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Portland cement solutions for ultra-high temperature wellbore applications

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ABSTRACT

Designing highly stable and low permeability high-strength oil well cement above 500 °F (>260 °C) is *extremely* difficult because the Portland cement undergoes strength retrogression starting at 230 °F (110 °C). Thus, fine crystalline silica stabilizer is required in the cement slurry design when cured until 400 °F (204.4 °C) to prevent this problem. However, the optimum particle size and the right practical dosage of silica in the cement slurry have not been clearly determined and studied for cement that will be subjected at such extremely high temperature (>500 °F), condition applicable for many ultra-deep geothermal and steam injection wells. Due to extreme heating conditions and tedious experimentation, there are only few published studies to date toward understanding the behavior of Portland cement used at that exceedingly high temperature; and thus, making the initial cement design highly challenging. Based on thorough experimental study, this paper presents new understanding and provides proper guidance to designing highly stable non-retrogressing and low steady permeability oil well cement for ultra-high temperature use. Moreover, this research carefully investigates the effect of the particle size of crystalline silica to the compressive strength, porosity and permeability of the cured cement. Finally, the substitution of crystalline silica with amorphous silica material in the ultra-high temperature cement is also exploited. Supplementary powder X-ray diffraction measurement identifies high temperature stable crystal phase Xonotlite ($Ca_6Si_6O_{17}(OH)_2$) in the silica-stabilized Portland cement. However, based from these current experimental results, it is observed that formation of Xonotlite crystal phase does not completely guarantee the longer term mechanical integrity of the cement sheath at ultra-high temperature, especially when the mixture contains amorphous-type silica in the blend.

1. Introduction

Neat Portland cement that is being used in cementing deeper, steam injection or geothermal wells [1–3] is known to experience strength retrogression at a critical temperature above ~230 °F (~110 °C). Briefly, strength retrogression is described as the decrease in the compressive strength of the set cement over time and is accompanied by increase in porosity and permeability. This phenomenon is prevalent with increasing temperature and is vastly severe at the early stage of high temperature heating (e.g. few days to a month) [4], which can be easily followed by the *in-situ* compressive strength measurements of the neat cement via Ultrasonic Cement Analyzer (UCA) testing (Fig. 1). The degrading cement has been reported to be mostly composed of weaker type of crystal phase like the lime-rich alpha-dicalcium silicate hydrate (α-C_2SH) that is denser than the usual calcium silica hydrate (C-S-H) product [5,6] and which can undergo deleterious bulk volume decrease either via shrinkage or in terms of porosity, resulting in a decrease in cement strength and upsurge permeability [7–9]. While Hillebrandite and β-tricalcium silicate hydrate are known to form in the neat cement subjected to much higher curing temperatures (ca above 300 °F or 149 °C), which are also classified as weaker type of cement crystal phases associated with higher permeability [2,10,11].

Cement strength retrogression is a serious problem that must be resolved for overall longer term well integrity of a very costly well and to ensure zonal isolation for the entire life of well. As an established chemical strategy, fine crystalline silica stabilizer is added to avert the strength deterioration of Portland cement when exposed to ultra-high temperature [12]. Portland cement has

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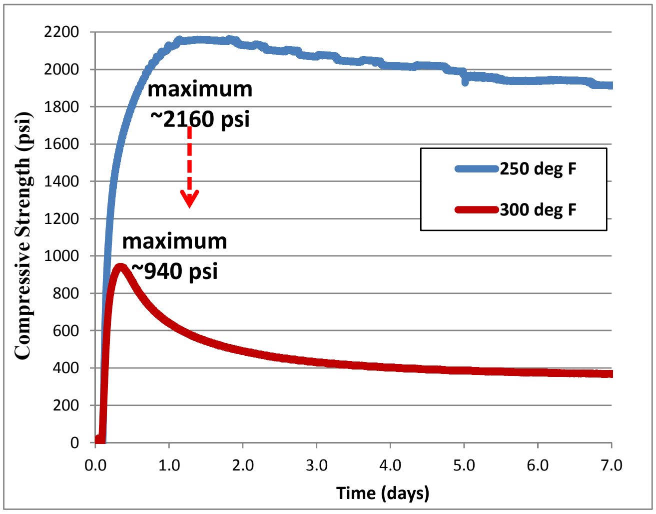

Fig. 1. Real time compressive strength measurements at 250 °F (121 °C) or 300 °F (148.9 °C) and 2500–3000 psi (17.2–20.7 MPa) pressure via Ultrasonic Cement Analyzer (UCA, OFITE Model 120-51) of the 15.9 ppg density (1.9 g/ml) neat cement slurry (0% bwoc silica) of Dyckerhoff class G.

calcium oxide to silicon dioxide (C/S) ratio close to 3.1 but upon addition of extra quantity of silica (typical dosage ~35% bwoc) [13,14] decreases the ratio close to 1.0, desirable for the stable formation of non-retrogressing stronger cement at temperature above ~230 °F (110 °C). For instance, the addition of adequate amount of silica to the cement design inhibits the reaction forming α-C_2SH and instead allows the development of silica-rich cement phases like Tobermorite or Xonotlite (depending on heating temperature), which give high compressive strength of cement when cured at that extreme temperature condition. Earlier published reports [2,15–17] highlighted the “cement hydration phase” diagram by Taylor [18], which emphasized the importance of strictly keeping the ratio of C-to-S to1.0 or less in order to form these temperature stable silica-rich cement phases that provide low permeability strong cement. Further information about the chemistry of Portland cement [19–21] and silica blends at high temperature is also discussed elsewhere [4,11,22–24].

Although strength retrogression was discovered in the mid-1930s [25], this problem was only given more attention and carefully disclosed in mid 1950s [26]. It was found out that all types of Portland and oil well cements have lower strengths when cured at 320 °F (160 °C) than at 200 °F (93.3 °C) [26], contrary to the earlier general notion that the strength of cement increases with an increase in temperature. However, this initial high temperature study was only limited to 7 days curing, and it only focused on the mechanical property of the resulting cement. Then this phenomenon was further confirmed by other studies [27,28], showing higher strength retrogression when increasing the curing temperature above 230 °F (110 °C). Then it was also described that retarded cements (API class E) will lose about 50% of their 24-h strength over time when cured at 320 °F (160 °C) while bentonite extended cement will severely lose strength to the point of catastrophic failure under the same heating temperature [29]. Thenceforward in 2007, more advanced *in-situ* synchrotron X-ray diffraction technique was used to study further the use of silica-rich mineral additives to prevent strength retrogression of class H Portland cement when heated at 356 °F (180 °C) at 7 MPa and 52 MPa pressure. Crystalline hydration product mostly Tobermorite is formed with cementing systems containing silica, zeolite or combination of both [30]. Former synchrotron study suggests a two-stage mechanism towards the formation of highly ordered crystalline Tobermorite or Xonotlite from a poorly crystalline C-S-H gel phase at a reaction temperature between 374 °F (190 °C) to 590 °F (310 °C) but there was no report about the permeability and compressive strength of the resulting material [31]. To date still only few studies are reported highlighting the significance of silica particle size to successfully prevent strength retrogression at temperature above 500 °F (260 °C) [32]. Moreover, there is no clear agreement yet on the right and practical dosage of silica in cement designs that will be exposed to such extremely high temperature. For instance, earlier published research mentioned that 35% bwoc to 40% bwoc silica is inadequate to create high-strength low permeability cement and excessive amount of silica was suggested (e.g. 60% bwoc to 80%bwoc) to provide long strength stability when the cement was subjected to 550 °F (287.8 °C) and above [33]. With increasing hotter oil and gas wells nowadays, knowing the optimum amount of silica needed for ultra-high temperature cement designs is highly important [34] since adding extremely less or more is detrimental to the strength of the cement sheath not to mention the relatively high price of crystalline silica material.

In this paper, firstly, we provide clear understanding about the optimum dosage of crystalline silica necessary to prevent the strength retrogression of class G Portland cement at ultra-high temperature (up to 550 °F or 287.8 °C) and for extended period of time (30 days). Our new findings suggest the optimal dosage of crystalline silica to fight strength retrogression and provide a high strength and low steady permeability cement at ultra-high temperature, as long as the correct size of silica particles is used. The exact chemistry of this strong cement is determined by X-ray diffraction analysis, confirming the formation of high temperature stable crystal phase. Then, gas permeability study indicates that the size of the silica particle is very crucial in obtaining high strength low steady permeability cement. Secondly, by varying the size of the crystalline silica, we have studied the relationship between the remaining SiO_2 peak versus particle size and the duration of thermal treatment. Finally, we have also investigated if one could really substitute certain amount of the crystalline silica by highly reactive amorphous silica (silica fume), keeping the total amount of silica in the cement mixture to ~40% bwoc and still provide a thermally stable cement slurry. The later study is equivalently important since several field practices utilize amorphous silica to adjust the rheology and prevent settling behavior of lower density (higher water/cement ratio) high temperature slurries. This study will provide insights if the amorphous silica can be taken into consideration while understanding the longer term cement sheath mechanical stability versus C/S ratio.

2. Experimental methods

2.1. Materials

American Petroleum Institute (API) class G cement sample (SG ~3.15) was obtained from Dyckerhoff, Germany. Commercially available drinking water (deionized water) from Ozarka was used as reactive water for preparing the actual cement slurry. The extra cement additives used in the cement slurry design were supplied by Lubrizol Oilfield Solutions (LZOS): (i) Copolymer of *N*,*N*-dimethylacrylamide and acrylamido-2-methylpropane sulfonic acid or commonly known as AMPS-based polymer fluid loss control (1.0–1.6% by weight of cement (bwoc)), (ii) magnesium oxide-based expansion additive (2% bwoc dosage), (iii) silicon-based defoaming agent (0.02 gallon per sack (gal/sk)), (iv) fine crystalline silica of varying sizes like 100 mesh, 200 mesh, and 325 mesh (dosage varied and exact amount is indicated in the discussion), and (v) amorphous silica (fumed silica) (dosage varied and exact amount is indicated in the discussion). No cement retarder was