 1:1 blend of the SCMs is reduced by approximately 1 pH unit over OPC. Addition of quartz makes little difference to the solution pH since at ambient temperatures, no reaction occurs with $Ca(OH)_2$, although there was some adsorption of hydroxyl ions onto the surface of the fine quartz reducing the pH slightly.

Table 2: pH of cement blends

	OPC	1:1 OPC + quartz	1:1 OPC + PFA	1:1 OPC + BFS	OPC + 20% MS600
pH	13.3	13.0	12.3	12.4	12.2

4.1.2 Phases formed upon autoclaving

OPC

Initially, $Ca(OH)_2$ was the only crystalline product formed from autoclaving OPC (Table 3) along with an amorphous C-S-H, but with increasing time of heating, crystalline α-C_2SH formed which increased in both amount and crystallinity with time. The samples became softer, so at 90 days could be scratched easily with a pencil.

Quartz addition

As expected, (Table 3) the final calcium silicate hydrate product formed at 1:1 addition of quartz was 11Å tobermorite but for this cement, it took 7 days before a well-crystallised product was formed at 160°C, although small peaks were visible at 1 day. At no time was $Ca(OH)_2$ detected after autoclaving. After 90 days, the predominant peaks present were those due to tobermorite but not all the quartz had reacted.

Table 3: Phases formed with OPC and quartz

Composition	1 day	3 days	7 days	90 days
OPC	CH + amorphous	CH + amorphous	CH, αC_2SH	CH, αC_2SH
OPC : quartz (1:1)	Quartz, tobermorite (tr)	Quartz, tobermorite	quartz, tobermorite	tobermorite, quartz

3.1.2 Samples with PFA additions

With a 1:1 ratio of OPC:PFA, tobermorite is eventually formed although it takes 7 days before there is any trace of it and 90 days before a significant amount is formed. (Table 4) With higher PFA additions (OPC:PFA = 1:3), tobermorite was not formed, even after 90 days autoclaving and the sample remained amorphous (Table 4). Free $Ca(OH)_2$ was not observed at any age by XRD. With flyash/quartz mixtures tobermorite did form, but the rate of reaction was slow and depended on the total amount of silica present. A typical XRD trace for the sample 1:0.5:0.5 OPC:PFA:qtz is shown in Figure 1. The ratio Ca/Si needed to be close to 1 with quartz present for crystalline tobermorite to form.

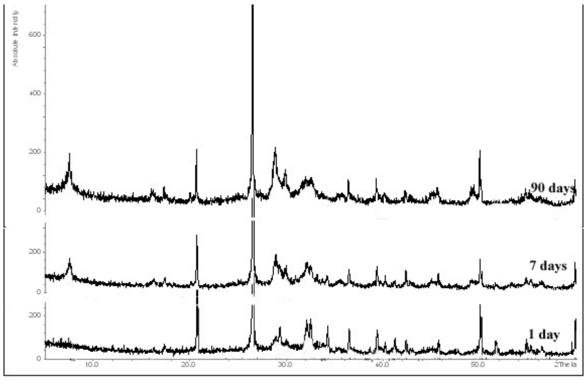

Figure 1: XRD traces of a 1:0.5:0.5 OPC:PFA:quartz blend autoclaved at 160°C. Diagnostic peak for tobermorite is at ~7° 2Θ

4.1.3 Samples with BFS additions

With slag additions only, the hydrogarnite phase, siliated katoite, C_3ASH_4, is ultimately formed (Table 5) indicating a different formation mechanism to that of tobermorite (Fig 2). This phase did not transform through to tobermorite, although it did coexist with αC_2SH indicating that the Ca:Si ratio has not been reduced far enough for the formation of tobermorite. The presence of $Ca(OH)_2$ confirms the high Ca:Si ratio. Gehlinite does not appear to react but small amounts of hydrotalcite are formed from the magnesium in the slag. With increasing amounts of quartz, αC_2SH_2 is formed until the Ca:Si ratio reduces to the level where tobermorite has formed in small amounts by 90 days. (Fig 3).

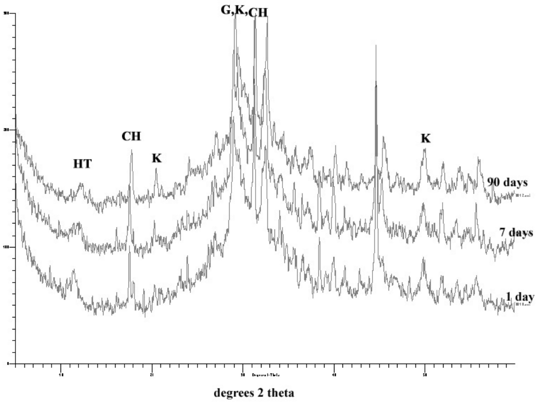

Figure 2: XRD traces of 1:3 OPC:BFS autoclaved at 160°C. HT, hydrotalcite; CH $Ca(OH)_2$; K katoite; g gehlinite

4.1.4 Additions of MS600

Compressive strengths of various addition rates of MS600 are shown in Table 6. These strengths are less than those obtained with 40% quartz addition but adequate for well cementing. The binder is amorphous and remains so for up to 6 months curing at 300°C. Carbonation of this binder is limited to a thin carbonation sheath.

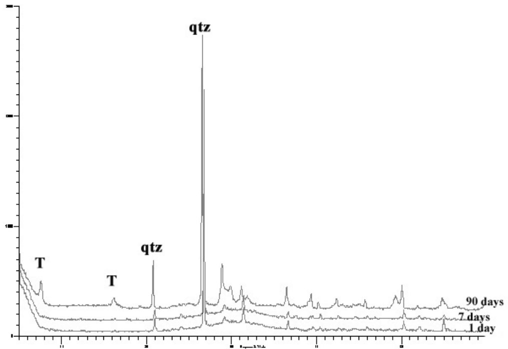

Figure 3: XRD trace of 0:5:2 OPC:BFS:quartz.

5. 0 DISCUSSION

The bulk of binder formed with additions of both PFA and MS600 after autoclaving is an amorphous calcium silicate hydrate with tobermorite, the preferred high strength binder, not forming. PFA, BFS and MS600 all contain reactive silica, so any available $Ca(OH)_2$ is rapidly bound into a calcium silicate hydrate, reducing the initial pH of the hydrating cement pore solution. This immediate removal of $Ca(OH)_2$ prevents a subsequent reaction with quartz and probably contributes to the lack of crystalline tobermorite formed since the pH is lowered. Ma and Brown (1997) showed that by increasing the pH with NaOH, tobermorite would form. This reduced pH could also provide some relief for cellulose degradation in autoclaved products. The small amount of quartz in the PFA does ultimately allow tobermorite crystallization but the amount formed is small. For BFS additions, while the initial binder is amorphous, it ultimately crystallises to α-C_2SH and katoite, a low strength calcium aluminosilicate. No product crystallises from MS600 addition even after 6 months of autoclaving at temperatures up to 300°C. Tobermorite will only form when additional quartz was added confirming that if there is not sufficient quartz present, a binder with lower strength is formed.

A cement/quartz ratio of 4:6 is now commonly used in industrial autoclaved products, giving Ca:Si molar ratios in the composite of 0.38. Tobermorite, $C_5S_6H_5$, has a Ca:Si ratio of 0.83 so in practice, this means that only the fine quartz will react leaving a significant quartz remaining. The quartz particles show only a small rim of reacted material by electron microscopy so a large proportion of the quartz remains as an inert filler. Despite this slow reaction, it is rare to find $Ca(OH)_2$ in freshly autoclaved commercial products although significant amounts of $CaCO_3$ are common. The boards are porous so low pressure steam curing probably accentuates carbonation, at least at the exterior of the stacks of sheets. The presence of $CaCO_3$ has been associated with increased amounts of

Table 4: Phases formed with PFA/quartz additions

Composition	1 day	3 days	7 days	90 days
OPC : PFA (1:1)	quartz* (tr)	Amorphous and quartz (tr)	tobermorite (tr) and amorphous	tobermorite and amorphous
OPC : PFA (1:3)	quartz (tr)	quartz (tr)	quartz (tr)	amorphous
OPC : PFA : quartz (1:0 5:0 0.5)	quartz	tobermorite (tr) quartz	Tobermorite, quartz	Tobermorite, quartz
OPC : PFA : quartz (1:1:1)	quartz	amorphous and quartz	tobermorite (poorly crystalline) quartz	tobermorite (poorly crystalline) quartz

Table 5: Phases formed with BFS/quartz additions

Composition	1 day	7 days	90 days
OPC:BFS =3:2	CH + amorphous	CH, katoite amorphous	CH, katoite, αC_2SH
OPC:BFS =4:3	CH + amorphous	αC_2SH(tr) amorphous	αC_2SH katoite, a
OPC:BFS =3:4	amorphous	katoite (tr), amorphous	αC_2SH, katoite
Pure BFS	amorphous	Amorphous	αC_2SH(tr)
OPC:BFS:Qtz =1:9:4	amorphous, qtz	amorphous, qtz	αC_2SH(tr), katoite
OPC:BFS:qtz =5:15:8	amorphous, qtz		Tobermorite (tr) qtz
BFS:Qtz = 5:2	amorphous + qtz	αC_2SH(tr), qtz	Tobermorite (tr) qtz

Table 6: Compressive strengths of MS600 additions

% Silica in Blend	168day UCS Mpa 20°C	84day UCS Mpa 90°C	168day UCS Mpa 90°C	28day UCS Mpa 150°C	84day UCS Mpa 150°C	168day UCS Mpa 150°C	28day UCS Mpa 300°C	84day UCS Mpa 300°C
0%	19	47	54		45	28	13	18
10%	55	47	42	7.7	3			
20%	45	47	53	65	38	57	38	30

tobermorite formation as it has the effect of lowering the available Ca. In geothermal wells, the carbonated fluids will rapidly carbonate $Ca(OH)_2$ from the hydrating cement making it unavailable to form a binder. By adding a reactive silica such as fly ash or MS600, any $Ca(OH)_2$ formed immediately reacts, reducing the pH by around 1 pH unit, so that while a lower ratio Ca silicate hydrate is formed, this product does not readily crystallise to tobermorite.

The mechanism by which tobermorite is formed from lime and quartz was deduced by Kalousek and Adams (1951). Its formation in the presence of more reactive forms of silica is still a subject of conjecture but it appears to form better with the slow dissolution of additional silica in a highly alkaline medium. It was not found in the BFS additions where the Ca:Si ratio remained high.

Klimesch (1999) showed that by using metakaolinite, a rapidly reacting silica, to replace some of the quartz, tobermorite was more rapidly formed via an initial hydrogarnet phase which formed within a few hours at 177°C. The ultimate tobermorite, which presumably contained significant quantities of substituted Al, is the anomalous tobermorite described by Komarneni et al. (1985). While katoite, a form of hydrogarnet, was formed with BFS additions, it did not go on to form tobermorite, no doubt because the Ca:Si ratio was too high.

Totally replacing the quartz with other more reactive siliceous materials does not lead to tobermorite formation. Work by researchers such as Goñi et al. (2003), Kropp et al. (1983) and Ma and Brown (2003) also showed that hydrothermal reactions of lime/OPC/flyash do not normally produce tobermorite, although Ma and Brown showed by raising the pH with NaOH it would form. Addition of large amounts of fly ash rapidly reduces the initial pH which retards the formation of tobermorite, although in this work it did ultimately form for the 1: 1 sample but not for the 1:3 sample indicating either the Ca:Si ratio of the initial calcium silicate hydrate was too low to form tobermorite or that the pH was too low to attack the quartz.

Addition of BFS to OPC, while slightly reducing the Ca:Si ratio in the initial mix, also provides a lower initial pH. The hydrothermal reaction only proceeds as far as the hydrogarnite, katoite, with formation also of α-C_2SH. This implies the Ca:Si ratio remains too high for tobermorite to form as α-C_2SH remains the main silicate binding phase except at high BFS additions when the product remains soft. Thus it too does not provide a method which both reduces the initial pH and allows tobermorite formation.

In the New Zealand geothermal fields, carbonation dominates with precured tobermorite samples carbonating rapidly and corroding in acidic waters. Lower strength, lower Ca/Si ratio binders, particularly if amorphous, prove carbonation resistant and have improved durability.

6.0 CONCLUSIONS

Addition of reactive forms of silica such as PFA, BFS or MS600 to OPC rapidly reduces the pH of the pore solution by at least one pH unit by removing any $Ca(OH)_2$ formed. This prevents the formation of tobermorite which requires high pH. This reduced pH is also likely to give improved performance of the cellulose fibres in autoclaved cement products if used in small amounts.

$Ca(OH)_2$ reacts quickly with these reactive forms of silica, competing with dissolved CO_2 for the available Ca. Thus more calcium silicate hydrate is formed. On autoclaving, the reduced pH does not lead to ready formation of tobermorite so a weaker binder is formed. If a strong binder is required then most of the added silica must be in the form of quartz.

The amorphous calcium silicate binder formed with reactive silicas, particularly MS600, while it has moderate strength gives good carbonation resistance and provides the best alternative if Portland cements are used in New Zealand geothermal fields.

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