A New Portland Cement Derived Composite Binder for Use in Geothermal Wells

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ABSTRACT

The shortcomings of regular grades of Portland cements used in service temperature environments above 110°C are well known. The metastable Calcium Silicate Hydrate reaction products recrystallise as generally denser, lower volume forms such as α-C_2SH, which leads to shrinkage and loss of compressive strength. In geothermal environments the associated cracking creates pathways for down hole fluid access. This process is known as strength retrogression. Modern type A cements also show additional volume loss with the conversion of ettringite into higher density forms.

Strength retrogression is traditionally controlled through the addition of 35-40 wt% silica to the cement which allows the preferential formation of tobermorite, xonotlite and gyrolite which give desirable well cementing qualities.

High levels of carbon dioxide are commonly found under geothermal conditions. The addition of excess silica to control strength retrogression results in a cement body very prone to rapid carbonation resulting in the deposition of lower volumes of aragonite, leading to shrinkage and reduced compressive strength. Associated cracking creates pathways for down hole fluids to accelerate this process further. To offset this the levels of silica are generally reduced but the result is a cement grout body that often rapidly degrades through both strength retrogression and carbonation processes.

This paper describes a new composite Portland derived cement designed to maximize durability and well life under geothermal conditions by taking advantage of the carbon dioxide concentrations to form desirable reaction products.

1. INTRODUCTION

In geothermal well cementing operations, a cement grout is pumped from the surface through the casing to the bottom of the borehole and from there injected into the annular space between the steel well casing and the strata through which the well is drilled. The grout (or slurry) needs to maintain working times as the temperature rises rapidly with increasing depth. The purpose of the grout is to hold the casing firmly while isolating different zones from communication and preventing leaks of fluid from the surrounding strata. The grout also provides protection to the steel casing from the geothermal fluid. The existing grout formulations try to balance loss of strength and integrity due to strength retrogression at high temperature against the rate of carbonation due to the extreme levels of carbon dioxide in the geothermal fluid.

Cement grouts used to install New Zealand geothermal wells need to endure harsh conditions very much outside of the original purposes for which Portland cement was engineered. Even at shallow depths temperatures are high enough to cause strength retrogression, together with acidic groundwater containing several atmospheres of carbon dioxide. Traditional solutions using type A cement (local OPC) and slag cements have demonstrated poor resilience to such conditions both in the laboratory and in the field. These traditional cementing systems have contributed to early well failures and the project's aim was to investigate alternative mix designs benchmarked against current designs.

Milestone, Grant-Taylor and St John demonstrated that slag cements in particular undergo very rapid carbonation. After relatively short exposure to New Zealand simulated geothermal conditions XRD determines the main components to be aragonite and katoite; a member of the hydrogarnet group formed where there is an excess of silica.

The main aim of this research is to quantify the effects that New Zealand Geothermal conditions have on current grout formulations, and to improve these through comparison of current formulations with new ones using optimized raw materials, tested in conditions simulating those at depth. The overall goal is to maximize the life of the well linings.

Current local Class A and Class G cements have been used as the basis for developing an improved cementing system for such conditions.

2. EXPERIMENTAL PROGRAMME

21 cement grout mixes have been evaluated, whose compositions are summarized in Table 1. The basic mix design was based on the industry standard, 15.6 pounds of cement per US gallon (3.785 Litre), with the workability and water content adjusted using BJ Services R-8 (water reducer/retarder) to maintain a grout density as close as possible to 15.6 ppg.

The control mix was that as currently used in New Zealand by BJ Services and was intended to provide a benchmark from which to measure cement grout 'life' for the subsequent mixes. The original design of this mix comprised a cement known as "Blast Furnace Slag Blend". This is a blend containing 35 wt% of the blend of ground granulated blast furnace slag (GGBS).

Even though bentonite was a component of the control mix, its inclusion was discontinued for other mixes as it was shown to rapidly accelerate the rate of carbonation. This behavior has been well documented by Milestone et al.

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Table 1. Composition of the 21 Mixes Tested.

Mix ID	Formulation					
	Cement	Silica	Slag%	Silica%	Lime%	Other
Control	BFS blend				0	Bentonite
1E	BFS blend		35		5	A300L
1F	BFS blend		35		10	A300L
1G	BFS blend		70		10	A300L
2	BFS blend				0	A300L
3	A	F		15	0	A300L
4	A	H		15	0	A300L
7	A	F		15	5	A300L
9	A	H		15	5	A300L
14	G	F		15	0	A300L
15	G	H		15	0	A300L
17	G	H		40	0	A300L
17A	G	R		40	0	A300L
18	G	F		15	5	A300L
18A	G	F		15	10	A300L
20	G	H		15	5	A300L
20A	G	H		15	10	A300L
20B	G	R		15	5	A300L
21	G	F		40	5	A300L
22	G	H		40	5	A300L
22A	G	R		40	5	A300L

In this series of experiments and to allow for easier comparison, additives are recorded as a percentage of the total binder weight. This differs from the API practice of specifying additives a percentage of the weight of cement.

Addition of bentonite and A300L is additional to the total blend.

A300L is a colloidal silica based additive used for control of free water. The silica types used are as follows:

Silica Type F = Crystalline Silica Flour
H = Amorphous Hydrothermal silica (Microsilica 600)
R = Recycled Glass Dust (Blast Glass)

2.1 Preparation of the Mixes

Each mix was prepared using a standard laboratory beater-type mixer. The samples were moulded using 100mm x 50 mm diameter cylindrical moulds and vibrated into place using a laboratory vibrating table. The moulds containing specimens for 20^oC cure were set aside, while the higher temperature specimen were placed in a 90^oC oven for three days before all moulds were stripped. The 20^oC samples were stored under water. The 90^oC specimens were wrapped in an absorbent cloth saturated with water, placed in heavy duty plastic bags and returned to the oven. The remaining specimens were placed in an autoclave containing a simulated geothermal fluid at either 150^oC or 300^oC for 7 and 28 day periods.

The simulated geothermal fluid is a brine (composition is given in Table 2) pressurized with carbon dioxide at 6 atmospheres for the 150°C cure samples and 8 atmospheres for the 300°C cure samples to maintain the pH at 5.0.

3. RESULTS

3.1 The Slag Based Mixes

The autoclave curing was terminated after 6 days as it was impossible to maintain the environment at pH 5.0 as determined by the down hole conditions, despite the large amount of carbon dioxide injected. The pH was regularly checked by bleeding out a small volume of fluid from the chamber containing the test grout cylinders. After dismantling the autoclave it was observed that the fluid around the grout cylinders was pH 7.0 while the thin layer of fluid between the stainless steel liner (which had no contact with the test cylinders) and the autoclave wall was pH 5, as predicted.

The cylinders removed were cracked and showed heavy carbonation which was evident from the significant loss of alkalinity according to the phenolphthalein test. In Fig 1, unstained areas have a pH of 10 or less. The carbonation was less in the interior, but the exposure time was very short. Corrosion of the autoclave walls was observed due to sulphide attack from the slag atmosphere.
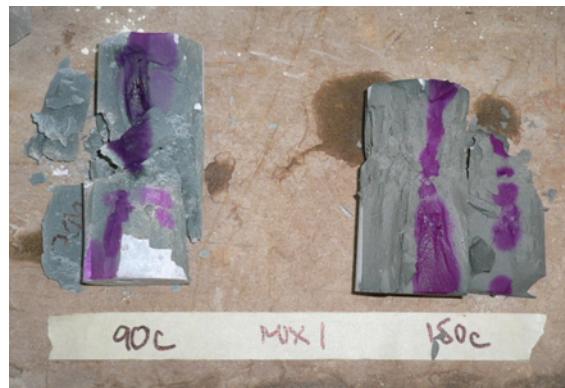
Figure 1: Slag based control mix after only 6 days showing loss of alkalinity

The autoclaved samples consumed CO_2 as fast as it was injected. This resulted in a very rapid rate of carbonation;

more rapid than expected, putting the effects of strength retrogression as a secondary problem. In these mixes rapid carbonation attack of both the (limited) hydrated lime component and the calcium silicate phases was observed.

X-ray diffraction (XRD) analysis of samples Control, 1E, 1F, and 2 cured in water at 20°C showed an increasing amount of portlandite (calcium hydroxide) with increasing hydrated lime content, as would be expected from adding additional lime to the mix; and decreasing C_3S content. Ettringite was also clearly seen.

At 90°C, XRD shows the disappearance of much of the ettringite which would be accompanied by shrinkage and cracking as it recrystallizes to form calcium monosulphoaluminate. Carbonated aluminates were not seen at 90°C.

For samples cured in the autoclaves at 150°C and six atmospheres CO_2, the cylinders showed extensive carbonation products and marked loss of alkalinity. Calcite resulting from the carbonation of portlandite and anhydrite were readily observed as were carbonated aluminate phases. Hydrogrossular garnet was seen at 150°C. Tri-calcium aluminate hexahydrate (C_3AH_6) or hydrogrossular garnet is the most stable of all calcium aluminate hydrates. It is very characteristic of blastfurnace slag cements cured at elevated temperatures. It will not undergo transformation into other hydrates as will CAH_{10} and C_2AH_8 but dehydrates at between 225 and 275°C forming $C_3AH_{1.5}$ before undergoing complete dehydration between 550-950°C.

All cylinders cured at 90 and 150°C demonstrated heavy crazing and cracking across their entire surface. These results display similar mineralogy to samples of hardened slag grout removed from failed wells.

3.2 Mixes Containing 15% Silica (by weight cement blend)

One of the aims of our programme was to investigate other forms of silica to find a substitute for crystalline silica flour. Two alternatives were investigated. Hydrothermal silica is a natural New Zealand resource. Large commercial deposits of amorphous silica, deposited from geothermal activity exist, some of which are mined and processed. Another silica-rich material examined was recycled glass (Blast Glass (Polish Grade)), which is more reactive than silica flour and has a low water demand thus greatly reducing the volumes of admixtures needed in grout design. These three sources of silica; Blast Glass, Hydrothermal Silica (as Microsilica 600) and Silica Flour (250FG) were tested with both Class A (OPC) and Class G cements.

Class A cement gives cause for concern due to its relatively high C_3A content (>8%) and therefore lower sulphate resistance. This cement has a proportion of ettringite, originating from C_3A hydration in the presence of gypsum, that, as temperatures rise above 90°C will convert to calcium monosulphoaluminate with a corresponding and readily observable volume loss. This will instigate cracking within the grout matrix and enable a more rapid rate of carbonation and ingress of solution from the aggressive ground waters. It also provides a more rapid path for the groundwater to reach the steel casing. Differences in compressive strength are shown in Figure 3. With respect to Class A cement; the rates of carbonation and cracking through loss of ettringite are probably more significant for durability than subsequent loss of strength due to (regression) strength retrogression. The degree and depth of

cracking was much greater in Class A cement compared to Class G cement having a C_3A content less than 3%.

Hydrothermal silica gave better high temperature results than silica flour with the hydrothermal silica appearing to preserve the portlandite (calcium hydroxide) content from carbonation. Cracking was generally reduced when using hydrothermal silica.

Addition of hydrated lime to the mixes further improves performance through the deposition of (expansive) calcite. The addition of hydrated lime to the mix provides a 'sink' for the CO_2 in the geothermal ground water. By providing an excess of hydrated lime the grout can form an expansive calcite phase which further helps to block up cracks and fractures and will help with bond to the steel casing. Addition of hydrated lime also helps the grout body provide passivity to the steel casing. Without the addition of lime there is a much more rapid carbonation of the calcium aluminate phases with accompanied shrinkage

Figure 2: Two cylinders (mix 9) welded together with high density calcite after autoclave curing, demonstrating healing of cracks and voids

XRD analysis showed that at 150°C hydrothermal silica based mixes had formed more of the stable higher temperature mineral phases than the less reactive silica flour, thereby offsetting strength retrogression to a greater extent. At 150°C, strength retrogression was more advanced in the silica based mixes. Another observation is that the addition of A300L (colloidal silica) favours the formation of beneficial scawtite at much lower than expected temperatures.

Table 2: Brine Composition:. Calculated chemistry at 300 m depth and 225°C. The chemistry matches that of groundwater in existing well RK9.

| Temperature	225°C
pH	5.1
Cl^-	1.62E-02M
SO_4^{2-}	6.76E-05M
HCO_3^-	7.57E-02M
HS^-	1.12E-03M
SiO_2 (aq)	1.3E-02M
Ca^{2+}	1.54E-05M
K^+	2.76E-03M
Na^+	1.51E-02M
Sulphur	Nil
P_{CO2}	6.9 bar

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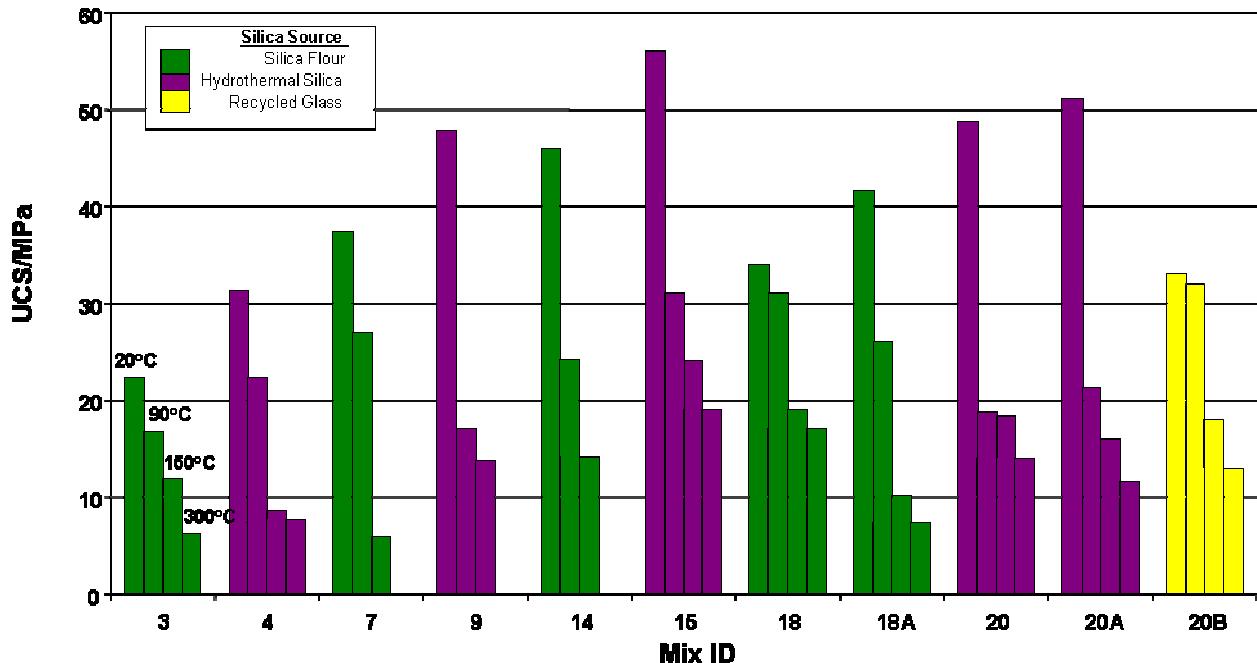
Figure 3: Compressive strength of 15% Silica mixes at 28 days age

3.3 Mixes containing 40% silica (by weight cement blend)

In general, the increased replacement of cement with silica will lower the compressive strength of a given mix, as silica is a low reactivity material and will not form strength contributing phases, particularly at lower temperatures. At higher temperatures, and in particular above 150°C, silica helps to form the important phases responsible for reducing loss of strength due to strength retrogression. However, this strength reduction has been further complicated by the varying water demands of the silica types used in the present mix program.

Microsilica 600 used in these trials is a milled hydrothermal silica. It has a very high water demand and cannot achieve the required 15.6 pounds per gallon slurry without high dosages of dispersants. The other two materials, silica flour and blast glass have very low water demands and produce very fluid slurries without the use of dispersants.

Of these 40 wt% of cement blend silica mixes tested, mix 17 (using hydrothermal silica) gave the best results even though extra water was required to achieve sufficient workability to place the mix in the moulds. Mix 17 had a water to binder ratio of 0.38 as opposed to 0.35 for all the other mixes using 40% silica. Differences in compressive strength are shown in Figure 4. Compressive strengths of 47 MPa at 150°C and 38 MPa at 300°C are some of the best attained in this study. XRD showed that the hydrothermal silica readily takes part in the formation of high temperature stable phases, preventing loss of strength due to retrogression. Addition of hydrated lime to 40 wt% silica mixes seems to offer little benefit in strength or durability compared to mixes based on 15 wt% of silica.

Carbonation effects were identified by the presence of calcite on the surface of the cured grout cylinders but were

not seen in the samples themselves suggesting longer term testing is needed to quantify service life improvements.

Mixes 17A and 22A were poor performers. Both contained 40% blast glass by weight of cement blend, but 22A also contained 5 wt% hydrated lime. Cylindrical samples of both materials withdrawn from the 300°C autoclave after 28 days showed extensive expansion and cracking. Expansion was estimated at 10% by volume. Low compressive strengths of 8MPa and 7MPa respectively were recorded due to the fractured matrix. Examination of these cylinders showed a low pH zone around the outside of the cylinder where carbonation had occurred. In the centre, pH remained in the 12 to 13 range and the Blast Glass had reacted with the alkali in the cement to form a (disruptive) silica gel. It is probable that the formation of the disruptive silica gel caused cracking, allowing for a much accelerated rate of carbonation. This is classic alkali-silica reaction and negates the use of recycled glass at 40 wt% cement blend.

Cylinders cured at 150°C did not show the large volumes of silica gel seen in the above but more detailed examination using SEM and XRD techniques identified reaction rims around the silica grains, suggesting at 150°C a 40 wt% cement blend blast glass mix would have a poor service life. This reaction also accounts for the low compressive strengths recorded.

Chemical analysis of the blast glass showed it to have a high alkali content. API specification 10A 2002 limits equivalent sodium oxide levels, $Na_2O(eq)$ to a maximum of 0.75% (by weight of cement) for use in concretes but in geothermal environments where silica is required to react with cement hydrates no such guides exist. Further work needs to be undertaken before recycled glass can be used in such applications.

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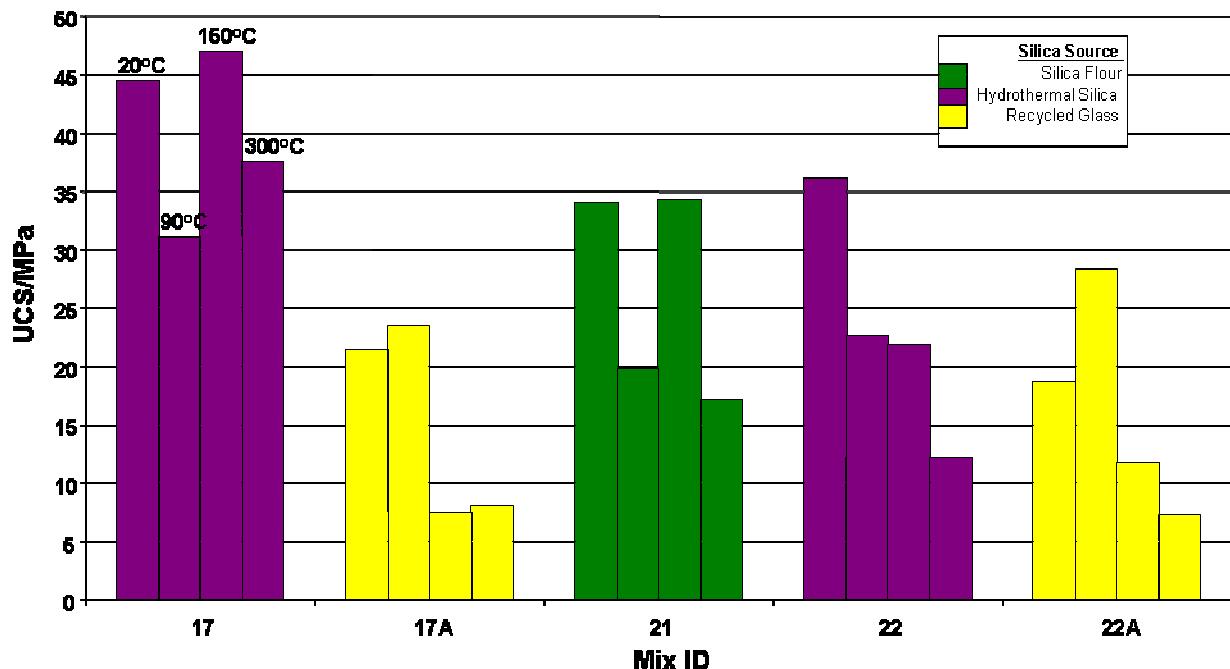
Figure 4: Compressive strengths for 40% Silica Mixes at 28 days age

3.4 The Effects of Hydrated Lime Addition

Hydrated lime (calcium hydroxide) was added to some mixes as a partial replacement of the cement component. As lime contributes little to the final compressive strength at lower temperatures, the reductions in strength observed match the reduction in the Portland cement component. However, at elevated temperatures, hydrated lime can react with CO_2 or carbonic acid, respectively, in the ground water that enables the formation of (strong) calcite.

The inclusion of hydrated lime (at 5 or 10 wt% of cement blend) to mixes containing 40 wt% of cement blend of silica would appear on first sight to be deleterious to compressive strength after curing at elevated temperatures. However this may not be conclusive as the marked reduction in strength in the mixes based on blast glass can be largely attributed to the generation of disruptive silica gel formed through alkali silica reaction**.**

3.5 Discussion of Results

3.5.1 Loss of Strength at 90°C

During normal (Class A) Portland cement hydration, the tricalcium aluminate (C_3A) mineral component reacts with available gypsum, in the presence of lime, to form ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$). At about 90°C the ettringite converts to the calcium monosulphoaluminate phase, with a net water loss. This results in a volume reduction of the cement paste causing shrinkage, cracking and a significant lowering of compressive strength.

The manufacture of Portland cements has evolved in recent years with the extensive use of chemical agents to provide production efficiencies. The addition of chelating agent based cement modifiers during cement clinker milling is a common procedure to lower power consumption during the milling stage by allowing a given clinker to achieve the required compressive strength at a lower cement specific surface area. In practice this means modern cements will

form more ettringite; and this is supported by our XRD results. These cements are even more prone to volume reduction and strength loss at 90°C than were Class A cements from several years ago.

If a grout based on Class A cement has undergone a paste volume reduction at 90°C, cracking will occur and it will more susceptible to the effects of carbonation and strength retrogression. A number of the Class A cement based mixes demonstrated such cracking after curing at 90°C.

Ettringite forms rapidly, with the reaction of added calcium sulphates to cement being used to control setting time. It is realistic to assume that under most geothermal grouting applications, a Class A grout will set and start to harden at temperatures that allow ettringite to form first. It will then convert to calcium monosulphoaluminate with a corresponding volume loss. The resultant shrinkage cracking that follows helps the acidic geothermal fluid get much faster access to the hardened grout matrix that adds another (new) stage in the strength loss process with Class A cements.

By contrast, Class G cement, with its very low C_3A content does not display this problem although some strength reduction was noted at 90°C.

3.5.2 Carbonation at 150°C

Although 20°C and 90°C curing was carried out at normal atmospheric CO_2 concentrations (0.03 vol%), samples tested at 150°C in an autoclave filled with a synthetic geothermal fluid were exposed to six atmospheres of CO_2. Carbonation occurred very rapidly as demonstrated by the XRD results. Little portlandite (hydrated lime) remained and large amounts of calcite were present.

At 300°C 8 atmospheres CO_2 were used to match our knowledge of down hole conditions.

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The hydrothermal silica based mixes seem less prone to carbonation between 20 and 90°C, more prone than silica flour based mixes at 150°C but appear to perform better than silica flour at 300°C. For both materials, our tests indicate that the problems of carbonation are worst at 150°C. It is unclear at this stage why carbonation is not more severe at 300°C. Again, longer term testing will help clarify this picture.

The addition of hydrated lime to the mix design appears to mitigate the effects of CO_2 attack. We have explored additions of lime at five and ten percent by weight of the cement blend. The added lime forms a sink for CO_2 and is rapidly carbonated to calcite. This occupies a larger volume and fills in the cracks with impermeable material, thus strengthening the matrix whilst making it less permeable to geothermal fluids. Addition of a small amount of hydrated lime greatly enhanced the performance of a number of grout mixes tested

3.5.3 Effects of Colloidal Silica Addition

An unexpected result from adding A300L colloidal silica to stabilize grouts made with the two cement types was the formation of the high temperature mineral, scawtite, a calcium silicate carbonate of general formula $Ca_7Si_6(CO_3)O_{18}\cdot 2H_2O$. X-ray diffraction analysis showed that scawtite was present in products formed at 150°C which is a lower temperature than previously supposed. The traditional view of strength retrogression is that scawtite appears at temperatures >200°C. Scawtite is responsible for the integrity of the bond between the grout and the steel well casing Its presence is more apparent in a Class A cement system than Class G.

Bjornstrom has shown that the use of nanosized silica has a nucleating effect, accelerating the precipitation of calcium silicate hydrate gel in Portland cements.

Bentonite, as discussed previously, when used as a stabilizer for geothermal grouts has a very deleterious effect on the strength, durability and potential service life of such grouts under (NZ) geothermal conditions (Milestone et al. and Grant-Taylor et al.).

CONCLUSIONS

After comparing the performance of two series of grout mixes based upon locally available Class A (OPC) cement and Class G cement, which have been combined with 3 different forms of silica, the following conclusions may be drawn:

- When comparing all parameters examined in this programme, mix 20 based upon a blend of 80 wt% class G cement plus 15 wt% hydrothermal silica together with 5 wt% hydrated lime gave the best overall result. Potentially the degree of cracking (that is a measure of how the cement blend matrix survives the simulated geothermal conditions) is the best measure of overall performance. In future research this will be measured as water permeability.

- Blast glass is an alternative form of silica, with a low water demand which greatly reduces the need for additives to maintain workability. Its performance is similar to hydrothermal silica and its non-crystalline morphology makes for safer use than silica flour. However, our programme has highlighted that at 40 wt% of the cement blend, a serious risk of ASR (alkali silica reaction) is demonstrated. The use of blast glass in geothermal grouts is not recommended until a much fuller investigation has been undertaken.

- The addition of hydrated lime to the cement blend mitigates the effects of carbonation, particularly at elevated temperatures.

- Colloidal silica (A300L) addition to the grout to replace bentonite as a stabiliser has the added benefit of producing scawtite at much lower than expected temperatures. Scawtite forms an excellent bond between the steel casing and the grout body. The use of nanosized silica has a nucleating effect, accelerating the precipitation of (higher silica) calcium silicate hydrate gel in Portland cements. It also assists the low temperature reaction between the calcium silicate hydrate gel and carbon dioxide to form calcium silicate carbonate hydrates or scawtite.

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