



Kinetic modeling of cement slurry synthesized with Henna extract in oil well acidizing treatments



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ABSTRACT

Acidizing treatment in petroleum reservoirs is a short-term and viable strategy to preserve the productivity of a well. There is a major concern for the degradation of cement sheath integrity, leading to poor zonal isolation and environmental issues. Therefore, it is essential to understand how the cement behaves when attacked by hydrochloric acid. In this study, a cement slurry by incorporation of the Henna extract, as an environmentally friendly cement additive, was synthesized as a potential solution to solve this problem. The characteristics of the treated cement slurry were compared with a reference slurry ($w/c = 0.44$) which is composed of only cement and water. A kinetic study was carried out to evaluate the adsorption behavior of the cement slurries exposed to an acid solution with 0.1 M HCl in a range of 25 to 55 °C conditions. The features of the cement slurries were evaluated by multiple analytical techniques such as XRD, FTIR, TG, and DSC analysis. From the experimental data, it is concluded that the second-order Lagergren kinetic model revealed to be the best in describing kinetic isotherms taken, because the margin between experimental and calculated values was minor for this model. The results of the characterization and HCl interaction kinetic studies underlined the prominent protective role of Henna extract-modified cement slurry in the enhancement of the cement resistance against acid attack and utilization in environmentally favorable oil well acidizing treatments.

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1. Introduction

Well cementing is a principal and substantial part among activities for the construction of oil and gas wells. The cement is pumped into the well, to be positioned in the annular space between a metal casing and geological formations. The cement sheath, in turn, has some responsibilities such as providing zonal isolation, supporting the casing from corrosion attack induced by

aggressive fluids, gas migration prevention, etc., along the annulus [1,2].

If the cement sheath does not meet these demands, loss of zonal isolation has negative impacts on the wellbore integrity and consequently life of the well. Also, from the economic viewpoint, decline in the hydrocarbon production rate and cost of remedial cementing operation should be considered as vital concerns [3]. Hence, the oil and gas industries have been led to confront the challenge of safety and catastrophic environmental problems. The permanence of the materials used for the process of well completion, especially cementing materials, is of superior significance to ensure long-term performance. In the recent decades, the researchers have paid special attention to the stability of wellbore materials, especially on cement, in an effort to better anticipate the influences of exposure condition experienced by cement. For instance, degradation of well cement was evaluated for carbon sequestration [4–9].

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Acidizing treatment is an effective technique routinely employed in oil and gas reservoirs in order to produce at higher rates. This operation is called well stimulation. Typically, for carbonate reservoirs, hydrochloric acid (HCl) is used for stimulation of the oil wells. In the common well stimulation procedure, acid is injected into the well and is pushed into the nearby subsurface geological formations. Acid fluid reacts with acid-soluble components such as calcium carbonate, magnesium carbonate, etc. As the well cement is exposed to the acid, it will dissolve and become vulnerable, at some time, deteriorated. This way, if acidizing operation is performed on a well, it will be considerable to understand how cement behaves in this harsh environment. With regard to this concept that the cement will react with acid solutions, multiple pathways are probably created for the leakage of the formation fluid. These provided routes consist of leakage through the pores of the cement which construct the primary cement in the well, migration along the annular space between cement sheath and geological formations, traveling through the trajectory at the interface of the casing and cement. The latter causes damage to the casing wall and flows into the wellbore and escapes upward into the well. The probable leakage scenario is presented in Fig. 1.

The main corrosion aspect in oil and gas wells focuses not only on the casing, but also corrosion occurs in the cement slurries if adequate precautions are not taken. Proper slurry design is of great concern in order to provide environmental protection. However, ecological side effect impacts are an inevitable part of exploitation of oil and gas fields. As mentioned above, several oil wells have been ascertained to exhibit fluids exchange problems that may cause contamination by the explosion of potable aquifers or even up to the surface. It is attributed to reaction of set cement with acid. A great number of scientific studies have been devoted to deterioration of cement slurries exposed to CO₂ environment and evaluations are well documented in the literature [4–9]. However, published data on exposure of the cement to the acid solution, are seldom and scattered. The growing interest in wellbore integrity issues in this condition has highlighted the requirement for more research on the cement system that can sustain the acid attack. In this way, the new solution is proposed to retain wellbore stability through the long-term integrity of cementing materials. As a key

opinion, incorporation of additives has potential solution in practice to cope with environmental problems. The purpose of this work is to achieve this solution. A few studies have been dedicated to modify protective characteristics of cement slurries by the addition of some additives resistant to aggressive environments [10–13]. Surprisingly, to our knowledge, no study has been performed by natural occurring substances.

In the margin of natural substances, plant extracts application for a wide range of corrosion prevention has grown through the recent decades and promised to further progressions [14–22]. So, finding naturally occurring substances as a readily available, environmentally friendly, and renewable sources of materials is of major practical subjects in the petroleum industry. Henna, a plant, also has been referred to as "*Lawsonia inermis*". This herb has been used for centuries to remove stain from the skin and hair. Its trait was attributed to the drying properties of its leaves. Some researchers have deduced corrosion inhibition of Henna extract in various aspects such as different metals and solutions [23–28]. Also, recently, Moslemizadeh et al. [29] indicated the swelling inhibition of Henna extract. However, the inhibitive action of Henna extract as a cement additive in acidic media is still unclear. Ostovari et al. [26] declared the main constituents of Henna extract by gas chromatography and mass spectrometry (GC–MS) analysis (see Fig. 2) and also GC–MS analysis was performed after methanolysis with sulfuric acid and methanol (see Fig. 3). It has been observed that the Henna extract contains lawsone (2-hydroxy-1,4-naphthoquinone, C₁₀H₆O₃), tannic acid, gallic acid (3,4,5-trihydroxybenzoic acid, C₇H₆O₅), and dextrose (α -D-glucose, C₆H₁₂O₆).

In this paper, a new cement slurry with the contribution of Henna extract as a non-hazardous, readily available, and naturally occurring substance cement additive was synthesized and characterized. For comparison purposes, in the same manner, reference cement slurry in the absence of Henna extract was also prepared and tested. The features of the cement slurries were analyzed by XRD, FTIR, TG, and DSC which were conducted to gain better comprehension of the changes of samples before and after acid attack. Additionally, the kinetic interaction of cement slurries/HCl solution was evaluated and experimental data were fitted to the traditional Lagergren models, both pseudo-first and second order.

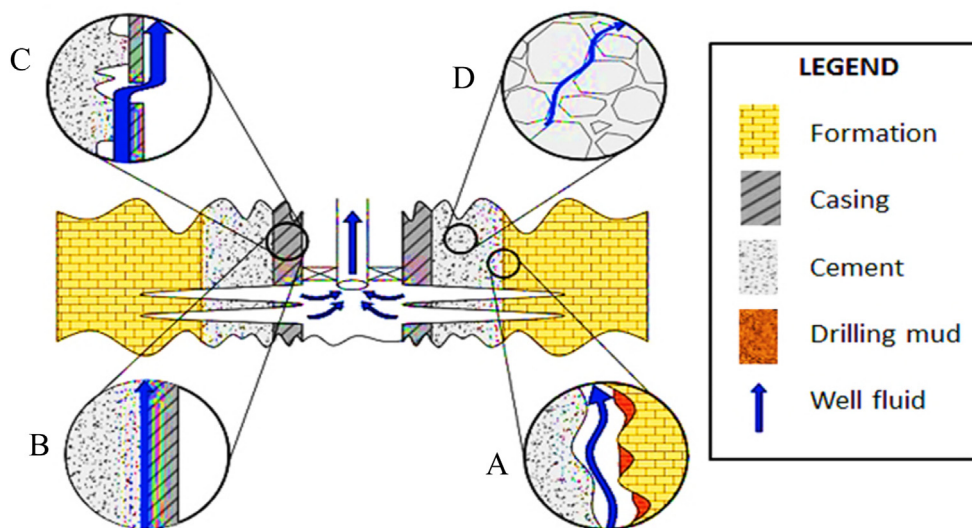


Fig. 1. (A) Migration along the annular space between cement sheath and geological formations, (B) traveling through the trajectory at the interface of the casing and cement, (C) well fluid entering the annulus through a damaged casing and traveling up the inside of the well, (D) well fluid migration through the pores or pathways of the well cement in the primary cement.

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