

Organic and synthetic cement slurry retarding additives for oil well cementing operations: a review

Abstract

Cementing operations within the context of crude oil production represent a crucial facet of the oil well completion process. However, a significant challenge encountered in high-temperature and high-pressure wells is that the cement slurry exhibits a reduced thickening time, demanding careful consideration and tailored solutions. As a result, the integration of chemical additives, in this case, retarders, becomes essential to tailor the behavior of the cement slurry to these good conditions. Over the years, different types of retarders that are applied to delay the thickening time of cement slurries to allow for more operational time during cementing activities have been developed and applied as oilfield chemicals. This review paper, using secondary data sources from academic journals, conference papers, textbooks, and unpublished studies from recognized websites, has categorized the different types of retarders into two broad classes: organic and synthetic retarders. The proposed theories involved in the mechanism of the cement slurry retardation process were elucidated. Also, the advantages and disadvantages of these retarders, the differences between the two categories, and the summary of the behaviors were stated. Although synthetic retarders are preferred in cement operations because they give predictable accuracy from time to time, however, because of strict environmental requirements in the oil and gas industry, organic retarders are encouraged as alternatives.

Keywords: retarders, cement-slurry, organic, synthetic, thickening time, cementing

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Ibifuro A,¹ Akuma O,² Joel F. O,³ Tonye O. E²

¹Chemical/Petrochemical Engineering Department, Rivers State University, Port Harcourt, Nigeria

²Centre for Gas, Refining and Petrochemical Engineering Department, University of Port Harcourt, Nigeria

³World Bank African Center for Excellence, Center for Oil Field Chemicals Research (ACE-CEFOR), University of Port Harcourt, Nigeria

Correspondence: Akuma O, Centre for Gas, Refining and Petrochemical Engineering Department, University of Port Harcourt, Nigeria, Email akuma.oj@uniport.edu.ng

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Introduction

Cementing operations within the context of crude oil production represent a crucial facet of the well completion process for oil and gas wells. This vital procedure encompasses the placement of cement slurry within the annular spaces between the casing and the wellbore, serving to ensure effective zonal isolation throughout the well's operational lifespan. The primary objective of cementing is to establish a secure seal in the annular spaces, thereby impeding the migration of fluids from the formation into the surrounding geological formations or the ground.¹ Typically, the cement slurry is introduced into the well using pumping, allowing it to descend through the casing to reach the bottom of the well. Subsequently, it is returned to a designated depth within the wellbore via the annular spaces situated between the casing and the formation, or potentially, another casing.² This controlled process of cementing operations is of paramount importance in guaranteeing the structural integrity and productivity of the oil and gas wells in question.

Sometimes, cement slurries are pumped down to a depth of 5000m where the temperature and pressure can be above 150°C (302°F) and 100MPa, respectively.³ In this depth of a high-temperature, high-pressure well, cementing operations sometimes encounter significant temperature differences between the upper and lower sections during extended cementing intervals.^{4,5} A significant challenge encountered in high-temperature and high-pressure wells is that the cement slurry exhibits a reduced thickening time, demanding careful consideration and well-designed solutions.³ This circumstance necessitates specialized approaches to address the unique demands of cementing operations under such extreme thermal and pressure environments.

Consequently, in high-temperature and high-pressure wells, the formulation of cement slurries necessitates precise engineering and design to meet specific requirements.⁶ As a result, the integration of certain chemical additives becomes essential to tailor the behavior of the cement slurry by these well conditions.⁷ Over the past decades, a

diverse array of chemical additives has been employed to optimize the design of cement slurries, ensuring successful annular space filling between the casing and geological formation. These additives serve a range of purposes, including:

- (i) Altering the setting time of the cement slurry to suit the demands of high temperature and pressure conditions.
- (ii) Dispersing cement particles evenly throughout the slurry.
- (iii) Controlling fluid loss from the slurry during placement.
- (iv) Managing cement shrinkage once it thickens or sets.
- (v) Enhancing the interfacial bonding between the casing and geological layer.
- (vi) Regulating fluid migration into the cement column during the setting process.^{8,9}

The strategic implementation of additives contributes to the development of specialized cement slurries that can perform optimally in challenging high-temperature and high-pressure well environments. One such additive often applied in cementing operations is the retarder.

Retarders are cement additives designed to delay the thickening time of cement slurries. The thickening time denotes the duration during which the cement slurry can be manipulated following its mixing with water.^{10,11} The problem of inadequate thickening times can yield significant operational challenges, as the premature setting of the cement may occur within the casing or pumping equipment.¹² Consequently, several crucial factors must be taken into account, namely, mixing time, displacement time, plug release time, and safety time. A comprehensive understanding of the well's temperature conditions is of utmost importance.³

As a result, the oil and gas industry has witnessed the development of various types of retarders over the years, serving as essential oilfield chemicals utilized in well operations. Within this study,

these retarders are categorized into two principal groups: organic, that is those formulated from plant biomass, and synthetic retarders. Accordingly, this paper undertakes a review of these classifications, with a particular emphasis on elucidating the common types of retarders and the nature of their compositions.

Materials and methods

This research was carried out using secondary data sourced from academic papers, conference papers/proceedings, text books and recognized websites. The method applied involves the reviewing of the main classes of oil well cement set retarders especially the major types and nature of the basic component in the cement set retarder.

Common categories of retarders

Retarders can be divided into two different categories: organic and synthetic retarders. The organic retarders include the following:

- a) Lignosulphonates,
- b) Hydroxycarboxylic (HC) acids
- c) Saccharides (sugar) compounds
- d) Cellulose derivatives
- e) Organophosphates (OP)^{5,7}

While the synthetic or inorganic retarders include:

- A. Acids and salts (Borates, sodium chloride etc)
- B. Oxides (Zinc, lead etc).¹²

Organic retarders

Retarders can originate from organic sources, such as plant biomass (grass, wood, roots, bark, leaves, etc.). These organic materials comprise untreated calcium, sodium, ammonia salts of lignosulphonic acids, hydroxycarboxylic acids, and carbohydrates. The majority of these organic retarders primarily contain hydrophilic active agents like sugar, starch, and cellulose, along with water-reducing effects. Consequently, they are often referred to as retarding water-reducing agents.^{12,13} Thus, the following represent retarders derived from natural or organic materials:

Lignosulphonates (LS)

Lignosulphonates (LS) are metallic sulphonate salts produced from lignin obtained through a sulfonation process applied to processed wood biomass. The resultant solution, termed lignin liquor, encompasses lignosulphonic acid, simple sugars, starches, and natural gums extracted in the course of the process. The exact composition of this liquor is dependent on the type of wood biomass utilized and the specific conditions prevailing in the reaction environment. The efficacy of the liquor as a retarder is subject to the relative proportions of its constituents, along with factors such as molecular weight and degree of sulfonation.^{14,15} Hence, three distinct classifications of lignosulphonates are applied in retarding cement set slurries: filtered, purified, and modified lignosulphonates.^{14,16} The filtered lignosulphonates grade is acquired by segregating cellulose and hemicellulose from the extracted lignin through a filtration method. Typically employed at temperatures approximately 93.3°C (200°F) Bottom Hole Circulating Temperature (BHCT) and at a concentration of about 0.6% Bottom Weight of Cement (BWOC), this filtered grade, in either calcium or sodium salt form, has usage limitations at higher temperatures, guided by economic considerations.^{14,15} Purified lignosulphonates, following an impurity removal process, exhibit the

lowest retarding potency among the various grades. The retarding effect is commonly attributed to the presence of impurities in the material.¹⁶ These impurities include low-molecular-weight carbohydrates such as pentoses (xylose and arabinose), hexoses (mannose, glucose, fructose, rhamnose, and galactose), and aldonic acids, particularly xylonic and gluconic acids.¹⁷ This grade, utilized as either calcium or sodium salt at a Bottom Hole Circulating Temperature (BHCT) exceeding 200°F (93.3°C), operates at a concentration of around 0.5% Bottom Weight of Cement (BWOC).

The modified variant of lignosulphonates entails a purposeful modification of its characteristics through physical or chemical treatments, with the aim of achieving specific objectives. In this context, lignosulphonates undergo combination or reactions with two or more components, such as boric acid, hydroxycarboxylic acids, or salts.¹⁴ When deployed, the modified lignosulphonates are employed at a Bottom Hole Circulating Temperature (BHCT) surpassing 93.3°C (200°F); notably, they demonstrate superior efficacy compared to the purified grade, particularly at temperatures exceeding 121.1°C (250°F). The resultant blended or reacted product offers several advantages, including heightened stability at temperatures beyond 150°C (300°F) BHCT, increased dispersing activity, and a synergistic effect with fluid-loss additives.^{14,15} Through this modification, lignosulphonates acquire properties that render them well-suited for applications in challenging high-temperature conditions, displaying improved performance and compatibility with other additives utilized in cement slurries.²⁶

Recently, studies have been carried out on the use of biomass biodegradable waste as cement additives to reduce operating costs, prevent environmental risks and enhance local content.^{3,5,10} Some of the types of biomass waste and compositions used as chemical additives especially retarders are as shown in Table 1. Hence, a study conducted by¹³ delved into the application of coffee powder as a cement retarder, encompassing a comprehensive evaluation of its influence on various properties of cement grouts. The investigation revealed that coffee powder displayed a consistent and linear behavior concerning thickening time in response to alterations in concentration and temperature. In this particular study¹⁸, an investigation was conducted on the utilization of palm spirit, sourced from the abundant palm trees in the Niger Delta region of Nigeria, with the aim of exploring its potential applicability as a retarder admixture in tropical hot weather concrete. Additionally, the investigation sought to assess the viability of employing palm spirit as a cost-effective alternative.

Table 1 Composition of some selected biomass

| S/No | Biomasses | Hemicellulose (%) | Cellulose (%) | Lignin (%) |
|------|-------------------|-------------------|---------------|------------|
| 1 | Wood | 20 – 30 | 35 - 50 | 25 - 30 |
| 2 | Sugarcane bagasse | 32 – 48 | 19 - 24 | 23 - 32 |
| 3 | Hazelnut shell | 30.4 | 28.8 | 42.9 |
| 4 | Corn cob | 31 | 50.5 | 5 |
| 5 | Tea waste | 19.9 | 30.2 | 40 |
| 6 | Walnut shell | 22.7 | 25.6 | 52.3 |
| 7 | Nut shell | 25 – 30 | 25 - 30 | 30 - 40 |
| 8 | Paper | 0 | 85 - 99 | 0 - 15 |
| 9 | Rice straw | 24 | 32.1 | 18 |
| 10 | Leaves | 80 – 85 | 15 - 20 | 0 |

Once more,¹⁹ conducted an investigative study centered on the utilization of agricultural processing waste for the generation of valuable products. The study's objective was to examine the

effectiveness of Carboxymethyl lignin as a cement paste retarder specifically tailored for application in oil wells. The experimental results demonstrated a direct and proportional relationship between the concentration of CML in cement slurries and the corresponding increase in thickening time. Again,²⁰ studied the alternative use of sawdust in the oil and gas industry. The sawdust was hydrolyzed using sulphuric acid and the product was sulphonated by sodium bisulphite in a chemical reaction. Product formed was used to retard cement slurry at different concentrations. Results show that there was over 50% retardation of the cement slurry from 4hrs 31 minutes to 7hrs 25minutes at 2ml and to 8hrs 35 minutes at 3ml by volume of the sample produced.

Although lignosulphonates (LS) serve as the predominant retarders, their application in high-temperature and high-pressure (HTHP) wells is not feasible due to their carbohydrate content and chemical structure.⁴ In HTHP conditions, organic acids and water-soluble borates emerge as the preferred retarders. An illustrative instance is Sodium tetraborate decahydrate (borax), frequently employed as a retarder, exhibiting the ability to expand the temperature range of most lignosulfonate retarders up to 315°C (600°F).¹⁶ Given the constraints posed by LS in HTHP wells, the adoption of alternative retarders with enhanced thermal stability and performance becomes imperative to ensure the efficacy of cementing operations in demanding wellbore conditions.

Hydroxyl carboxylic (HC) acids

Hydroxyl carboxylic acids, derived chiefly from naturally occurring sugars like citric acid and tartaric acid, play a pivotal role in retarding when employed in their salt forms. The retarding mechanism is rooted in the presence of alpha or beta hydroxycarboxylic acid groups.²⁰ These groups possess the ability to form stable ring structures, notably five or six-membered rings, through chelation with calcium ions. These rings, characterized by remarkable stability, tend to partially adsorb onto the hydrated cement surface, effectively impeding the nucleation sites of hydration products.¹⁸ Furthermore, hydroxyl carboxylic acids (HC acids) are renowned for their antioxidant and sequestering properties, bestowing favorable effects on the performance of cement slurries.¹³

Hence, in the investigation documented by,²¹ a thorough examination was conducted to assess the effectiveness of tartaric acid as an additive in alleviating the setting of oil well cement under elevated temperature conditions. The study's findings underscore the considerable promise of tartaric acid in addressing the undesired delays in setting encountered during high-temperature well cementing, thereby contributing to the improvement of safety and efficiency in cementing operations. Moreover,²² conducted an exploration to investigate the interaction of tartaric acid in the hydration process of Portland cement, utilizing various analytical techniques. The observed retardation in hydration was ascribed to the precipitation of calcium tartarate hydrate on the surface of cement grains. Similarly,²³ carried out an extensive inquiry into the inhibition of cement hydration through the application of sucrose, tartaric acid, and lignosulfonate, employing a variety of analytical and spectroscopic techniques. The study revealed that tartaric acid emerged as the most potent agent for retarding C₃A hydration and inhibiting the formation of ettringite.

Saccharide (sugar) compounds

Saccharides, the elemental constituents of carbohydrates with a general formula of C_nH_{2n}O_n, encompass both simple sugars and polymers such as starch and cellulose. These compounds display diverse configurations, adopting either a ring or short-chain structure,

commonly comprising five or six carbon atoms. Notably, among saccharides, the five-membered ring structures represented by sucrose and raffinose exhibit significant retardation properties within this category.²³ Research has highlighted that the retardation extent is contingent upon the susceptibility of these compounds to alkali hydrolysis, which hampers hydration by impeding nucleation sites.²⁴ The exploration of saccharides as potential retarders provides valuable insights into their distinctive structural attributes and their ability to influence the hydration process, holding promise for optimizing cementing operations in oil wells. Further delving into the specific mechanisms that underlie the retarding effects of saccharides on cement hydration may facilitate the development of improved cement formulations tailored to meet the challenges of high-temperature and high-pressure well environments.

In this specific investigation,²⁵ the efficacy of sugarcane juice (SCJ) as a cohesion-inhibiting agent was meticulously examined. The research outcomes indicated that the inclusion of SCJ in the concrete mix resulted in a noticeable prolongation of the concrete's final setting time. Similarly,²⁶ delved into the impact of sugar on the curing duration of Ordinary Portland Cement (OPC) paste and the compressive strength of concrete. The introduction of sugar effectively retarded the setting time of the cement, achieving a setting time of 1.33 hours with a dosage of 0.06% by weight of cement.

Moreover, an empirical investigation by²⁷ systematically evaluated the influence of cellulose sugar acids on cement hydration, comparing their effects with commercially available raw starch sugar derived from agricultural starch sources. The study disclosed significant postponements in the cement hydration reaction and the formation of cementitious products upon the introduction of sugar-cellulosic acid. These observations underscore the potential feasibility of employing a cellulosic product derived from cost-effective agricultural waste as a promising alternative to conventional commercial vegetable starch products when integrated into cement formulations.

Cellulose based

Cellulose polymers, derived from wood or other plant materials, display resilience under the basic (alkaline) conditions prevalent in cement slurries. The retarding mechanism is thought to entail the adsorption of these cellulose products onto the surface of hydrated cement, effectively impeding further hydration processes.²⁸ The active sites responsible for this adsorption process include the ethylene oxide links and carboxyl groups present in cellulose. A widely utilized cellulosic material with retardant properties is Carboxy-Methyl-Hydroxy-Ethyl-Cellulose,^{29,30} known for its effectiveness at temperatures up to approximately 121°C (250°F).

Cellulose-based polymers have demonstrated successful applications across various realms of petroleum engineering, notably in endeavors such as enhanced oil recovery, the formulation of drilling fluids, fracturing, and cementing operations.³⁰ In the realm of oil well cementing, these polymers have been harnessed to enhance the characteristics of cement slurries. However, when subjected to high temperatures, certain limitations of these polymers become evident.³ Specifically, they struggle to achieve an adequate thickening of viscosity in cement slurries under such elevated conditions, resulting in challenges like fluid loss, gas migration, and cost inefficiencies. Therefore, it becomes imperative to employ polymer types capable of augmenting viscosity at heightened temperatures.³¹

In accordance with the study conducted by,³¹ an examination of the application of cellulose-based polymers in oil well cementing operations was undertaken. The empirical findings indicated that

among a range of cellulose-based polymers, HPMC (hydroxypropyl methylcellulose) exhibited notable efficacy in enhancing viscosity at a temperature of 90°C (194°F). These encouraging outcomes underscore the capacity of cellulose-based polymers to elevate the overall performance and quality of cement slurries employed in oil well applications.^{32,33}

Organophosphonates (OP)

Organophosphonates constitute a category of chemical compounds formed through the esterification process involving phosphoric acid and alcohol. In specific conditions, hydrolysis of organophosphonates can occur, resulting in the release of alcohol from the ester bond.²⁰ While organophosphates, with a few exceptions, stand out as highly effective retarders in cement formulations, their limited utilization in well cementing applications is attributed to certain challenges. Notably, the requirement for low concentrations poses difficulties in accurate measurement.^{34,35} Furthermore, the sensitivity of these retarders to concentration levels adds complexity to their application. Nonetheless, organophosphates present distinct advantages, particularly in ultrahigh-temperature wells exceeding 230°C (450°F) or when extended thickening times of 24 hours or more are essential.³⁶

Alkylene phosphonic acids and their corresponding salts have gained recognition as additives that retard the setting of well cements.²² These substances exhibit notable hydrolytic stability, and their efficacy remains intact at Bottom Hole Circulating Temperatures (BHCT) as high as 230°C (450°F), contingent upon their molecular structure.

Table 2 Summary of the characteristic behavior of organic retarders

| S/No | Retarders | Behavior |
|------|--------------------------------|---|
| 1 | Lignosulphonates (LS) | The addition of lignosulphonate facilitates the acceleration of ettringite formation, and as hydration occurs, calcium ions bind to the polymer matrix, leading to the creation of a diffusion barrier. Consequently, the CSH (Calcium Silicate Hydrate) gel structure undergoes a morphological change upon the adsorption of lignosulphonate, resulting in the formation of an impermeable layer that effectively retards the hydration process. ^{15,16} |
| 2 | Hydroxyl Carboxylic (HC) Acids | The retarders function by forming complexes with calcium ions, wherein they engage in chelation with the calcium ions to create stable ring structures. These highly stable five or six membered rings are subsequently partly adsorbed onto the hydrated cement surface, effectively hindering the nucleation sites of hydration products. ^{21,23} |
| 3 | Saccharides (sugar) compounds | The process of cement set hydration experiences deceleration when the nucleation sites of the CSH phase are rendered inactive or "poisoned" due to the presence of adsorbed anions from sugar acids. ^{37,38} |
| 4 | Cellulose based | Cellulose products undergo adsorption on the surface of hydrated cement, thereby impeding subsequent hydration processes. ^{25,31} |
| 5 | Organophosphonates (OP) | The retardation of hydrate growth is attributed to the adsorption of phosphonate groups onto the nuclei of cement hydrates. This phenomenon involves the poisoning of active nuclei sites through adsorption, resulting in the deceleration of setting or thickening time. ²⁰ |

Synthetic retarders

The term synthetic retarder can be somewhat misleading, given that the mentioned retarding compounds are, to some degree, synthesized.¹⁶ However, the term is employed to denote a category of low-molecular-weight vinyl polymers sharing similar functional groups with conventional retarders (such as sulfonate, carboxylic, or an aromatic ring). The advantage of synthetic retarders lies in their ability to regulate the number and relative arrangement of main chains containing functional groups along the polymer backbone.¹³

Several inorganic compounds are recognized for their retarding effects on the cement hydration process, particularly in the context of well-cementing applications. The major classes of these compounds are listed as follows:

- i. Acids and salts: boric, sodium chloride, phosphoric, hydrofluoric, and chromic
- ii. Oxides: zinc, lead, etc.

Furthermore, compounds phosphomethylated with quaternary ammonium salts display significant retardation properties.¹⁹ Despite the limited documentation on the precise mechanism of retardation, it is commonly hypothesized that, similar to other retarders, the deceleration is attributed to an adsorption process. This process inhibits active nuclei sites, consequently delaying the setting or thickening time. As per the proposed mechanism of retardation, the growth of hydrates is impeded by the adsorption of phosphonate groups onto the nuclei of cement hydrates.³⁶

Similarly, Nitrilotris Methylene Phosphonic Acid (NMPA) engages with calcium ions within the pores by precipitating on the surface of cement grains, thereby impeding the formation of Calcium Silicate Hydrate (CSH) nuclei.²² Derivatives of Methylene Phosphonic Acid (MPA) can also be utilized to formulate cement slurries with considerably extended thickening times. While Methylene Phosphonic Acid (MPA) derivatives exhibit limited retardation effects on tricalcium aluminate and tricalcium aluminoferrite phases at temperatures surpassing 110°C (230°F), they manifest robust retarding properties on silicates and dicalcium phases during the hydration of cement.²⁹

In the context of well cementing operations, the benefits of employing OP cement retarders are apparent, as they exhibit relative insensitivity to minor fluctuations in cement composition and possess the capability to diminish the viscosity of high-density cement slurries (Table 2).²⁰

Acids and salts

Inorganic acids, encompassing boric acid, phosphoric acid, hydrofluoric acid, and chromic acid, alongside their corresponding salts, exhibit the capacity to impede the hydration process of Portland cement. Within this category, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and other borates, such as boric acid (H_3BO_3) and its sodium salt, are frequently employed as cement retarders.³⁶ Borates manifest notable retarding efficacy, particularly at elevated temperatures, typically up to a Bottom Hole Circulating Temperature (BHCT) of around 149°C (300°F). Although their retarding effectiveness diminishes at even higher temperatures, a synergistic effect is observed when combined with other retarders like lignosulfonates, resulting in enhanced retardation compared to the use of either retarder in isolation.³⁶

Additionally, water with salt concentrations surpassing 20% Bottom Weight of Water (BWOW) exerts a retarding influence on cement slurries. This retardation is discernible in the viscosity profile of saturated salt slurries, characterized by a sharp increase in Bearden units of consistency before setting.

Oxides

Zinc, characterized as a heavy metal, is acknowledged for its retarding influence on the setting and solidification of cement slurry, with its effects varying based on the dosage applied. In natural settings, zinc exhibits amphoteric behavior, manifesting diverse forms in alkaline solutions. These forms encompass both aqueous and precipitated Zinc Hydroxide ($Zn(OH)_2$) and zincate ions [$Zn(OH)_3^-$ / $Zn(OH)_4^{2-}$], with $Zn(OH)_4^{2-}$ emerging as the more prevalent species [37]. Furthermore, the solubility of zinc in alkaline solutions rises with the pH up to a certain alkali concentration, after which it starts to decrease.^{37,38}

In the context of well cementing procedures, Zinc Oxide (ZnO) is occasionally employed to decelerate less viscous cements, preserving the rheological properties of the cement slurry and the hydration of the Tricalcium Aluminate - gypsum system.²² The retarding mechanism of ZnO is ascribed to the formation of $Zn(OH)_2$ precipitates within the cement particles.²⁶ Zinc Hydroxide, characterized by low solubility ($K_s = 1.8 \times 10^{-14}$), precipitates as a colloidal gel, yielding a precipitate with minimal permeability. The retarding impact diminishes as the Zinc Hydroxide gel undergoes transformation into crystalline calcium hydroxyzincate.³⁹

The addition of $Ca(OH)_2$ to a solution containing zincate ions triggers the formation of a compound identified as calcium zincate ($CaZn_2(OH)_6 \cdot 6H_2O$ or CZ). Researchers have endeavored to analyze the kinetics of CZ development. In a specific inquiry led by,³⁶ it was observed that the CZ precipitation did not occur instantaneously, marking a distinct timeframe referred to as the incubation period. Furthermore, it was noted that the rate of CZ formation intensified with increased CZ precipitation, and the introduction of CZ to nucleation sites resulted in the inhibition of active sites, thereby retarding the hydration process of cement.³⁹

Consequently, numerous investigations have concentrated on the formulation of synthetic retarders designed for application in oil well scenarios. Notably, SDH-2, a synthetic cement retarder

Table 3 Advantages and disadvantages of organic retarders

| S/No | Advantages | Disadvantages |
|------|--|--|
| 1 | Waste disposal technique is safe and lead to reduction in land use for landfills | Inconsistent quality of wastes due to different quality of wastes composition |
| 2 | Sequestering the lignocellulosic material which contains about 50% carbon leads to reduction in CO_2 | Do not provide the consistency needed to control thickening time accurately except design and operational control is included. |
| 3 | Lightweight, bio and fire-resistant composites | No real predictability of results |
| 4 | Cost of production is lower | Large space required for the storage of wastes materials |

Table 4 Advantages and disadvantages of synthetic retarders

| S/No | Advantages | Disadvantages |
|------|---|--|
| 1 | Provides reproducible results | Environmental concerns for these substances when released to the environment |
| 2 | Increased safety through additive engineering | High capital required for production |
| 3 | Offers predictable results based on the system designed linearity | |
| 4 | Thermal stability and can perform in high temperature, high pressure (HTHP) well conditions | |

Table 5 Summary of the differences between organic and synthetic retarders

| S/No | Organic retarders | Synthetic retarders |
|------|-----------------------------------|--|
| 1 | Environmentally friendly (safe) | Environmental concerns associated with these substances when applied in well cementing operations |
| 2 | Lower cost of production | High cost associated with the production of these substances |
| 3 | No real predictable results | Provides predictable/reproducible results |
| 4 | Do not provide consistent results | Provides consistent results |
| 5 | No thermal stability | Provides thermal stability and hence can perform in high temperature, high pressure (HTHP) well conditions |

developed by³⁷ specifically for deep oil well cementation, has undergone comprehensive assessment. Its attributes, encompassing responsiveness to temperature, resistance to salt, additive distribution, and compressive strength, were meticulously examined. The outcomes revealed that SDH-2 effectively demonstrated retarding properties for oil well cement slurries within the temperature spectrum of 40°C (104°F) to 204°C (399.2°F). Furthermore, addressing the need for retarding cement slurries in the upper segments of deep and ultra-deep wells with prolonged cementing intervals, researchers introduced a novel high-temperature retarder (HTR) - 300L, which underwent thorough evaluation.⁴⁰ The findings indicated that HTR - 300L showcased remarkable temperature-resistance capabilities and maintained a stable molecular structure.

Organic versus synthetic retarders

The application of organic retarders in oil well cement scenarios presents notable fluctuations, lacking the requisite uniformity essential for accurate control of thickening times across diverse cement types, despite effectively prolonging cement setting intervals in well operations. This variability primarily stems from the inherent inconsistency in the production of natural organic retarders, evident in batch-to-batch and source-to-source variations. Additionally, factors such as down-hole conditions, process control, and variations in cement compositions significantly contribute to the observed irregularities in natural organic retarders and other biopolymers utilized in the industry.¹³ Consequently, the employment of organic retarders in oil well cementing entails both advantages and disadvantages, as elucidated in Table 3.

The synthetic retarders are based on the same functional groups as those of conventional retarders (e.g. sulfonate, carboxylic acid, or an aromatic compound). The synthetic products, like any other inorganic product, are man-made, so the reaction environment is controlled and consistent reaction environment.⁴¹ Consequently, the use of synthetic retarders in oil well cementing offers both advantages and disadvantages, as outlined in Table 4 (table 5).

Cement retardation theories

In recent times, the importance of retarders has intensified, particularly with the growing depths of wells, accompanied by a substantial increase in temperature and pressure levels.³ In conventional oil well cementing practices, Portland cement is the predominant material, composed of four principal constituents: tricalcium silicate (C_3S) and tricalcium aluminate (C_3A), contributing to early strength development; dicalcium silicate (C_2S), responsible for achieving final strength; and tetracalcium aluminoferrite (C_4AF).⁴¹ Gypsum is added during the cement manufacturing process to regulate the setting time. However, standard cement exhibits inadequate thickening time for applications in temperatures exceeding 38°C (100°F) at depths surpassing 3000 meters. Consequently, the inclusion of retarders as additives becomes imperative to extend thickening time and meet the demands of such challenging conditions.⁴²

As indicated by,⁴³ the retardation phenomenon, while not entirely elucidated, is linked to the binding of retarders with calcium ions, resulting in a deceleration of ettringite crystal growth.^{43,44} Despite ongoing investigations, the exact mechanisms governing the retardation process remain a subject of exploration, with multiple theories proposed, none of which have provided a comprehensive explanation. The effectiveness of retarders hinges on two primary factors: the chemical composition of the retarder itself and the specific cement phase (silicate or aluminate) targeted by the retarder. Furthermore, the retarding impacts of these additives are subject to various factors, including the applied dosage, curing conditions, and other relevant parameters.⁴⁵ Consequently, the intricacies associated with retardation necessitate further research and exploration to attain a comprehensive understanding of the underlying processes.

Therefore, the five theories which have been used to explain the mechanism of retardation are summarized below:

Adsorption theory

The Adsorption theory proposes that a retarding admixture is adsorbed onto the surface of cement particles, forming a protective layer. This layer acts as a diffusion barrier, hindering the access of water molecules to the surface of unhydrated cement particles, thus slowing down the hydration process. Consequently, the cement paste maintains its plasticity for an extended period due to the limited availability of hydration products needed for paste solidification. Essentially, the retarder becomes adsorbed onto the surfaces of hydration products, diminishing their contact with water and imparting hydrophobic characteristics to the cement paste.⁴⁴ This phenomenon elucidates how the adsorption of the retarding admixture influences hydration kinetics, resulting in the observed hydrophobic behavior of the cement paste.

Precipitation theory

The generation of certain insoluble byproducts resulting from the interaction of the retarder with the alkaline solution (pH exceeding 12) bears resemblance to an adsorption mechanism. These insoluble byproducts precipitate as protective layers around the cement particles, inducing a deceleration in the cement hydration process. The protective layer acts as a diffusion barrier, impeding the efficient interaction between water molecules and the cement particles. More precisely, the retarder reacts with either calcium or hydroxyl ions, or both, present in the aqueous phase, leading to the creation of an impermeable and insoluble sheet enveloping the cement grains. This process effectively retards the ingress of water toward the cement surface.⁴⁶ The establishment of these protective layers by the retarder

influences the hydration kinetics of the cement, resulting in the observed slowdown of the hydration process through the formation of an impermeable barrier.

Nucleation theory

Upon the introduction of water to the cement, calcium ions and hydroxyl ions are released from the surface of the cement particles. Once a critical concentration of these ions is reached, the crystallization process for hydration products is initiated. The addition of a retarding admixture to the cement causes the adsorption of this admixture onto the calcium hydroxide nuclei, effectively impeding their growth until a certain level of supersaturation is achieved. Essentially, the retarder becomes adsorbed onto the nuclei of hydration products, occupying the reactive faces and thus retarding the subsequent growth of these nuclei.⁴⁷ The inclusion of the retarder modifies the kinetics of nucleation and growth of hydration products, leading to the observed deceleration in the overall hydration process.

Complexation theory

In this context, during the initial stages of the process, certain complexes involving calcium ions released by the cement grains are formed. These complexes contribute to an increase in the solubility of the cement. As hydration proceeds, especially in the presence of a retarding admixture, there is a noticeable elevation in the concentration of calcium and hydroxyl ions within the aqueous phase of the cement paste. The accumulation of these ions in the solution hinders their precipitation to form calcium hydroxide, leading to a deceleration of the hydration process. The retarder operates by chelating the calcium ions, resulting in a reduction in the concentration of calcium ions in the pore solution, thereby impeding the formation of nuclei.⁴⁸ Through this mechanism, the retarder effectively modulates the kinetics of hydration by regulating the availability of calcium ions crucial for the nucleation and growth of hydration products.

Dissolution - precipitation theory

This mechanism is principally applied in retarders utilizing organic phosphonic acid. In the initial stage, the process involves the extraction of calcium ions, resulting in their dissolution. Subsequently, a precipitate forms, identified as insoluble calcium phosphonate, which acts as a diffusion barrier to water, effectively retarding nucleation by binding to the surface of the CSH (Calcium Silicate Hydrate) gel.⁴⁹ Through this approach, the retarder significantly influences the kinetics of hydration, and the formation of insoluble calcium phosphonate plays a pivotal role in modulating the hydration process by impeding the nucleation and growth of hydration products.

Concerning any particular retarder, accurately establishing the exact mechanism poses a challenge. Nevertheless, it is conceivable that all the mechanisms expounded upon are involved to varying extents in the retardation process, with the different theories synergistically contributing.⁴⁹ Despite the uncertainties surrounding the precise mechanisms of retardation, the technology has undergone extensive development and refinement.^{50,51}

Conclusion

Controlling cement set is one important factor to the success of any cementing job. Too much thickening time will increase the costs with waiting on cement (time needed to wait for cement sheath to develop compressive strength) and delay the development of the oil well construction process. Similarly, very short operational times also generate associated risks and costs, due to premature set risk during displacement of the slurry inside the case which, in extreme cases,

can lead to total loss of investments in the well. Several retarders have been developed over the past few decades which are classified mainly into organic and synthetic retarders. Performance of the organic retarders varies depending on the source. However, synthetic retarders are preferred because they perform more consistently compared to organic retarders.

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Conflicts of interest

The authors declare that they have no competing interests.

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References

- Nelson EB, Guillot D. Well cementing, 2nd edn. Schlumberger, Sugar Land. 2006.
- Smith DK. Cementing. SPE Monograph Series. 1987;4:2.
- Salam KK, Arinkoola AO, Ajagbe B, et al. Evaluation of thickening time of oil field class g cement slurry at high temperature and pressure using experimental design. *International Journal of Engineering Sciences*. 2013;2:361–367.
- Salim P, Amani M. Special considerations in cementing high pressure high temperature wells. *International Journal of Engineering and Applied Sciences*. 2013;1:120–143.
- Eric B, Joel F, Grace O. Oil well cement additives: A review of the common types. *Oil and Gas Research*. 2016;2:112.
- Oriji AB, Zakka SB. Effects of thickening time on the application of cement slurry for high temperature, high pressure drilling. *Innovative systems design and engineering*. 2013;4(3).
- Anon. Types of Retarders slurry retarders Cellulose derivatives.
- Anon. Drilling engineering lecture notes on cementing. Institute of Petroleum Engineering. Herriot Watt University; 2009:1–40.
- Shahriar A. Investigation of oil well cement slurries. Ph.D. Thesis, University of Western Ontario, School of Graduate and Postdoctoral Studies. 2011.
- Joel OF, Ademiluyi FT. Modelling of compressive strength of cement slurry at different slurry weights and temperatures. *Research Journal of Chemistry Science*. 2011;1(2):128.
- Abbas G, Irawan S, Memon MK, et al. Hydroxy propyl methyl cellulose as free water and settling control agent in oil well cement slurry. Springer, Singapore; 2015:121–128.
- Shuker MT, Memon KR, Tunio SQ, et al. Laboratory investigation on performance of cement using different additives schemes to improve early age compressive strength. *Research Journal of Applied Sciences Engineering and Technology*. 2014;7:2298–2305.
- Angelini S, Ingles D, Gelosia M, et al. One-pot lignin extraction and modification in γ -valerolactone from steam explosion pre-treated lignocellulosic biomass. *Journal of Clean Production*. 2017;151:152–162.
- Yao L, Yong-Chao L, Hong-Qin H, et al. Structural characterization of lignin and its degradation products with spectroscopic methods. *Journal of Spectroscopy*. 2017.
- Joel OF. The secondary effects of ligno sulfonate cement retarder on cement slurry properties. *Journal of Engineering and Applied Sciences*. 2009;4:1–7.
- Anjos MA, Martinelli EA, Dulce MA, et al. Hydration of oil well cement containing sugarcane biomass waste as a function of curing temperature and pressure. *Journal of Petroleum Science and Engineering*. 2013;109:291–297.
- Otoko GR, Ephraim ME. Concrete admixture and set retarder potential of palm liquor. *European International Journal of Science and Technology*. 2014.
- Moreira PH, Freitas JC, Braga RM, et al. Production of carboxymethyl lignin from sugar cane bagasse: A cement retarder additive for oilwell application. *Industrial crops and products*. 2018;116:144–149.
- Anaele JV, Joel OF, Chukwuma FO, et al. Alternative utilization of sawdust for oilfield chemical additive (Cement Retarder) Production: A Case Study of Local Cement. *International Journal of Science and Engineering Investigations (IJSEI)*. 2019;8(85):33–37.
- Guo S, Bu Y, Lu Y. Addition of tartaric acid to prevent delayed setting of oil-well cement containing retarder at high temperatures. *Journal of Petroleum Science and Engineering*. 2019;3(4).
- Sarita R, Singh NB, Singh NP. Interaction of tartaric acid during hydration of Portland cement. *Indian Journal of Chemical Technology*. 2006;13:255–261.
- Hou W, Bao J. Evaluation of cement retarding performance of cellulosic sugar acids. *Construction and Building Materials*. 2019;202:522–527.
- Nelson EB, Baret JF, Michaux M. Cement additives and mechanism of action an well cementing. Nelson Elsevier Science Publishers Amsterdam; 1990:3–37.
- Otunyo WA, Koate I. Sugar cane juice as a retarding admixture in concrete production. *Global Journal of Engineering Research*. 2015;14:17–23.
- Peschard A, Govina A, Pourchez J, et al. Effect of polysaccharides on the hydration of cement suspension. *Journal of the European Ceramic Society*. 2006;26:1439–1445.
- Usman ND, Chom HA, Salisu, C, et al. The impact of sugar on setting –Time of ordinary portland cement (OPC). *FUTY Journal of the Environment*. 2016;10(1).
- Bermudez M. Effect of sugar on the thickening time of cement slurries. *SPE Annual Technical Conference and Exhibition SPE 113024 Anaheim California USA*. 2007:11–14.
- Roshan H, Asef M R. Characteristics of oil well cement slurry using CMC. *Journal of Society of Petroleum Engineers Drilling and Completion SPE*. 2010;25:328–335.
- Abbas G, Irawan S, Memon KR et al. Application of cellulose-based polymers in oil well cementing. *Journal of Petroleum Exploration and Production Technology*. 2020;10:319–325.
- Ahmed A, Mahmoud AA, Elkhatatny S, et al. Improving Saudi class g oil – well cement properties using the tire wastes material. *ACS Omega*. 2020;5:27685–27691.
- Ismail AA, El Sabbagh, AM, Adawy AI et al. Effect of some plasticizers on the rheological properties of oil well cement slurries. *Egyptian Journal of Petroleum*. 2018;27(4).
- Yimlamai B, Choirit W, Christi Y et al. Cellulose from oil palm empty fruit bunch fiber and its conversion to carboxymethylcellulose. *Journal of Chemical Technology & Biotechnology*. 2021;96(6).
- Liu K, Du H, Zheng T, et al. Recent advances in cellulose and its derivatives for oilfield applications. *Carbohydrate Polym*. 2021.
- ZhiGang QI, Xiaoming ZHU, Huilian CAO. Applications and study on organophosphate acids (Salts) for oil well cement retarder. *Energy Science and Technology*. 2013;6(2):79–83.
- Peng Z, Zhang J, Feng Q, et al. Synthesis and retarder mechanism study of a novel amphoteric composite high temperature-resistant retarder for oil well cement. *RSC Adv*. 2018;8:14812.

36. Sabins FL, Sutton DL. The relationship of thickening time, gel strength, and compressive strength of oilwell cements. *SPE Production Engineering*. 1986;1(02):143–152.
37. Michaux M, Nelson EB, Vidik B. Chemistry and characterization of Portland cement in well cementing. *Nelson Elsevier Science Publishers Amsterdam*. 1990:8–25.
38. Khalid NHA, Hussin MW, Ismail M, et al. Evaluation of effectiveness of methyl methacrylate as retarder additive in polymer concrete. *Construction and Building Materials*. 2015;93:449–456.
39. Jintang GUO, Xiujian XIA, Shuoqiong LIU, et al. A high temperature retarder HTR–300L applied in long cementing interval. *Petroleum Exploration Development*. 2013;40(5):656–660.
40. Norfadhilah H, Koji T, Kunio Y. solid fuel from oil palm biomass residues and municipal solid waste by hydrothermal treatment for electrical power generation in Malaysia: a review. *Sustainability*. 2019;11:1060.
41. Taylor HF. Cement chemistry. Academic Press London; 1997. 475 p.
42. Liu CJ, Huang BZ, Xu TT, et al. Oil and gas well cementing theory and applications. Petroleum Industry Press; 2001:84–90.
43. Magarini P, Lanzetta C, Galletta A. Drilling design. Manual Eni–Agip, Division. 1999:97–107.
44. Coveney PV, Humphries W. Molecular modelling of the mechanism of action of phosphate retarders on hydrating cements. *Journal of the Chemical Society Faraday Transactions*. 1996;92:831–841.
45. Khan B, Ullah M. Effect of a retarding admixture on the setting time of cement pastes in hot weather. *Journal of King Abdulaziz University Engineering Sciences*. 2004;15:63–79.
46. Double DD, Hewlett PC, Sing KSW. New developments in understanding the chemistry of cement hydration (and discussion). *Phil Trans R Soc Land A*. 1983;310:53–66.
47. Brothers LE, Chatterji J, Childs JD. Synthetic retarder for high strength cement. *Presented at SPE/IAOC Drilling conf. Amsterdam, the Netherlands*. 1991:11–14.
48. Thomas NL, Bichall JD. The Retarding action of sugars on cement hydration. *Cement Concrete Research*. 1983;13(6):830–842.
49. Ramachandran VS, Feldman R, Beandoin J. Concrete science: Treatise on current research. Philadelphia Pennsylvania; Heyden and Son Ltd; 1981.
50. Bishop M, Barron AR. Cement hydration inhibition with sucrose, tartaric acids and lignosulfonates analytical and spectroscopic study. *Industrial Engineering Chemical Research*. 2006;45(21):7042–7049.
51. Rahul J, Tamal KS, Sumukh D. Coffee as a cement retarder. Conference held in Manama, Kingdom of Bahrain; 2017.