



Effect of sodium carboxymethyl celluloses on water-catalyzed self-degradation of 200 °C-heated alkali-activated cement



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ABSTRACT

This paper investigates the usefulness of sodium carboxymethyl celluloses (CMC) in promoting self-degradation of 200 °C-heated sodium silicate-activated slag/Class C fly ash cementitious material after contact with water. CMC emitted two major volatile compounds, CO₂ and acetic acid, creating a porous structure in cement. CMC also reacted with NaOH from sodium silicate to form three solid reaction products, disodium glycolate salt, sodium gluconic salt, and sodium bicarbonate. Other solid reaction products, such as sodium polysilicate and sodium carbonate, were derived from hydrolysates of sodium silicate. Dissolution of these products upon contact with water generated heat that promoted cement's self-degradation. Thus, CMC of high molecular weight rendered two important features to the water-catalyzed self-degradation of heated cement: one was the high heat generated in exothermic reactions in cement; the other was the introduction of extensive porosity into cement.

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1. Introduction

To increase hot water or steam production the geothermal reservoirs are usually constructed in highly permeable formations that are poorly consolidated, naturally fractured or undergo through stimulation operations where large volumes of water are forced into the hot formation to open existing and create new fractures [1,2]. Consequently, lost circulation, when drilling fluid is partially or completely lost into the formation, is a common problem during construction of geothermal wells. Temporary sealing materials address this issue by plugging the fractures during the drilling operations and opening them later by disintegration when the drilling is completed.

Presently, Ordinary Portland Cement (OPC) is used as a well-casing cementing material; it is also often adapted as the binder in the sealing systems [3,4]. The major drawback of OPC use in corrosive geothermal wells is its limited resistance to the hot acidic environment created by the combination of concentrated dihydrogen sulfide (H₂S) and carbon dioxide (CO₂). As is well documented [5,6], the capacity of OPCs to withstand acid is very poor, and they suffer from severe acid erosion. To deal with this problem, acid-resistant cements are required. Alkali-activated cementitious materials (AACMs) prepared from industrial by-products with pozzolanic properties such as granulated blast-furnace slag and

sodium silicate with various molar ratios of Na₂O/SiO₂, as alkali activators of pozzolanic reactions, have low susceptibility to acid erosion [7,8].

The present work evaluates potential of these AACMs as temporary sealers for geothermal wells.

The drilling temperatures of geothermal wells seldom exceed 116 °C [9] with an average temperature being around 85 °C due to the cooling effect of circulating fluids. However, well temperature rises up to more than 200 °C under static conditions, when the drilling is completed. The ideal sealer must not only plug the fractures at a low temperature of 85 °C, but also it must self-degrade at the well temperature of ≥200 °C. In hot geothermal wells the sealer plugging the fractures may encounter two different environments: one is hydrothermal at the inlet of fracture; the other is hot and dry at its end. Thus, the sealer is required to disintegrate both in hot water at 200 °C and when coming in contact with water during stimulation operations after the dry heat of 200 °C.

Several biodegradable biopolymers are currently employed as additives for cements self-degradation; they include starch, cellulose acetate, gelatin, and poly(L-lactic acid) in the form of powder, microsphere, and fiber. All of them promote the partial biological degradation of biocompatible bone cements [10–15]. When these bone-cement additives come in contact with body fluids, they degrade, creating an interconnected pore network structure in the cement, allowing the bone-tissues to grow into the channels facilitating the cement degradation. For applications in geothermal wells, of particular interest is polymers' thermal degradation. The

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cellulose and cellulose-related compounds are degraded thermally in air at around 200 °C, yielding volatile CO₂ gas and acetic acid vapor [16–18]. Sodium carboxymethyl cellulose (CMC) and cellulose-related compounds are frequently used as additives in water-based drilling fluids to reduce fluid loss and to assure desirable rheological properties at elevated temperature [19–22]. Appropriate decomposition temperature along with the compatibility with drilling fluid make carboxymethyl cellulose to be a potential candidate for modifying the AACMs system for temporarily sealing applications. This study assesses the ability of CMCs of different molecular weights to degrade the 200 °C-heated AACMs after contact with water. The tested AACMs system of slag/Class C fly ash blend was activated with sodium silicate.

2. Experimental procedure

2.1. Materials

The four different sodium carboxymethyl celluloses (CMCs) evaluated for their ability to degrade sealing material were supplied by Dow Chemical Corporation under the commercial names “Walcofel CRT 30 PA, 100 PA, 2000 PA and 30,000 PA”. Two industrial by-products, possessing pozzolanic properties, were used as the hydraulic pozzolana cement: granulated blast-furnace slag under the trade name “New Cem” and Class C fly ash. The slag was supplied by Lafarge North America, and the fly ash was obtained from Boral Material Technologies, Inc. Their chemical compositions detected by micro energy-dispersive X-ray spectrometer (μ EDX) were as follows: Slag; 38.5 wt% CaO, 35.2 wt% SiO₂, 12.6 wt% Al₂O₃, 10.6 wt% MgO, 1.1 wt% Fe₂O₃, and 0.4 wt% TiO₂; Class C fly ash; 30.2 wt% CaO, 31.9 wt% SiO₂, 21.7 wt% Al₂O₃, 4.6 wt% MgO, 6.1 wt% Fe₂O₃, 1.7 wt% Na₂O, 0.7 wt% K₂O₃, and 3.1 wt% SO₃. An anhydrous sodium silicate granular powder under the trade name “Metso Beads 2048,” supplied by the PQ Corporation, was used as the alkali activator of these pozzolana cements; its chemical composition was 50.5 wt% Na₂O and 46.6 wt% SiO₂. The formula of the dry pozzolana cements employed in this test had slag/Class C fly ash ratio of 20/80 by weight. A 10% of this alkali activator by total weight of pozzolana cement was added to prepare the dry mix cementitious reactant. Further, 1.2% CMC by the total weight of pozzolana cement was incorporated into this dry mix. In preparing cement slurry with similar consistency, the water/blend (w/b) ratio depended on the particular CMC; namely, the ratio was 0.33, 0.39, 0.51, and 0.75, respectively, for 30 PA-, 100 PA-, 2000 PA-, and 30,000 PA-incorporated cement slurries. Higher molecular weight CMCs increased slurries' viscosities and required larger water amounts to be mixable. These slurries were left at room temperature in air for 72 h. Afterward, all set cements were autoclaved hydrothermally at 85 °C for 24 h under a pressure of 1000 psi. Since the ideal sealer not only plugs the fractures at 85 °C, but also self-degrades when the well temperature reaches \geq 200 °C, some 85 °C-autoclaved cements were further heated for 24 h in an oven at 200 °C. The heated samples were further exposed to water to simulate the stimulation operations when the sealer is expected to disintegrate.

To evaluate the susceptibility of CMCs to alkaline cement slurry at 85 and 200 °C, the cement pore solution was extracted from the slurry of sodium silicate-activated 20/80 slag/Class C fly ash cement by centrifuging slurries at 6000 rpm for 10 min. The pH of extracted pore solution was 13.7. The test samples were prepared in the following manner: first, 0.5 g CMC was immersed into 3 ml pore solution at room temperature; second, pore solution-wetted CMC was autoclaved for 24 h at 85 °C and 200 °C; and, finally the pore solution-treated CMC was dried at 100 °C for further testing.

2.2. Measurements

The molecular weight (MW) of the “as-received” 30, 100, 2000, and 30,000 PA CMCs was measured by High-Performance size-exclusion Chromatography/Laser Light Scattering (HPC/LLS). First, all the CMCs, except for 30,000 PA, were dissolved in running buffer at \sim 3.5 mg/ml concentration, then filtrated through a 200 nm Dura-pore membrane. The dissolved 30,000 PA formed a large aggregate, precluding its filtration so that there was no possibility to measure its MW. The High-Resolution Scanning Electron Microscopy (HR-SEM) was used to explore the different morphological features of CMCs. TAM Air Isothermal Microcalorimeter was employed to obtain the initial- and final-heat release times and to determine the cumulative heat of hydration evolved during the hydrolysis-hydration of these cementitious slurries at 85 °C. The initial- and final-heat release times were determined at the time of the cross point of extended baseline and the slope lines of the heat flow peak [23]. The total heat, J/g, was computed from the enclosed area of the curve with the baseline made between the initial and final setting times. Microcalorimeter was also used to measure *in-situ* heat evolution in a process of dissolution of sodium silicate activator and reaction products of CMC treated with cement pore solution; self-degradation of CMC-modified cement after contacting water.

The compressive strength for 85 °C–24 h-autoclaved cements was obtained using Instron Model 5967. The cylindrical (16 mm diameter by 35 mm length) specimens were solidified at room temperature for 72 h and autoclaved at 85 °C for this assessment. Some of the 85 °C-cured specimens were further heated at 200 °C for 24 h and their porosity was measured with the helium pycnometer. The measured values provided comparative porosity estimates for samples with different CMCs. The thermal decomposition-related properties of non- and pore solution treated-CMCs were investigated using Thermo Gravimetric Analysis (TGA) at the heating rate of 20 °C/min in a N₂ flow. Pyrolysis–Gas Chromatography/Mass Spectroscopy (Py–GC/MS) was employed to identify and quantify the volatile derivatives emitted by the decomposition of CMC. To accomplish this, a 5–10 mg sample was pyrolyzed at 450 °C by a CDS 2500 Pyrolysis Autosampler, and then, the volatile chemical compounds were identified and quantified using an HP 5890 Series II Gas Chromatograph coupled with an HP 5989 Mass Engine. The chromatographic peaks were identified by referencing them to the NIST MS library and data in the literature, and by comparing their chromatographic retention times to those of the available reference chemical compounds. Some solid compounds remained after CMC decomposition. Fourier Transform Infrared (FT-IR) spectroscopy was adapted to identify them and to define their reaction products with sodium silicate at 200 °C. In preparing the FT-IR samples, the dry mixtures with 100/0, 89/11, 86/14, 80/20, 67/33 CMC/sodium silicate ratios by weight were dissolved in a constant amount of water at room temperature, and then placed in an oven at 200 °C for 24 h; thereafter, the dry samples were ground up for FT-IR analysis.

3. Results and discussion

3.1. CMCs

The viscosities of solutions made by dissolving 1 g CMC in 200 g water were 200, 300, 1010, and 6950 cp for the 30 PA, 100 PA, 2000 PA, and 30,000 PA, respectively, suggesting that the increase in number of PA corresponds to an increasing molecular weight (MW) and rising viscosity, while the pH of all CMCs ranged from 7.45 to 7.87. As expected, the MW of 30 PA, 100 PA, and 2000 PA CMCs determined by HPC/LLC were 80,500, 133,400, and

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