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# IMPACT OF STEAM TREATMENT ON THE MICROSTRUCTURE AND CHEMISTRY OF CURED OIL WELL CEMENTS

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## Abstract

The cement sheath in thermal recovery oil wells is subjected to elevated temperatures up to about 320°C during the injection of steam to stimulate high viscosity crude oil production. Initially the cement sheath in these wells is pre-cured at formation temperature ( $\leq 40^\circ\text{C}$ ) prior to being exposed to steam treatment. Steam treatment can be performed anytime from immediately after the cement has set to years later. It is generally assumed that the cement chemistry and microstructure resulting on steam injection is similar to that obtained for geothermal cements where the cement sheath is heated directly to elevated temperatures as it is pumped downhole and cured at those temperatures. The objective of this study was to determine the impact of steam treatment on the microstructure and chemistry of pre-cured cement pastes.

Thermal cement samples composed of Class G well cement and 40% silica flour by weight of cement were cured at 35°C for 1 and 14 days followed by steam curing at 230°C and 20.7 MPa pressure for 1 day and then allowed to cool to ambient temperature over 48 hours. A variety of analytical techniques were used to determine the mineralogy and microstructure of hydrated cement phases. Comparison was made with baseline samples that had been cured at 4 and 17 days at 35°C and a sample heated to and cured at 230°C for 1 day and cooled over 48 hours to ambient temperature without prior curing at 35°C.

Cements cured at 35°C prior to heating at 230°C showed significant differences in chemistry and microstructure compared to the baseline samples. On heating the pre-cured samples to 230°C complete conversion of the amorphous C-S-H gel,  $\text{Ca}(\text{OH})_2$ , ettringite and unreacted  $\text{SiO}_2$  flour to crystalline C-S-H occurred. Xonotlite and 1.1nm tobermorite were the predominant phases with other minor identifiable and non-identifiable phases present. Fracture surfaces also showed different features occurring between samples pre-cured for 1 and 14 days at 35°C. More notable was the fact that the baseline sample heated directly to 230°C contained a mixture of amorphous and crystalline C-S-H and  $\text{Ca}(\text{OH})_2$  as well as unreacted  $\text{C}_4\text{AF}$  and silica flour. In that sample aluminium substituted tobermorite was the predominant crystalline C-S-H phase with indications of xonotlite and other crystalline phases. The impact of pre-curing on the chemistry cement sheath integrity in comparison to direct cure at 230°C is discussed.

## Originality

The work in this paper is part of a more extensive study to investigate the impact on cement sheath microstructure, chemistry and physical properties resulting from steam treatment processes used in enhanced oil recovery. In the case of enhanced steam recovery, the well is cemented at temperatures  $\leq 40^\circ\text{C}$  and only once the cement has set and the well is in production is it exposed to elevated temperatures that can reach up to 320°C from steam injection. Steam injection treatments can occur immediately on production or years later depending on rate of oil recovery.

No study has been reported that specifically investigates the effect of steam injection on cement that has first been allowed to set at  $\leq 40^\circ\text{C}$ . It has generally been assumed that the phase assemblage, microstructure and long term stability are similar to those of cements cured at temperature and pressure as in deep or geothermal wells. The originality of the present work is that it shows that there are some notable differences in the stable phases and in the microstructure produced by the two curing conditions that may impact the integrity of the cement sheath.

## Chief contributions

Cement research typically examines the behaviour of cementitious materials when they are hydrated under a single temperature regime (i.e. close to room conditions or at a constant, higher temperature and pressure). This type of temperature regime is not representative of conditions during enhanced oil recovery operations in oil well, where the cement is typically hydrated initially at temperatures  $\leq 40^\circ\text{C}$ , but is later exposed to temperatures of up to 320°C. It has generally been assumed that cements hydrated under these conditions are similar in properties to those hydrated entirely at the high temperature and pressure conditions seen in deep or geothermal wells. The chief contribution of this work is to demonstrate that the two curing conditions produce hydrated cements with substantially different properties. The phase assemblage and microstructure of the hydrated cements produced when cements are allowed to set at  $\leq 40^\circ\text{C}$  and then heated to high temperatures are unique and significantly different from those produced when the cement is hydrated entirely at the higher temperature. These differences suggest that the impact of changing temperature regimes needs to be considered in sheath design and placement.

**Keywords:** well cements, phase transformation, thermal cements, mineralogy, mechanical properties

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## Introduction

Cyclic steam injection and steam flood techniques have been used throughout the world to enhance heavy oil recovery from oil wells (Chu, 1985). Cyclic steam injection follows a pattern of heating a vertical production well over short periods of time, followed by return to production of oil (Earlougher, 1969). The most prevalent steam flood technique, steam assisted gravity drainage (SAGD) (Butler, 1998) involves drilling two shallow wells vertically then extend horizontally into the base of the reservoir with one well above the other. Steam is injected into the top well into the reservoir, where it condenses and heats the surrounding heavy oil. The viscosity of the oil decreases and gravity drains it to the lower production well. Temperatures in the wells can reach up to 320°C.

Both techniques use a cement sheath to seal the annulus between the well casing and the rock formation in order to prevent unwanted fluid migration, especially of oil, gas or steam (Nelson and Barlet-Gouédard, 2006). Zonal isolation and cement sheath integrity are considered to be key requirements for enhanced heavy oil recovery (DeBruijn, 2009). The sheath is typically composed of a special thermally stable oil well Portland based cement blended with silica flour at 35-40 % the mass of cement (Eilers and E.B. Nelson, 1979). This procedure reduces the calcium to silica (C/S) ratio of the material to approximately 0.8 and produces crystalline calcium silicates hydrates that are stable over a range of temperatures and which provide good compressive strength and low permeability (Nelson, 1980).

Although the behaviour of crystalline calcium silicate hydrates over the temperature range of 110 - 320°C has been well documented (Taylor, 1980; Harker, 1964; Mellor *et al.*, 2009), most studies to date have been on cement heated to and cured at those temperatures. In enhanced recovery wells the cement is cured at temperatures  $\leq 40^\circ\text{C}$ , producing C-S-H,  $\text{Ca}(\text{OH})_2$ , ettringite and other lower temperature hydration products. The degree of hydration of the cement sheath is dependent on the curing temperature and time prior to steam injection, which can be from days to years. Conversion of low temperature hydrated cement phases to crystalline hydration products on steam injection may not necessarily produce the same reaction kinetics or physical properties as those from cement hydrated immediately at the higher temperatures. Here we report on the differences in hydration products in terms of chemistry and morphology that result from heating thermal cements cured for 1 and 14 days at 35°C to 230°C from the behaviour observed in samples hydrated only at 35°C and only at 230 °C.

## Experiment

Class G oil well cement (Lehigh Inland, Calgary, AB, Canada) was dry blended with silica flour (Sil Industrial Minerals Inc., Calgary, AB, Canada) at a 1:0.4 mass ratio and mixed with water at a water/(cement + silica flour) ratio of 0.4 in a Waring blender according to API/ISO 10426-2-2003 (API 2005). Details of the cement and silica flour are presented elsewhere (Makar and Luke, 2011). The resultant slurry was conditioned in an atmospheric consistometer for 20 minutes at ambient temperature. It was then placed in sealed 2cm x 2cm x 16 cm bar brass molds. Molds containing the experimental samples were cured at 35°C in a water bath for 1 (sample 1LT-1HT-2C) or 14 days (sample 14LT-1HT-2C), demolded and then placed in a curing chamber (CTE, Tulsa, OK, USA). The curing chamber was 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. The sample labeling indicates the number of days at low temperature (LT), at high temperature (HT) and cooling (C).

Low temperature control samples were cured at 35°C for the same total curing times as the experimental samples, 4 days for sample 4LT and 17 days for sample 17LT. The high temperature control sample 1HT-2C was put directly into the curing chamber and cured at 230°C under the same curing regime as the pre-cured experimental samples. All high temperature sample production was performed at a pressure of 20.7 MPa.

Samples for SEM analysis (Hitachi S4800, Tokyo, Japan) were taken from exposed fracture surfaces after the bar samples had been broken. They were 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  $\mu$ A emission current and at ~9 mm working distance. Vacuum dried internal fragments taken from crushed bars were used to determine the mineralogy by X-ray diffraction (XRD) with CuK $\alpha$  radiation (Rigaku DMAXB, Woodlands, TX) and mass loss by thermogravimetric analysis (TGA) (TA Instruments SDT-Q600, New Castle, DE, USA).

## Results

### 1. XRD and TGA

XRD data for the low temperature control samples 4LT and 17LT showed the phase assemblage that would be expected from the hydration of an oil well cement at near ambient temperatures, including the presence of crystalline Ca(OH)<sub>2</sub> and ettringite, a C-S-H created hump in the background of the spectra 36–44° 2 $\theta$ , and unreacted C<sub>3</sub>S, C<sub>2</sub>S and C<sub>4</sub>AF. As would be expected, unreacted silica flour was also present. The spectra for samples 4LT and 17LT can be found elsewhere (Makar and Luke, 2011).

Part of the recorded spectra for the high temperature control sample 1HT-2C and the two experimental samples is shown as Figure 1. As expected (Nelson, 1980; Taylor 1980; Harker 1964; Huang, *et al.*, 2002) sample 1HT-2C appears to be predominantly 11Å tobermorite, with a relatively small amount of xonotlite and katoite (dashed arrow) in the sample. Unreacted silica flour, unreacted C<sub>2</sub>S and some residual C-S-H were also present.

The experimental samples 1LT-1HT-2C and 14LT-1HT-2C had similar phase assemblages to each other (Figure 1), but had substantial differences from that observed for sample 1HT-2C. In both cases the predominant phase observed was xonotlite, with 11Å tobermorite present in much lower quantities. The solid arrow at ~39.4° 2 $\theta$  shows an example where a tobermorite peak was apparent in 1HT-2C sample, but not in the two experimental samples. It also appears that more tobermorite was present in sample 1LT-1HT-2C than in sample 14LT-1HT-2C. The solid arrow at ~30.2° 2 $\theta$  indicates a tobermorite peak that clearly shows the change in tobermorite peak intensity between the three high temperature samples. Conversely, the dotted arrows indicate examples of xonotlite peaks that show increasing intensity as the length of pre-curing time increases.

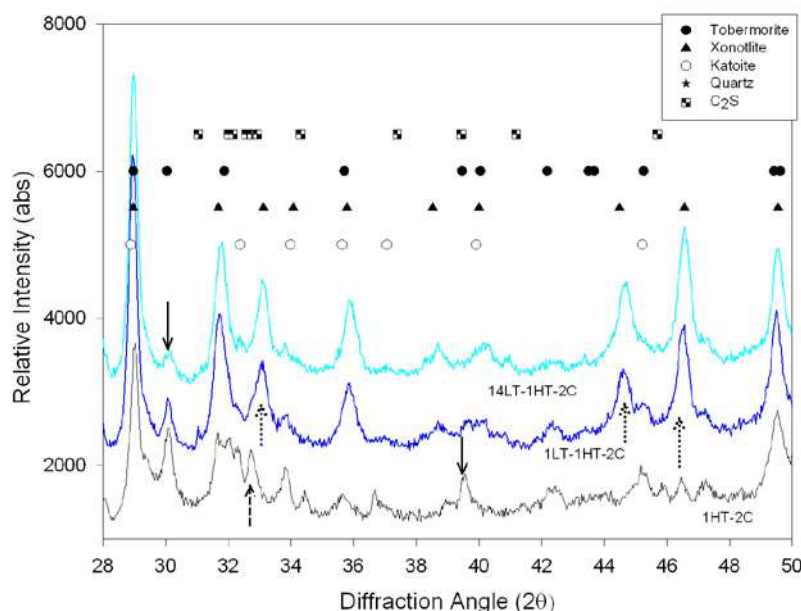


Figure 1: X-ray diffraction spectra for high temperature samples

The results of the thermogravimetric analysis are shown in Figure 2. The three control samples show considerable mass losses between 0 and 140 °C, which may be attributed to the disassociation of C-S-

H and ettringite in the low temperature samples 4LT and 17LT and tobermorite in the high temperature control 1HT-2C. Comparison to the results in Figure 2 for the two experimental samples suggests that much of the water in the tobermorite was driven off during the initial heating of the sample. Residual C-S-H would also disassociate in this temperature range. Above 145 °C the mass loss in sample 1HT-2C slows as the remaining water is removed. At about 750 °C an abrupt mass loss (Figure 3) occurs that can be associated with the topotactic decomposition of both tobermorite and xonotlite to wollastonite (Taylor, 1959, Buckner *et al.*, 1960).

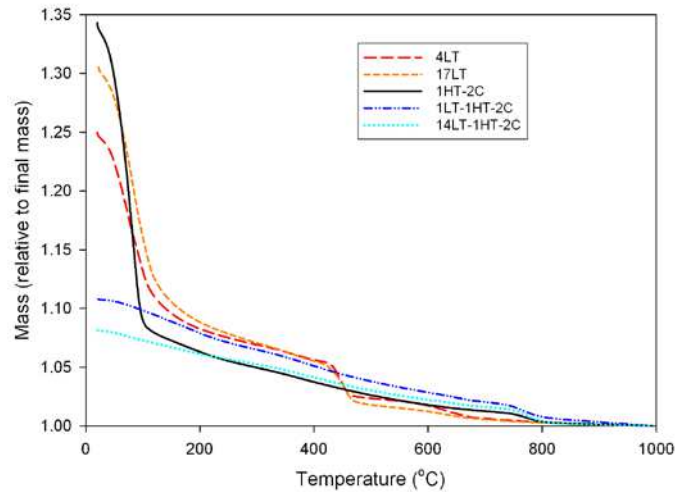


Figure 2: Mass loss due to disassociation upon heating

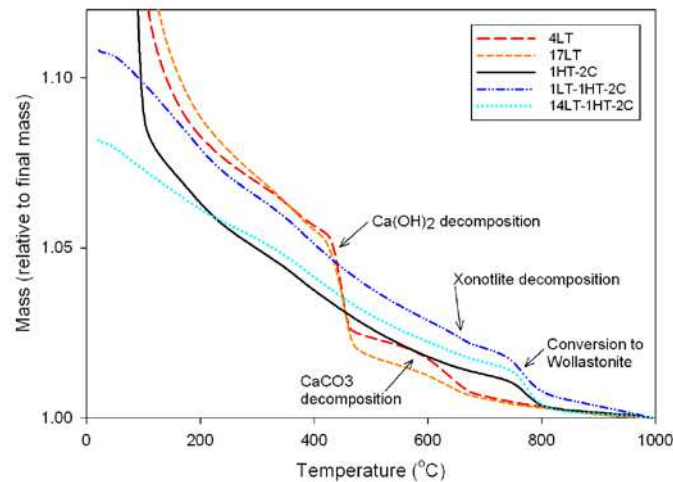


Figure 3: Mass loss due to disassociation upon heating (lower third of Figure 2)

Both samples 1LT-1HT-2C and 14LT-1HT-2C do not have high initial loss of mass upon heating, instead having a much shallower slope that is not dissimilar to that followed by the same samples between 200 and 600 °C. Sample 1LT-1HT-2C does have a higher total mass loss, which may be due to the increased presence of tobermorite noted in Figure 1 and the possible presence of residual C-S-H. The pattern of mass loss for the two high temperature experimental samples above 200 °C is similar to that of 1HT-2C in the same range (Figure 3), although there is a higher degree of mass loss in 1LT-1HT-2C than in 14LT-1HT-2C. Water contained in the experimental samples before heating appears to have been driven off during the heating process, with the calcium hydroxide that would have been present in the sample taken up during the conversion process. Partial decomposition of the xonotlite in the two experimental samples may be taking place at about 650 °C (Huang, *et al.*, 2002). The latter



result is more readily observed in the derivative TGA data for the samples, published elsewhere (Makar and Luke, 2011).

## 2. Scanning Electron Microscopy

Imaging of the fracture surfaces from the low temperature samples produced results that were consistent with those reported in the literature for hydrating cements (Diamond, 1976). All of the high temperature samples showed regions of dense calcium silicate hydrates along with more crystalline hydration products. However, the morphology of the calcium silicate hydrates varied depending on the curing regime. Examples of the dense calcium silicates from each sample are shown in Figure 4. Although the XRD and TGA results show differences in composition, there appears to be little difference between the observed morphologies for samples 1HT-2C (Figure 4a) and sample 1LT-1HT-2C (Figure 4b), but the dense calcium silicate hydrates in sample 14LT-1HT-2C (Figure 4c) appear to be more fibrous in structure. The fibrous morphology has been reported previously for xonotlite (Taylor, 1964) and its appearance in Figure 4c but not in Figure 4b suggests that the crystallite size was larger in sample 14LT-1HT-2C.

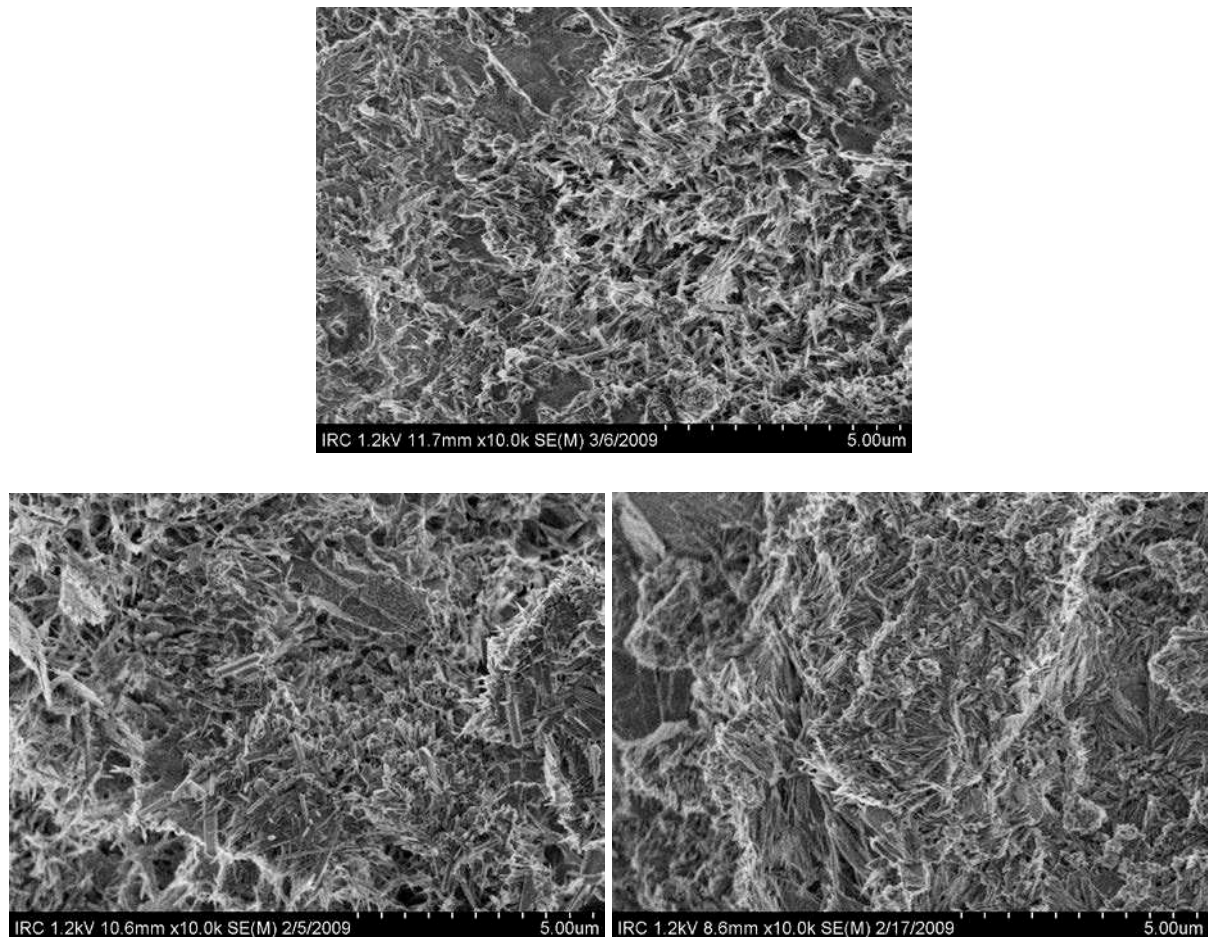


Figure 4: Dense calcium silicate hydrates in samples: a) 1HT-2C (top), b) 1LT-1HT-2C (lower left) and c) 14LT-1HT-2C (lower right)

While the dense calcium silicate hydrates in sample 1HT-2C seem to have similar morphology to sample 1LT-1HT-2C, the more crystalline hydration products in the same samples showed distinct differences. In sample 1HT-2C fine needle-like rods were seen on the surfaces of large pores (Figure 5a). The rods were too fine for analysis by energy dispersive spectroscopy (EDS) in the SEM, but



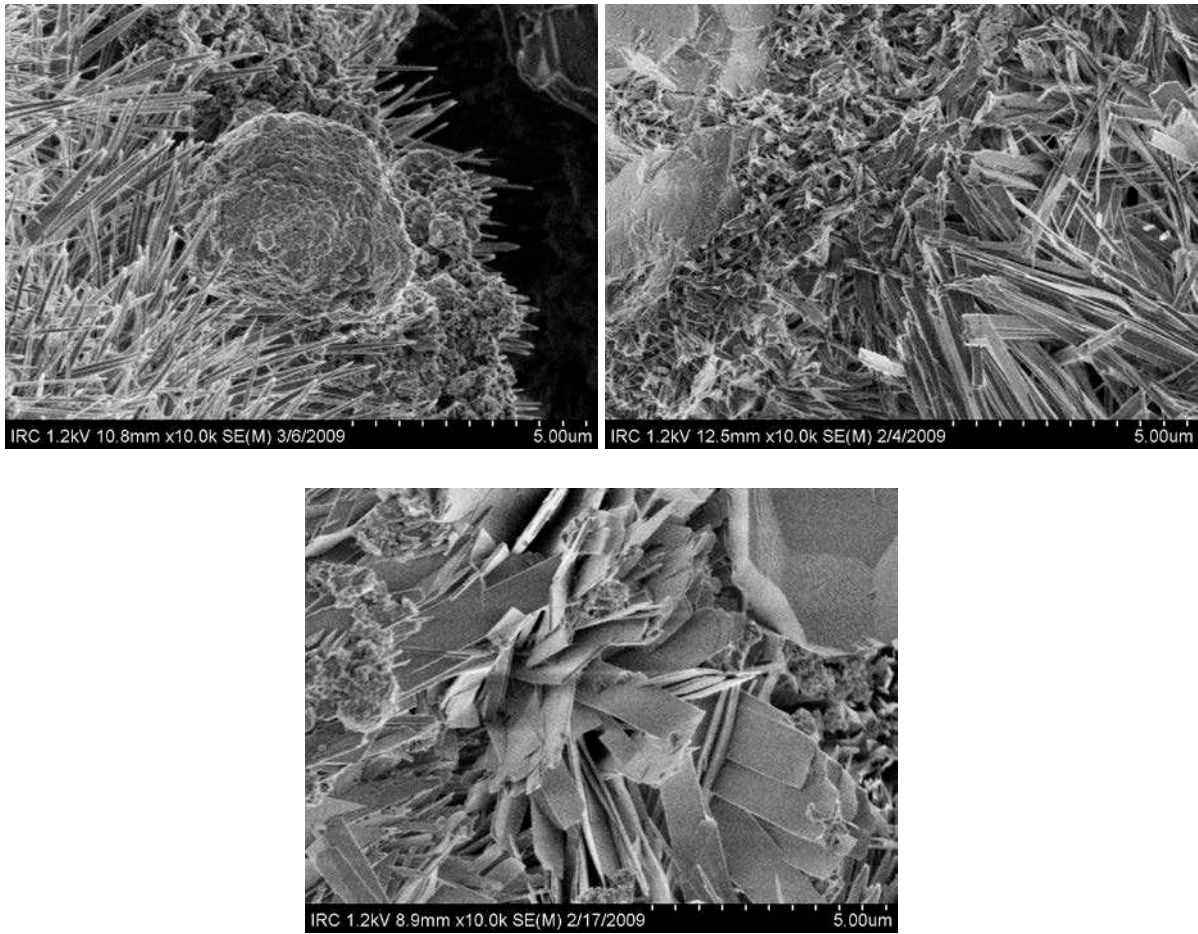


Figure 5: Observed crystalline morphologies indicated by white arrows: a) needles in 1HT-2C (upper left), b) laths in 1LT-1HT-2C (upper right) and c) plates in 14LT-1HT-2C (bottom)

Table 1: Composition of plates in Figure 5c

Element	Atomic %
O	70.8
Na	0.2
Al	1.7
Si	13.3
S	0.2
K	0.5
Ca	13.2
Fe	0.1

the morphology is one that is typically seen for tobermorite (Taylor, 1964). Both sample 1LT-1HT-2C and 14LT-1HT-2C, however, showed examples of lathe-like structures (Figure 5b), which may be either tobermorite or xonotlite (Taylor, 1964). All three samples also contained examples of platy

structures, which were often large enough for EDS analysis. The average results for four measurements on the structure shown in Figure 5c are shown in Table 1 and are consistent with aluminum substituted calcium silicate hydrates, indicating, along with the morphology, that they were xonotlite.

## Conclusions

While curing thermal cement blended with silica flour directly at 230 °C produced samples predominantly composed of tobermorite, the results from the different analytical methods presented here show that pre-curing the sample for either 1 or 14 days at 35 °C before heating to 230 °C produced samples that were predominantly composed of xonotlite, with the sample pre-cured for 14 days having a higher proportion of xonotlite and larger bulk crystallites than the sample pre-cured for 1 day. The analysis showed that heating the pre-cured samples caused most of the water they contained to be driven off from the material as the C-S-H, residual silica flour, residual C<sub>2</sub>S and calcium hydroxide was consumed. As xonotlite and tobermorite have different physical properties (Kyritsis *et al.*, 2009), the differences between the composition of the samples produced by the different curing regimes suggests that the curing regime can affect the performance of the cement sheath in steam treated oil wells.

## References

- API, 2005. API/ISO 10426-2-2003 Recommended Practice for Testing Well Cements. *API RP 10B-2 (Fifth Edition)*, Washington, DC, USA.
- Buckner, D.A., Roy, D.M. and Roy, R., 1960. Studies in the System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O, II: The System CaSiO<sub>3</sub>-H<sub>2</sub>O. *Amer. J. Sci.*, 258, 132-147.
- Butler, R.M., 1998. SAGD Comes of Age. *J. Can. Pet. Tech.* 37(7), 9-12.
- Chu, C., 1985. State-of-the-Art Review of Steamflood Field Projects. *J. Pet. Tech.*, 37(10), 1087-1902.
- DeBruijn, G., et al., 2009. Flexible Cement Improves Wellbore Integrity in SAGD Wells. *SPE/IADC 119960*.
- Diamond, S., 1976. Cement Paste Microstructure – An Overview at Several Levels. In *Hydraulic Cement Pastes: Their Structure and Properties*, (C.A. Association, ed.) Cement and Concrete Association, Wexham Springs, Slough, UK, 3-23.
- Eilers, L.H. and Nelson, E.B., 1979. Effect of Silica Particle Size on Degradation of Silica Stabilized Portland Cement. *SPE* 7875.
- Earlougher, R.C. 1969. Some Practical Considerations in the Design of Steam Injection Wells. *J. Pet. Tech.*, 21(1) 79-86.
- Harker, R.I., 1964. Dehydration Series in the System CaSiO<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. *J. Am. Ceram. Soc.* 47, 521-529.
- Huang, X., Jiang, D. and Tan, S., 2002. Novel Hydrothermal Synthesis Method for Tobermorite Fibers and Investigation on their Stability. *Matr. Res. Bul.*, 37, 1885-1892.
- Kyritsis, K., Hall, C., Bentz, D.P., Meller, N., and Wilson, M. A., 2009. Relationship Between Engineering Properties, Mineralogy, and Microstructure in Cement-Based Hydroceramic Materials Cured at 200°–350°C. *J. Am. Ceram. Soc.*, 92(3) 694–701.
- Makar, J.M. and Luke, K.E., 2011 Cement Sheath Stability In Steam Treated Oil Wells, in submission *J. Am. Ceram. Soc.*
- Mellor, N., Kyritsis, K. and Hall, C., 2009. The Mineralogy of the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (CASH) System from 200 to 350°C, *Cem. Concr. Res.* 39, 45-53.
- Nelson E.B., 1980. High Temperature Cement Compositions Pectolite, Scawtite, Truscottite or Xonotlite: Which Do You Want?, *SPE* 9286 .
- Nelson E.B. and Barlet-Gouédard V., 2006. Thermal Cements, in *Well Cementing*. Ed. Nelson, E.B. and Guillot, D., Sugarland Texas: Schlumberger, 335-336.
- Taylor, H.F.W., 1980. Structure and Composition of Hydrates. In: *7<sup>th</sup> International Congress on the Chemistry of Cement*, Moscow, Vol.1, PII 2/1-2/13.
- Taylor, H.F.W., 1959. The Transformation of Tobermorite into Xonotlite. *Mineral. Mag.*, 110-116.
- Taylor, H.F.W., 1964. *The Chemistry of Cements*, Academic Press: London.