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Thermal Stability of the Cement Sheath in Steam Treated Oil Wells

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Abstract

Considerable work has been done in the past on the phase equilibria and physical properties of thermal cements heated directly to high temperatures. In thermal recovery oil wells the cement sheath is, however, cured for days to years at temperatures of 40°C or less before it is subjected to steam injection temperatures of up to about 320°C. The effects of this alternative curing regime have not been well documented. Here, the impact of pre-curing samples for 1, 14 and 28 days at 35°C before heating to 230°C on phase assemblages, morphologies and physical properties of thermal cement were investigated. Control samples included thermal cements heated directly to high temperature as well as samples cured only at 35 °C. Xonotlite formed the predominant phase in the pre-cured thermal cements instead of the tobermorite found in the control sample heated directly to 230°C. Although all pre-cured samples were predominantly xonotlite, their morphological characteristics of the phase assemblages were found to vary distinctly with pre-curing time. Significant differences between the pre-cured and directly cured samples were also observed in terms of porosity, permeability and mechanical behaviour.

I. Introduction

Enhanced heavy oil recovery uses steam delivered to the production zone either by cyclic steam injection^(1,2) or steam flood techniques^(3,4) to heat the oil and allow easier extraction. As in conventional oil and gas wells, the annulus between rock formation and the metal casing pipe is filled with cement. In enhanced recovery wells the cement is cured at temperatures less than or

equal to 40°C, producing amorphous C-S-H gel, $\text{Ca}(\text{OH})_2$, ettringite and other low temperature hydration products. The degree of hydration, morphological characteristics and physical performance of the cured cement is dependent on the curing temperature and time prior to steam injection which can be from days to years after the cement has set. This differs from conventional high temperature wells such as geothermal wells where the cement is exposed to temperature before it sets. Steam temperatures in enhanced oil recovery wells can range as high as 320°C, although temperatures in the range of 230°C are more common.

Portland cement hydration undergoes significant changes on hydrothermal curing above 110°C with formation of meta-stable and stable crystalline calcium silicate hydrates⁽⁵⁾. Portland based oil well cements used above 110°C contain 35-45% silica flour by weight of cement (bwoc) to prevent formation of crystalline alpha-dicalcium silicate hydrate $\text{Ca}_2\text{SiO}_3(\text{OH})_2$ ($\alpha\text{-C}_2\text{SH}$), a phase that is associated with a reduction in solid volume, increased permeability and decrease in compressive strength over time⁽⁶⁾. Lowering the calcium to silica (C/S) ratio from between 2.0 – 3.0 in a neat Portland oil well cement to 0.8 - 1.0 in an Portland oil well cement/silica flour blend (thermal cement) produces crystalline calcium silicates hydrates that are stable over a range of temperatures and provide good compressive strength and low permeability.⁽⁷⁾ The resulting phase equilibria and stability fields of crystalline calcium silicate hydrates over the temperature range of 110 - 320°C have been well documented.^(5,8,9) Tobermorite, truscottite, gyrolite, xonotlite, foshagite and/or other calcium silicate hydrates have been reported depending predominantly on curing condition and C/S ratio.^(9,10) Hydrogarnet⁽¹¹⁾ anorthite⁽¹²⁾ and calcium aluminium silicate hydrates such as aluminium substituted tobermorite⁽⁵⁾ may also form due to the aluminate phases present in cement. Although the phase equilibria are well studied the literature on the effect of the phases formed on physical properties is minimal⁽⁷⁾.

In studies reported to date the cement has been heated to and cured at elevated temperature, whereas in the case of enhanced recovery wells the cement is cured at temperatures less than or equal to 40°C prior to steam injection. In general, the oil well industry considers that the use of thermal cement in enhanced recovery wells should provide a phase assemblage similar to that of the same thermal cement heated directly to temperature. However, from studies in the pure CaO-SiO₂-H₂O system it is known that the starting material can have a significant impact on the phase assemblage^(13,14) and stability at elevated temperature. Conversion of pre-existing low temperature hydrated cement phases to crystalline hydration products may not necessarily produce the same phase assemblages or physical properties as those of an anhydrous cement mixed with water and heated directly to temperature. The steam induced phase conversion of an already established cement hydration matrix may also cause stresses that can affect the matrix's integrity. As cement sheath performance is considered to be a key requirement for enhanced heavy oil recovery,^(15,16) understanding the potential effects of steam treatment is of considerable importance to the industry. At the same time, the absence of information on the effects of heating of this type of "pre-cured" samples suggests the need for investigation at a fundamental level. The purpose of this study was therefore to investigate the effects on phase equilibria, morphology and physical properties that result from heating thermal cements cured at 35 °C for 1, 14 and 28 days to 230°C in order to understand the results of phase conversion of hydrated cement matrices pre-cured at low temperatures and the potential for impact of the phase conversion on the well sheath. The results were interpreted by comparison to control samples that were immediately heated to 230 °C or cured only at 35 °C.

II. Experimental Procedure

(1) Materials and Sample Preparation

Lehigh Inland (Calgary, AB, Canada) Class G oil well cement⁽¹⁷⁾ was used for the study. Details of the chemical and physical characterization data are summarized in Table 1. Mineralogical composition was determined from XRF oxide analysis provided by the manufacturer using the Bogue calculation and from XRD data using Rietveld whole-pattern fitting using TOPAS (Bruker, Billerica, MA, USA) software. Silica flour (Sil Industrial Minerals Inc., Calgary, AB, Canada) was used in the cements to provide thermal stability at temperatures above 110°C. Compositional data produced by petrographic analysis and other data on the silica flour are provided in Table 1.

The Class G cement was dry blended with 40% bwoc silica flour and mixed with water at a water/(cement + silica flour) ratio of 0.4 in a Waring blender and conditioned for 20 minutes in an atmospheric consistometer at 25°C according to API/ISO 10426-2-2003.⁽¹⁸⁾ The mixing and conditioning regime was intended to be representative of mixing and pumping cement down hole in an oil well. Stability of the mix design in relation to particle settling had previously been determined using the API/ISO 10426-2-2003 well-simulation slurry stability test method.⁽¹⁸⁾ The slurry was poured into conventional 5cm x 5cm x 5cm cube brass molds for compressive strength measurement and air permeability samples and 2cm x 2cm x 16 cm bar stainless steel molds for samples for the other measurements. The molds were then placed in a water bath at 35°C for time periods as indicated in Table 2 before demolding. Demolded samples were examined to ensure that sedimentation of the samples had not taken place. Samples for thermal curing were placed in a curing chamber (CTE, Tulsa, OK, USA) heated to 230°C over a 4 hours period, maintained at 230°C for 24 hours and then allowed to cool to 25°C over 48 hours to

prevent thermal shocking. Pressure of the curing chamber was maintained at the maximum possible value, 20.7 MPa, in order to ensure the water in the samples remained liquid. High temperature control samples were put directly into the curing chamber and cured at 230°C under the same curing regime as the pre-cured experimental samples. The total time of cure was the same for both the experimental and low temperature control samples. Table 2 summarizes the test conditions and associated nomenclature used in this paper. Tests on the low temperature samples were carried out immediately after curing was completed. Tests on the high temperature samples, which would not be expected to undergo further hydration, were carried out within 4 days of the end of the curing cycle, with samples kept in sealed containers until needed.

(2) Mineralogical and morphological analysis

Samples for SEM analysis (Hitachi S4800, Tokyo, Japan) were prepared from exposed fracture surfaces cut with a saw (Buehler Isomet, Lake Buff, Illinois) in isopropanol, dried in a convection oven at 100°C for 2 hours to ensure all remaining water was removed, cooled and then mounted on aluminum stubs for imaging, with the SEM operating at 1.2 kV accelerating voltage, 7 μ A emission current and at an approximately 9 mm working distance. The combination of the field emission gun technology in the SEM with the operating conditions meant that high resolution imaging could be undertaken without metallization⁽¹⁹⁾. Vacuum dried internal fragments taken from crushed bars were ground to pass a 75 micron sieve and used to determine the mineralogy by X-ray diffraction (XRD) (Rigaku DMAXB, Woodlands, TX) with $\text{CuK}\alpha$ radiation, a 5° to 85° 2 θ range, 0.03° step size and an 18 second/step count rate. Duplicate samples were tested to ensure the results were consistent.

(3) Measurement of physical parameters

Compressive strength data was obtained on duplicate cube samples using a hydraulic press (M&I Testing Equipment, Dundas, ON, Canada with Admet, Norwood, MA, USA, Precise Digital Controller) at a load rate of 30 Kg/s. With the exception of the sample material and bar dimensions, flexural strength measurements were carried out on sets of three bars according to ASTM C348⁽²⁰⁾ using a mechanical testing system (Instron Model 5566, Universal Testing Machine, Norwood, MA, USA) with a 2kN load cell and sample bars loaded in 3 point bending at a rate of 300 N/min. Before flexural testing the bars were dry polished using 600 μm grit paper to remove surface defects that might cause premature failure.

Two cross-sections for each sample were cut from untested bars using a diamond saw. One of the cut surfaces of each sample was polished to ensure a smooth contact surface when the sample was mounted in an automated microhardness tester (Microhardness Tester, CSM Instruments, Peseux, Switzerland). The surface to be tested was left unpolished. After mounting, force was applied to the samples using a diamond Vicker's hardness point at a rate of 6.000 N/min to a maximum value of 3.000 N, and the depth of penetration simultaneously recorded for each measurement. The load was held constant for 15 seconds before reducing at a rate 6.000 N/min. Hardness and elastic modulus values were then calculated by the instrument software using the method of Oliver and Pharr⁽²¹⁾. A total of twenty-five measurements were made on a 5 x 5 grid with a 2 mm separation between measurement points on each cross section giving a total of 50 measurements per sample.

The microhardness measurements were examined and results that did not exhibit a smooth, monotonic increase in hardness with increasing displacement into the sample were removed to ensure the measurements did not include large scale porosity or silica flour. The

average modulus of elastic modulus and Vicker's microhardness values were determined for each specimen. Standard deviations of the results for each data were determined. Each data set was tested to determine if it could be considered a normal distribution using the Lilliefors test⁽²²⁾. The null hypothesis that the sample sets were normal was accepted at the 0.05 significance level for all of the samples.

Variances [the square of the standard deviation]⁽²³⁾ were then calculated. Comparisons between the data calculated for each sample were made using a two tailed standard normal (Z) test with the null hypothesis that the two distributions were really the same⁽²³⁾. This test evaluated the probability that two separate sets (for example, 4LT and 1LT-1HT-2C samples) were really subsets of the same data set. High calculated values of Z correspond to a high probability that the sample sets are not the same.

Reserved sample material of approximately 0.5 g were analysed in a porosimeter at low and high pressure by Quantochrome Inc. (Quantochrome Poremaster GT Porosimeter, Boynton Beach, FL, USA) and at the National Research Council Canada. Duplicate tests were performed on the samples to confirm the results, with typical values being shown. Permeability testing was performed at Core Laboratories Canada Ltd, Calgary, AB, Canada, on cores cut from cubes. Air permeability was measured at ambient pressure and at three incrementally hydrostatic net confining pressures of 5520, 6900 and 10340 kPa using an automated system (Core Laboratory Instruments, CMS 300 Automated Permeameter, Houston, TX, USA). The expense of this test precluded full duplicate samples, but duplicates measurements were made on the 31LT and 28LT-1HT-2C samples and used to provide the experimental uncertainty shown for the measurements.

III. Results

(1) Mineralogy and Morphology

XRD and TGA measurements were used to follow the changes in the anhydrous phases, the development of the hydration products and the mineralogy of the heat treated samples. The phase development in the low temperature samples occurred as would be expected from the literature⁽¹¹⁾, with the anhydrous phases reacting with the mix water to produce calcium silicate hydrate (C-S-H), calcium hydroxide ($\text{Ca}(\text{OH})_2$) and ettringite (Figure 1a). Amounts of reaction product increased with time of cure as seen in sample 17LT as compared to sample 4LT (Figure 1a) with the anhydrous phases being correspondingly reduced compared to the anhydrous sample. The phases seen for sample 31LT (not shown) were similar to those seen for sample 17LT.

Sample 1HT-2C also shows the phase assemblage (Figure 1b) that would be expected from the literature^(5,8,9,24,25). Curing the sample at 230 °C produced 11 Å tobermorite with some xonotlite. Katoite was also present in this sample. In addition, the data suggests the presence of some residual C-S-H, based on a broad background hump in the range 25-35° 2 θ . Peaks from unreacted silica flour and C_2S were also identified. In contrast, the predominant phase in pre-cured experimental samples was xonotlite (Figure 1b). Tobermorite peaks at 16.3°, 30.0° and 39.4° 2 θ were only identifiable in sample 1LT-1HT-2C, which also showed a small unreacted silica flour peak at 26.7° 2 θ . Samples 14LT-1HT-2C and 28LT-1HT-2C had very similar phase assemblages and therefore only the former is shown in the figure. The XRD results were confirmed by TGA measurements⁽²⁶⁾, which also showed that only a small amount of tobermorite was present in sample 1LT-1HT-2C as compared to 1HT-2C. Further details on the mineralogy of the samples and minor phases appear elsewhere.⁽²⁶⁾

The results of phase analysis suggest that the amount of anhydrous phases present in the sample at the time of heating is directly related to relative degree of formation of tobermorite and xonotlite upon heating. Immediate curing produced mostly tobermorite, curing after 1 day of hydration produced xonotlite with some tobermorite, while curing after 14 or 28 days of hydration produced almost entirely xonotlite. This route to producing xonotlite by pre-curing samples has not been reported previously in the literature, where xonotlite has been synthesized directly from silica and calcium hydroxide⁽¹³⁾ or by conversion of tobermorite⁽²⁷⁾.

Although the pre-cured samples were primarily composed of xonotlite, SEM examination of sample fracture surfaces showed that their morphology depended on the length of pre-curing. Typical 1LT-1HT-2C fracture surfaces showed what appeared to be regions of blunt needles and dense calcium silicate structures in addition to regions of an elongated platy material (Figure 2). Taylor⁽¹⁰⁾ indicated that both xonotlite and tobermorite may have a lath or needle like morphology, but that $11\text{\AA}$ tobermorite can also have the form of elongated plates and xonotlite a dense structure in the form of a aggregated needles. The plates in Figure 2b may therefore be tobermorite, the blunt needles in Figure 2a tobermorite or xonotlite and the dense hydration product in Figure 2a either xonotlite or amorphous C-S-H.

The 14LT-1HT-2C fracture surface images also showed a high number of regions with flat lath structures (Figure 3a), but also regions of dense, fibrous appearing hydration product (Figure 3b). The flat laths in Figure 3a could be examples of either tobermorite or xonotlite, however, phase analysis suggests that an identification as xonotlite is more appropriate. In contrast, the dense structure in Figure 3b appears to consist of aggregated needles and was also identified as xonotlite. The fracture surfaces for sample 28LT-1HT-2C were similar to those for sample 14LT-1HT-2C and are not shown.

The three control samples did not have similar fracture surfaces to those observed for the three experimental samples. SEM imaging of the sample 4LT fracture surface showed regions of flat platy structures consistent with $\text{Ca}(\text{OH})_2$, ettringite needles and regions of porous C-S-H that at higher magnification had a globular structure (Figure 4, arrow) similar to that reported in the literature.⁽²⁸⁾ The 17LT and 31LT fracture surfaces (not shown) had a similar, but denser microstructure, as would be expected from longer curing times. Dense hydration products were common throughout the examined sample 1HT-2C fracture surfaces (Figure 5a) with needle-like structures predominating at the edges of the larger pores (Figure 5b). The layered plate morphology of the dense material in Figure 5a is typical of tobermorite⁽¹⁰⁾ and would be expected from the phase analysis. The needle-like structure⁽¹⁰⁾ as seen in Figure 5b can be either tobermorite or xonotlite.

In addition to changes in phase assemblage and fracture surface morphology, the different curing methods also affected the pore size distribution of the samples (Figure 6). The low temperature samples had pore size distributions typical of those found in the literature⁽²⁹⁾, with most of the pores being between 0.5 μm and 0.02 μm in diameter. The sample cured directly to temperature, 1HT-2C, showed a much tighter pore size distribution and had ~1.8% of its total volume filled with pores greater than 200 μm in diameter, with a rapid increase in pore volume below a diameter of 0.04 μm . The experimental samples all had similar rapid increases in pore volume, but they occurred at a higher diameter, around 0.08 μm . Sample 1LT-1HT-2C had a total intrusion volume of ~30%, but samples 14LT-1HT-2C and 28LT-1HT-2C had much higher total intrusion volumes of ~40% and ~46% respectively. In each case the experimental samples total intrusion volume was much higher than that seen in the corresponding low temperature control sample.

(2) Mechanical Properties

All of the experimental samples had compressive strengths that were significantly higher than those of the corresponding low temperature controls (Table 3), although increasing pre-curing times resulted in decreasing strengths. Their compressive strengths were also higher than that of high temperature control sample 1HT-2C. Samples 1LT-1HT-2C and 14LT-1HT-2C also had flexural strengths that were higher than their corresponding low temperature controls (Table 3), but the flexural strength of sample 28LT-1HT-2C was the same as the low temperature control 31LT within the experimental uncertainty. Increasing pre-curing time again produced reduced strengths in the pre-cured samples.

The differences between control and experimental samples were also apparent in the modulus of elasticity (Table 4) and the Vicker's microhardness values (Table 5). Moduli of elasticity were lower for the experimental samples 1LT-1HT-2C and 14LT-1HT-2C than the corresponding low temperature controls at a statistically significant level. In contrast, the statistical analysis of the comparison between samples 31LT and 28LT-1HT-2C suggested the modulus of elasticity values should be treated as being statistically the same. All of the experimental samples also had modulus of elasticity values that were lower than the those of the high temperature control (confidence levels 98%+).

The Vicker's hardness measurements followed a more complex pattern, with the 4LT sample having the highest hardness, followed by the high temperature samples and then samples 17LT and 31LT. The higher Vicker's hardness values measured for the 4LT sample compared to 17LT and 28LT were anomalous, since it would be expected that the longer curing times would have the higher values. The degree of confidence that the hardness values for 1LT-1HT-2C were statistically different from those of the corresponding controls was relatively low (73% for 4LT,

and 67% for 1HT-2C), but the differences between the remaining experimental samples and the controls were found to be different at a much higher level (93%+).

IV. Discussion

The differences in microstructure, morphology and mechanical properties between sample 1LT-1HT-2C and both the low and high temperature controls were significant. Differences between the low temperature control samples and the hydrothermally treated samples were expected due to transformation of amorphous silicate phases to high temperature crystalline phases.⁽⁵⁾ The differences observed between the high temperature control 1HT-2C and experimental sample 1LT-1HT-2C, however, demonstrated that even a short period of pre-curing can have significant impact on the results of the phase conversion process. Although the total porosity of 1LT-1HT-2C was higher (Figure 6) it had a lower percentage of very large diameter pores. In addition, while the predominant phases in both samples are tobermorite and xonotlite (Figure 1), sample 1LT-1HT-2C had a much higher ratio of xonotlite to tobermorite than 1HT-2C⁽²⁶⁾. It also had a lower content of unreacted silica flour and does not appear to have any katoite. Finally, the appearance of the morphology of the phases in the two samples was quite different. Both samples have lath like structures located near pores, but those in sample 1LT-1HT-2C are blunter and more compact and flat and elongated plates were also seen (Figure 2). Regions of dense hydration product were fibrous in appearance in sample 1LT-1HT-2C, while they had a layered appearance in sample 1HT-2C (Figure 4).

These differences may all play a role in the differences between the measured mechanical properties of samples 1LT-1HT-2C and 1HT-2C. Strengths in cementitious materials are dependent both on the properties of the material itself and on their pore size distribution. In material of the same or similar composition, such as cements hydrated at a constant temperature,

pore size distribution plays a predominant role in material strength. It has been shown that pores greater than 10 nm in diameter are the most significant in some cementitious systems⁽³⁰⁾, but recent work⁽³¹⁾ has also suggested that the smaller diameter pores can also significantly affect the response of hydrated cement to mechanical loads. The role of porosity here is unclear, but on balance the high percentage of large diameter pores in sample 1HT-2C was likely to contribute significantly to its relative weakness. In addition, if it were not fully bonded to the matrix, the unreacted silica flour in the sample would allow cracks to propagate easily around its perimeter, effectively acting as an additional source of large diameter porosity.

The morphology of the samples may also make a difference in performance. While examples of plates such as Figure 3b are seen in sample 1LT-1HT-2C, the bulk of the structure is made up of dense blunt needles or what appears to be small xonotlite aggregates⁽¹⁰⁾ such as are seen in Figure 2a. These structures may be more resistant to fracture than the layered plates seen in Figure 4b for sample 1HT-2C. Finally, it is possible that the difference in composition between the two samples affected the mechanical properties. Recent work⁽³²⁾ suggests that increasing xonotlite content at the expense of tobermorite is likely to result in an increase in compressive strength, which would fit with the differences observed here. Previous research^(7,33), however, has shown that xonotlite was weaker than tobermorite, making difficult to draw conclusions about the effect of composition on the strengths observed here.

The reduction in strength produced by longer pre-curing times was likely due to the differences in porosity in the samples. As noted earlier, the phase assemblages (Figure 1) and the microstructure of the three experimental samples (Figures 2 and 3) do not appear to be highly dissimilar from each other. Many of the differences that do exist would tend to suggest that samples 14LT-1HT-2C and 28LT-1HT-2C should be stronger than 1LT-1HT-2C. The more

complete reaction of silica flour eliminated a possible source of weakness, while the apparent lack of tobermorite in samples 14LT-1HT-2C and 28LT-1HT-2C would not be expected to produce a significant strength change. Finally, the plates seen on the fracture surfaces of sample 1LT-1HT-2C (Figure 2b) do not appear in the other two experimental samples, with the longer laths in Figure 3a appearing instead. This change would also be expected to increase the strength of the material, not reduce it.

While the phase assemblages and microstructure do not appear to show mechanically significant differences between the experimental samples, the difference in porosity between 1LT-1HT-2C on one hand and 14LT-1HT-2C and 28LT-1HT-2C on the other was more than enough to produce a difference in mechanical strength. A subsequent examination of the air permeability of the samples (Table 6) showed that 14LT-1HT-2C and 28LT-1HT-2C also had high air permeabilities compared to any of the other samples. Mercury intrusion porosimetry measures the minimum pore diameter in a pore and will not measure closed pores. The air permeability measurements suggest that some of the increased porosity seen in the samples with longer pre-curing times was due to the opening of closed pores, rather than solely due to increased porosity. Both the increased porosity and the opening of closed pores would be expected to have contributed to the reduced strengths of those samples.

The differences between the results of the phase transformations thus suggest that the extent of the hydration process before the transformation takes place is a key factor in determining the resulting mechanical performance. Additional work is needed to fully understand the mechanisms behind this finding. It is speculated, however, that the combination of the amount of unreacted calcium silicates in the system, the ease of access to those calcium silicates and the available free or loosely bound water all play a role in the final properties. In

sample 1HT-2C, the cement grains were unreacted before heating and therefore at full size, as was the silica flour. Packing of the constituents of the blend would have resulted in many gaps between particles, which would have been filled by the mix water. The resulting composition upon heating was largely tobermorite and the sample had significant large diameter pore content. In sample 1LT-1HT-2C, the partial reaction of the cement at low temperatures produced both C-S-H and Ca(OH)_2 . At that stage in the hydration reaction, diffusion processes would have just become predominant⁽¹¹⁾ and unreacted calcium silicates would be present in the material covered by inner hydration products. Gaps between the silica flour and the inner products would have been filled with porous outer product material. A considerable amount of free water would have remained in the sample. Here the phase conversion produced xonotlite with some tobermorite, with the excess water entering the pores in the sample. The greater density of xonotlite (2.7 gm/cm^3) versus tobermorite ($\sim 2.4 \text{ gm/cm}^3$)⁽³⁴⁾ likely contributed to the observed increase in pore diameter. Finally, in samples 14LT-1HT-2C and 28LT-1HT-2C, the low temperature reaction had progressed to a significantly higher degree, reducing the amount of unreacted calcium silicates and minor phases, producing denser inner and outer hydration products and leaving little free water. The resulting phase conversion in this case produced xonotlite without significant tobermorite being present, resulting in a further increase in porosity. The remaining excess water again entered the sample pores. The difference in the results of the conversions suggests that the preliminary formation of C-S-H and Ca(OH)_2 may create an environment where xonotlite formation is favoured over tobermorite. Work in a pure synthetic C-S-H- Ca(OH)_2 - SiO_2 -water system would confirm this possibility.

V. Summary

Changing the starting composition or continuous curing temperature of a cement can alter its resulting mineralogy, morphology and physical properties. The results presented here show that changes in the curing temperature part way through the curing process can have as significant an effect. Pre-curing a sample for 1 day at 35°C and then raising it to temperature 230°C produced a phase assemblage primarily composed of xonotlite with higher flexural and compressive strength compared to a sample which was immediately heated to 230°C and was primarily composed of tobermorite. The changes in strength appear to be due to differences in phase assemblage, morphology and porosity of the hydration products. Pre-curing samples for 14 or 28 days before raising their temperature to 230°C produced a phase assemblage that was similar to that of the sample pre-cured at 35°C for only 1 day, but samples that were weaker in both flexural and compressive strength. The strength differences appeared to be due to the presence of a much higher degree of porosity and a higher degree of pore interconnectivity in the samples that were pre-cured for longer time periods.

In an industrial context, permeability and matrix strength are considered important parameters in relation to well cement sheath integrity⁽¹⁵⁾. Pre-curing for 14 or 28 days produced samples with reduced strength and heightened air permeability. Although the latter parameter was still well below the values quoted in literature as being detrimental⁽³⁵⁾, it is possible that longer pre-curing times may be more problematic. The data here, although limited, therefore show that changes in the phase equilibria need to be considered when designing methodologies for cement sheath integrity on exposure to steam stimulation.

Finally, it is important to note that the improved flexural and compressive strengths seen in the sample pre-cured for 1 day were obtained using a standard oil well industry cement/silica

flour mix and curing regimes intended to reflect steam treatment conditions. It is therefore possible that modifications to the approach followed here could be used to produce high levels of performance in cementitious materials intended for above ground construction or industrial applications. Further work is underway to explore this possibility.

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Tables

Composition (wt%)	Glass G Cement	Silica flour
SiO ₂	21.0	87.5
CaO	62.0	1.64
Al ₂ O ₃	3.93	4.47
Fe ₂ O ₃	4.34	1.18
MgO	2.83	0.40
Na ₂ O	0.30	1.25
K ₂ O	0.49	1.25
SO ₃	2.87	n/a
S	n/a	0.24
L.O.I. (1000°C)	1.23	n/a
Insoluble Residue	0.21	n/a
Total Alkalis (as Na ₂ O)	0.62	n/a
Blaine Fineness (m ² /g)	2.88	
Passing 45 µm mesh (%)	53	89
Density (g/cm ³)	3.15	2.63
Mineralogy		
	Bogue	Rietveld
C ₃ S	52.0	54.1
C ₂ S	20.7	24
C ₃ A	3.11	3.2
C ₄ AF	13.2	13.9

Table 1 – Raw material analysis

Sample Identification	Sample Type	Curing Conditions	Total Curing Time
4LT	Control	4 days at 35°C, cooled to 25°C	4 days
17LT	Control	17 days at 35°C, cooled to 25°C	17 days
31LT	Control	31 days at 35°C, cooled to 25°C	31 days
1HT-2C	Control	1 day at 230°C, 2 days cooling to 25°C	3 days
1LT-1HT-2C	Experimental	1 day at 35°C, 1 day at 230°C, 2 days cooling to 25°C	4 days
14LT-1HT-2C	Experimental	14 days at 35°C, 1 day at 230°C, 2 days cooling to 25°C	17 days
28LT-1HT-2C	Experimental	28 days at 35°C, 1 day at 230°C, 2 days cooling to 25°C	31 days

Table 2 – Sample identification and curing conditions. Note that sample 1HT-2C was only cured for 3 days total time in order to maintain a consistent high temperature curing and cooling regime.

Sample	Compressive Strength (MPa)		Flexural Strength (MPa)	
	Mean	Standard Deviation	Mean	Standard Deviation
4LT	23.9	0.5	5.9	1.0
17LT	30.5	2.2	6.2	0.4
31LT	34.6	1.1	8.1	0.7
1HT-2C	30.0	3.0	10.4	2.1
1LT-1HT-2C	55.6	1.7	12.6	1.0
14LT-1HT-2C	51.0	1.6	8.4	0.9
28LT-1HT-2C	44.0	1.6	7.8	0.2

Table 3 – Results of strength measurements

Sample	Average Modulus of Elasticity (GPa)	Standard Deviation (GPa)	Variance/ sample (GPa)	Test of Mean Value / Probability of Rejection of Null Hypothesis		
				Comparison	Result	
4LT	16.0	1.7	0.13	4LT vs. 1LT-1HT-2C	-1.41	84%
17LT	14.3	2.8	0.33	17 LT vs. 14LT-1HT-2C	-7.61	>99.9%
31LT	14.4	2.0	0.11	31LT vs. 28LT-1HT-2C	0.29	22%
1HT-2C	16.6	2.0	0.14			
1LT-1HT-2C	15.2	2.3	0.19	1LT-1HT-2C vs. 1HT-2C	-2.34	98%
14LT-1HT-2C	9.8	1.0	0.03	14LT-1HT-2C vs. 1HT-2C	-16.6	>99.9%
28LT-1HT-2C	14.6	2.2	0.20	28LT-1HT-2C vs. 1HT-2C	-4.27	>99.9%

Table 4 – Results of modulus of elasticity measurements

Sample	Average Vicker's Hardness (MPa)	Standard Deviation (MPa)	Variance/ sample (MPa)	Test of Mean Value / Probability of Rejection of Null Hypothesis		
				Comparison	Result	
4LT	30.0	5.7	1.6	4LT vs. 1LT-1HT-2C	-1.1	73%
17LT	24.3	5.2	1.1	17 LT vs. 14LT-1HT-2C	1.89	94%
31LT	23.8	5.8	0.9	31LT vs. 28LT-1HT-2C	2.56	99%
1HT-2C	29.8	6.4	1.5			
1LT-1HT-2C	28.1	6.7	1.7	1LT-1HT-2C vs. 1HT-2C	-0.97	67%
14LT-1HT-2C	27.0	5.8	0.9	14LT-1HT-2C vs. 1HT-2C	-1.82	93%
28LT-1HT-2C	27.3	5.0	1.0	28LT-1HT-2C vs. 1HT-2C	-3.70	>99.9%

Table 5 – Results of Vicker's hardness measurements

Confining Pressure (MPa)	Permeability to Air (mD)						
	4LT	17LT	31LT	1HT- 2C	1LT- 1HT-2C	14LT- 1HT-2C	28LT- 1HT-2C
Ambient	0.09	0.06	0.12	0.07	0.09	0.21	0.20
5.516	0.04	0.01	0.03	0.02	0.02	0.08	0.07
6.895	0.04	0.01	0.03	0.02	0.02	0.06	0.06
10.340	0.03	0.01	0.03	0.02	0.02	0.04	0.06

Table 6 – Air permeability values at different confining air pressures. Experimental uncertainties are ± 0.02 for the ambient measurements and ± 0.01 for the non-ambient measurements.

Figures

Figure 1a – Crystalline phases present in the unhydrated OPC and in samples hydrated at 35 °C as determined by X-ray diffraction. Results for sample 31LT are similar to those for 17LT and not shown.

Figure 1b – Crystalline phases present in samples hydrated at 230 °C as determined by X-ray diffraction. Results for sample 28LT-1HT-2C are similar to those for 14LT-1HT-2C and not shown.

a)

b)

Figure 2 - Morphology of fracture surfaces for sample 1LT-1HT-2C: a) Typical surface: blunt needles and dense calcium silicate hydrates; b) platy hydration products

a)

b)

Figure 3 – Morphology of typical fracture surfaces for sample 14LT-1HT-2C: a) lathe structures; b) dense calcium silicate hydrates. Sample 28LT-1HT-2C has similar morphology.

a)

Figure 4 - Morphology of typical fracture surface for sample 4LT (arrow – typical globular structure). Samples hydrated for longer times at 35 °C have a similar, but denser morphology.

a)

b)

Figure 5 - Morphology of typical fracture surfaces for sample 1HT-2C: a) dense hydration products; b) needle-like structures associated with large pores.

Figure 6 – Effects of curing regime on pore size distribution