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Development of silica-enriched cement-based materials with improved aging resistance for application in high-temperature environments

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ABSTRACT

Understanding the effects of high temperature (HT) and high pressure (HP) conditions on the microstructure of cement-based materials is critical to the construction and safe operation of deep oil and gas wells. Under such conditions, the persistence of calcium-silicate-hydrate (C-S-H) gel is compromised by ongoing crystallization that, if not controlled, may adversely affect the durability of the cement sheath. This work investigates the effect of silica content > 35% by-weight-of-cement (BWOC), silica particle size, and solid volume fraction (SVF) on the microstructure and phase composition of cement-silica blends cured hydrothermally at 200 °C and 20.7 MPa. The results of X-ray diffraction and electron microprobe analysis revealed significant impact of these three mix design parameters on the final phase assembly, and on the conversion rate of semi-crystalline C-S-H to gyrolite and 11 Å tobermorite. Incorporation of more fine siliceous material suppressed dissolution of coarse silica particles, resulting in a matrix with improved homogeneity and dominated by fine gel pores. Mixes with lower SVF showed greater formation of 11 Å tobermorite, a higher degree of crystallinity and/or greater crystallite size. Prolonged HTHP curing of all systems (up to three months in this study), irrespective of the initial SVF, increased the fraction of capillary pores, indicating void coalesce caused by crystal growth. However, we find that this coarsening is less pronounced in systems with less pore space available for crystallization.

1. Introduction

In recent years there has been increased interest in oil and gas production from unconventional resources [1]. Shale gas, a natural gas trapped within low permeability shale formations, and heavy oil, an asphaltic, dense and viscous crude oil, are two examples of fossil fuels whose recovery has become technologically feasible and economically sound [2]. However, recovering these energy reserves often requires overcoming hostile downhole conditions, such as high-temperatures (HT) and pressures (HP). The HTHP environment amplifies the risks that exist in conventional wells. Therefore, a higher demand is placed on the reliability of the materials and technologies employed in the well production system.

A vital part of the well system is the cement sheath. Its role is to support the casing and to provide the zonal insolation during well operation and even beyond the well's productive life. When subjected to harsh HTHP downhole conditions, the cement must be capable of resisting a variety of potentially damaging mechanical and physico-chemical processes such as mineralogical transformations, excessive crystal growth, thermal stresses or pressure changes. Long-term stability of the cement sheath in HTHP conditions is of critical importance for well safety and maintenance.

It has long been known that the addition of silica to Portland cement, such that the overall Ca/Si molar ratio is decreased to about 1, avoids the early strength retrogression experienced by neat cement slurries cured at temperature above about 100 °C [2, 3, 4]. However, the long term durability and structural performance of silica-enriched cement is still an issue that may compromise the operation of the entire well system leading to failure. In recently published work [5, 6], we identified a 'coarsening mechanism' that negatively affects the microstructure and long-term performance of conventional oil-well cement systems containing 35% silica flour (ground quartz) by weight of

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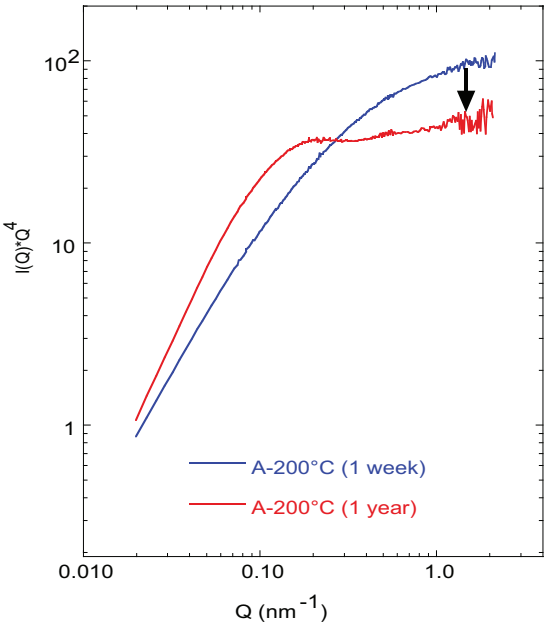
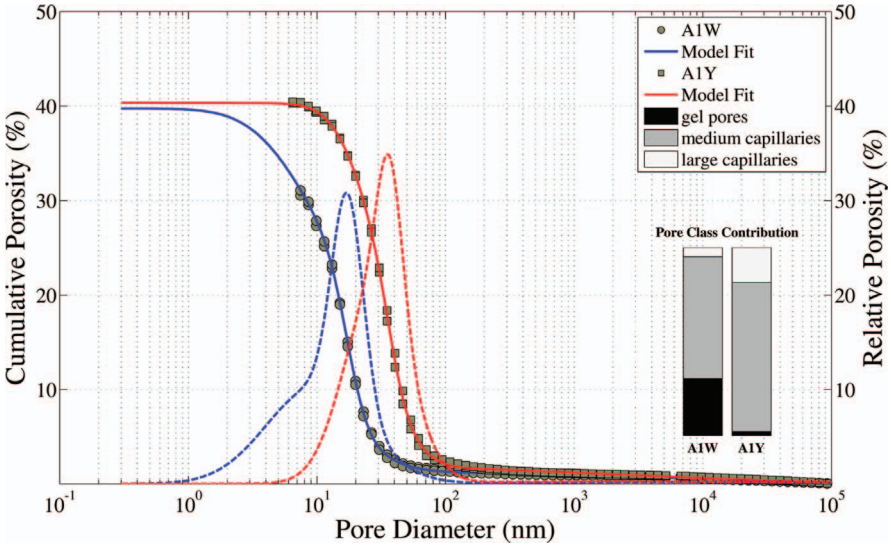


(a)



(b)

Fig. 1. Coarsening of a binder consisting of Class G cement with 35% bwoc silica flour and exposed to hydrothermal curing at 200 °C for one week (A1 w) or one year (A1 y), after [5]. a) Small-angle neutron scattering (SANS) results showing a decrease in the scattered intensity at the highest Q-values (marked by a downward arrow), which indicates a reduction in the specific surface area, SSA. The horizontal shift of the high-Q Porod scattering regime with time toward lower Q-values indicates the growth of the smallest solid features generating scattering. b) Mercury Intrusion Porosimetry (MIP) results showing an increase in the median pore diameter and a significant reduction of the gel porosity in favor of medium and large capillaries with time.

cement (BWOC), and subjected to HTHP hydrothermal conditions. This microstructure coarsening consists of changes in the nanometer-level microstructure of the cement sheath; specifically, an increase in the size of the fundamental particles (comprised of crystalline CSH, e.g. xonotlite) of the binding matrix as the cement sheath ages (Fig. 1a). As a consequence, the pore space undergoes pore coalescence such that fine gel pores are replaced by medium and large capillary pores (Fig. 1b), causing a reduction of the specific surface area (SSA). These microstructural changes cause a gradual decline in the compressive strength and fracture toughness of the cement sheath material [5].

In this work we investigated the effects of adding silica in amounts greater than the commonly accepted and used value of 35% BWOC. This includes analysis of phase evolution and composition with X-ray powder diffraction (XRD) and electron microprobe (EPMA) techniques. Additionally, small angle neutron scattering (SANS), mercury intrusion porosimetry (MIP), and electron microscopy (SEM) were used to study the effects of silica particle size and the solid volume fraction of the mix design on the nanotexture evolution during prolonged HTHP treatment.

2. Materials and methods

2.1. Materials synthesis

All samples were prepared using Class G Portland cement (Dyckerhoff, Wiesbaden, Germany). All of the silica used was crystalline α-quartz. Two distinct silica particle sizes were used (see Fig. 2). For the D-type specimens, fine and coarse silica powders developed for commercial oilwell cementing, with median particle size $d_{50} \approx 2\,\mu m$ and $d_{50} \approx 110\,\mu m$ respectively, were used. For the T-type specimens, a technical grade silica (MIN-U-SIL®5, US-Silica) with a particle size slightly finer than the fine silica was used.

The mix designs for all specimens are given in Table 1. Systems D1 and D2 contain both fine and coarse silica, and thus have a bimodal distribution of silica particles. While D1 and D2 systems have the same total silica content of 65% by volume of the blend, system D2 contains more fine silica (and thus less coarse silica). The overall Ca/Si molar ratio of the D-system is 0.38, which is low enough to ensure that the