

Synthesis, characterization and hydration analysis of a novel epoxy/superplasticizer oilwell cement slurry – Some mechanistic features by solution microcalorimetry

Antonio R. Cestari*, Eunice F.S. Vieira, Ellen C.S. Silva, Fernanda J. Alves, Marcos A.S. Andrade Jr.

Laboratory of Materials and Calorimetry, Department of Chemistry/CCET, Federal University of Sergipe, 49100-000 São Cristóvão, Sergipe, Brazil

ARTICLE INFO

Article history:

Received 26 January 2012

Accepted 16 April 2012

Available online 27 April 2012

Keywords:

Oilwell cement slurries

Epoxy resins

Polyacrylates

Solution microcalorimetry

Eco-friendly materials

Superplasticizers

Solution calorimetry

Kinetic modeling

ABSTRACT

A new epoxy/polyacrylate-modified oilwell cement slurry was synthesized. The features of the new slurry were evaluated in relation to a standard cement slurry ($w/c = 0.5$). The characterization of the slurries was performed by Raman, XRD, TG/DTG and solid-state diffuse reflectance spectroscopy. The main morphological features of the new slurry were preserved, even after long-term contact with HCl in aqueous solution. The hydration of the slurries was studied by heat-conduction microcalorimetry. The exothermic microcalorimetric outputs were well fitted to a three-parameter kinetic model. The analysis of both thermodynamic and kinetic results from microcalorimetry have pointed out that diffusional growth from non-stoichiometric mixtures is the main mechanistic feature of the hydration of the cement slurries. The results of this study underline the excellent features of the new epoxy/superplasticizer-modified cement slurry for using in severe acidic environments of oilwells.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Oilwell cementing is used for providing zonal isolation of subterranean formations to prevent exchange of gas or fluids among different geological formations, as well as for protecting oil producing zones from collapse. Oilwell cementing is less tolerant to errors than conventional cementing works [1,2]. If the cement does not provide a good seal, gas or liquid fluids can migrate to the surface and lead to work accidents or environmental problems [1]. So, fully understanding of interfacial phenomena behind oilwell cement procedures has scientific, economic and environmental importance.

In order to increase the production of oilwells, one such method commonly employed in oil and gas industry is known as acidizing stimulation [3]. Typically, a non-oxidizing mineral acid is introduced into the well and is forced into subterranean formations to remove acid-reactive components, such as carbonates of alkali metals and others. The usual acid employed in such acidizing procedures is hydrochloric acid. However, several oilwells have been observed to exhibit well zonal intercommunication problems due to problems in the cement slurries. It is due to reactions between the hardened slurries in the oilwell annulus and the acidic solution. As a consequence, acid (even oil) spill may cause long-term environmental problems [3,4]. In this way, cementing of oilwells requires new materials that provide long-term stability in acidic

media. The protective characteristics of oilwell cements may be controlled by the addition of polymeric additives [5].

The use of specific polymeric nets has been highly effective in preventing destruction and increasing the internal cohesion of oilwell cement packs. In this way, epoxy resins are useful to promote physico-chemical interactions and ensure excellent levels of adhesion between the mineral and organic phases of polymer-modified cement slurries [5,6]. In this way, polymeric nets of epoxy resins are typically insoluble in the aqueous mineral acid solutions employed in acidizing operations of oilwells. Epoxy cements are composed of epoxy resin, cement and fine aggregates. Epoxy resin systems are made up of an epoxy resin and a curing agent (also called a hardener or catalyst). Common epoxy formulations are based on diglycidyl ether of bisphenol A resins that can be cross-linked with a wide variety of hardeners such as amines, organic acids, anhydrides and others [7].

It is well known that hydration phenomena at cement and water interfaces drive the characteristics of oilwell cement slurries. The knowledge of the heat-producing properties during oilwell cement hydration is required to choose a suitable cementitious system for a given specific project. The kinetic and thermodynamic features of the early hydration stages are essential for the performance of hardened cements and can be monitored by microcalorimetry [8,9]. Heat-conduction microcalorimetry has been used to obtain and analyze the features of heat evolution evolved in the early stages of hydration of cement slurries, with the objective of increasing understanding of the hydration mechanisms at cement

* Corresponding author. Fax: +55 79 21056684.

E-mail address: cestari@ufs.br (A.R. Cestari).

and water interfaces. However, there is relatively little research on early cement hydration, that is, the initial hours after adding water.

In this work, it is intended to use sodium polyacrylate as a superplasticizer agent in a new epoxy-cement system for use in routine oilwell operations. Superplasticizers can be used for three different purpose, namely (a) to increase workability without changing the mixture composition, (b) to reduce the amount of mixing water in order to reduce the water-to-cement ratio and then to increase strength and/or improve durability, and (c) to reduce both water and cement in order to reduce cost in addition to reducing creep, shrinkage and thermal strains caused by heat of cement hydration [10]. As far as we known, nothing is known about the role of the epoxy/superplasticizer system in oilwell cement procedures. The features of the new slurry were evaluated in relation to a standard cement slurry ($w/c = 0.5$). The structural characterization of the slurries, before and after contact with aqueous HCl solution, is also presented and discussed.

2. Experimental section

2.1. Materials and reagents

Water was used after double distillation. Powder cement (200–325 mesh, Class A special for oilwell cementation) from Cimesa Special Cements (Laranjeiras, Brazil) and silica gel of 150–300 mesh (particles diameter) from Schumberger Petroleum Services (Nossa Senhora do Socorro/SE, Brazil) were used in the slurries preparations. The bisphenol A epoxy resin, commercially available as Araldite GY279, as well as its hardener (Aradur 2963), was supplied by The Huntsman Co Special Resins. Sodium polyacrylate was obtained from Sigma–Aldrich. The idealized chemical structures of the epoxy resin, the hardener and sodium polyacrylate are shown in Fig. 1.

2.2. Preparation of the cement slurries

The mixing procedure adopted in accordance with the American Petroleum Institute (API) practice was described earlier [8,9]. It was consisted of mixing the cement, epoxy resin and hardener, sodium polyacrylate and water for 30 s at 12,000 rpm. The amounts

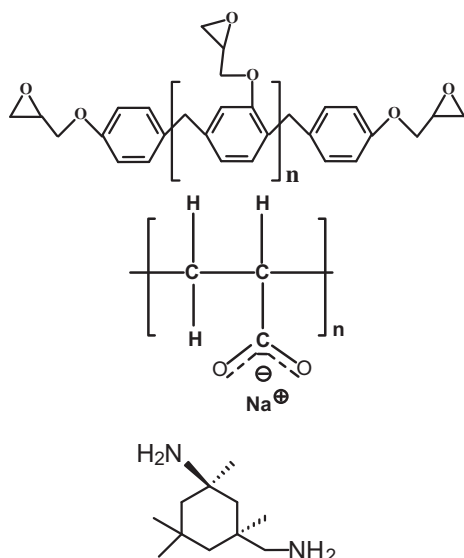


Fig. 1. Idealized chemical structures of the epoxy resin (above) and sodium polyacrylate (center) and the hardener (below).

of the components of the slurries were calculated in relation to a final density of the cured slurries from 1.50 to 2.00 g cm^{-3} [8,9].

In order to avoid uncompleted polymerization, the proportion of epoxy resin/hardener was 1:2. The cement, silica and water were used to obtain the standard cement slurry ($w/c = 0.5$) for comparative purposes. The cement slurries were cast into cubic molds with 5.08 cm sides and cured in water for 28 days before use. For simplicity, the slurries are hereafter denominated as epoxy-sp (cement, water, silica, epoxy resin, hardener and superplasticizer) and standard (cement, silica and water).

2.3. Characterization of the cement slurries

The Raman spectra were acquired with a Bruker Senterra Raman System equipped with an Olympus microscope with a 50 \times objective to focus a Melles Griot laser beam on the sample. The spectra were excited by the 785 nm line from an air-cooled He–Ne laser. The laser power measured after the microscope objective was ca. 50 mW. The thermogravimetric analyses (TG and DTG) were made using about 10 mg of material, under synthetic air atmosphere from 25 to 800 $^{\circ}\text{C}$, in a SDT 2960 thermoanalyzer, from TA Instruments. DRX-ray analyses were performed in a Shimadzu diffractometer, in the 2θ range from 5 $^{\circ}$ to 60 $^{\circ}$ (accumulation rate of 0.02 $^{\circ}\text{ min}^{-1}$), using Cu K α radiation. The solid-state diffuse reflectance spectra of the samples were recorded on an Ocean Optics UV–Vis spectrophotometer from 400 to 900 cm^{-1} at a resolution of 4.0 cm^{-1} .

The cement samples were also characterized after 40 h in contact with a 0.1 mol L^{-1} aqueous solution of HCl. From earlier studies [8,9], this contact time is sufficient to reach the maximum HCl amounts sorbed on oilwell cement slurries.

3. Results and discussion

3.1. Some considerations on cement chemistry, epoxy resins and superplasticizers

Cured cements have a range of sizes and complex internal microstructures, with the result that different clinker phases hydrate at different rates. The composition of oilwell cement slurries is usually based upon four principal mineral phases [1]: tricalcium silicate (Ca_3SiO_5 , or C_3S), dicalcium silicate (Ca_2SiO_4 , or C_2S), tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$, or C_3A), and a calcium aluminoferrite (C_4AF) of variable composition. These mineral phases are intimately mixed in the form of cement grains, with little or no pore space.

At ambient temperature, the most important cement hydration process is the conversion of the silicate phases to an almost amorphous C–S–H and portlandite ($\text{Ca}(\text{OH})_2$). The calcium silicate hydrate (C–S–H) formed is typically a poorly crystalline non-stoichiometric material consisting principally of dimeric units at first, but which subsequently slowly polymerizes after a few days. The portlandite released during cement hydration is partially consumed as a result of interaction with active silica fume to form C–S–H phases. In general, sulfate is added to all cements in the form of calcium sulfate. If not, the C_3A and C_4AF phases may quickly hydrate and cause loss of workability [11].

The most rapid reaction during the early hours of cement hydration at ambient temperature is due to the formation of ettringite, a hydrous calcium aluminosulfate mineral ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$). The C_2S phases react at a much slower rate to form similar hydration products. Some portlandite is present at the beginning of hydration, where the aqueous phase of the cement slurry can be considered for simplicity as essentially a

Download English Version:

<https://daneshyari.com/en/article/7000555>

Download Persian Version:

<https://daneshyari.com/article/7000555>

[Daneshyari.com](https://daneshyari.com)