THE SECONDARY EFFECTS OF LIGNOSULFONATE CEMENT RETARDER ON CEMENT SLURRY PROPERTIES

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ABSTRACT

The primary function of retarders in cement slurry design is to increase the thickening time at higher temperature to allow time for placement of the liquid slurry. This has been the focus in the oil Industry on cement slurry design using retarders. However, test results from this research work using different retarder concentrations indicated that not only the thickening time was affected but the compressive strength, rheological as well as the free fluid properties. Increasing retarder concentration not only resulted to increase in thickening time, but a decrease in both rheological properties and early strength development as well as increase in free fluid results. It is therefore imperative that to optimize a cement slurry design to meet up with design objectives and all boundary conditions, the choice of optimum retarder concentration is critical.

INTRODUCTION

Chemistry of Portland cement slurry reaction

The most widely used cement is Portland cement. The four major clinker phases present in Portland cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetra calcium aluminoferrite (C_4AF); the clinker is ground with gypsum (CH_2). The formulae in parentheses use the standard cement chemistry abbreviations [1]:
$C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $= SO_3$, and $H = H_2O$. The reactions involved when cement is mixed with water are complex. Each phase hydrates by a different reaction mechanism and at different rates. The reactions, however, are not independent of each other because of the composite nature of the cement particle and proximity of the phases. When cement and water are mixed together, the reactions which occur are mostly exothermic-heat is produced. The evolution of hydrating cement can be qualitatively characterized by the heat evolution curve sketched in (Figure-1) [2]. Five principal reactions occur.

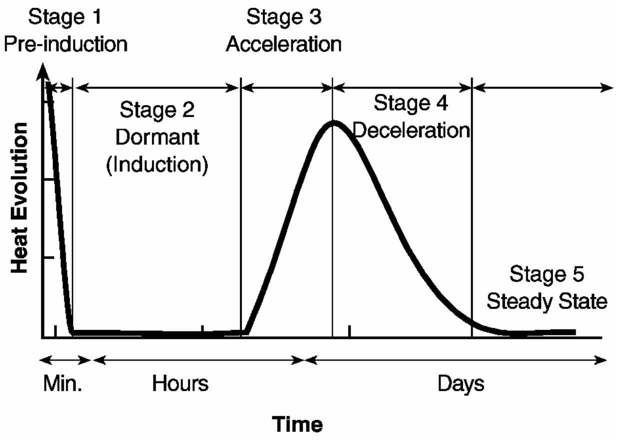

Figure-1. Schematic of heat evolution for Portland cement at 68°F.

Almost immediately on adding water, some of the clinker sulphates and gypsum dissolve, producing an alkaline, sulfate-rich solution. Soon after mixing, the Tricalcium aluminate (C_3A) phase-the most reactive of the clinker minerals- reacts with the water to form an aluminate-rich gel. The gel reacts with sulfate in solution to form small rod-like crystals of ettringite. Tricalcium aluminate (C_3A) hydration is a strongly exothermic reaction but it does not last long. Typically only a few minutes and is followed by a period of a few hours of relatively low heat evolution. This is called the dormant, or induction period. The first part of the dormant period-up to perhaps half-way through-corresponds to when concrete can be placed. As the dormant period progresses, the paste becomes too stiff to be workable. At the end of the dormant period, the alite and belite in the cement start to hydrate, with the formation of calcium silicate hydrate and calcium hydroxide. This corresponds to the main period of cement hydration during which slurry strength increases. The cement grains react from the surface inwards, and the anhydrous particles become smaller. Tricalcium aluminate (C_3A) hydration also continues, as fresh crystals become accessible to water. The period of maximum heat evolution occurs typically between about 10 and 20 hours after mixing and then gradually tails off. In a mix containing Portland cement as the only cementitious material, most of the strength gain occurs within about a month. Ferrite hydration also starts quickly as water is added, but then slows down, probably because a layer of iron hydroxide gel forms, coating the ferrite and acting as a barrier, preventing further reaction.. Portland cement is composed largely of four types of minerals: alite, belite, aluminate (C_3A) and a ferrite phase (C_4AF).

Cement hydration

The reaction of cement with water is referred to as cement hydration. As hydration occurs, the cement sets as a compact solid and consequently develops compressive strength. The process of hydration could take several days or even weeks at low temperatures. However, at high temperatures, maximum strength is attained after a few hours. The rate at which hydration occurs when water is mixed with cement can be altered using chemical additives [3]. Chemicals used to increase the speed of hydration are called accelerators. Each of the cement constituents participate in hydration reactions in the presence of water, but the rate of hydration can differ for each constituent. For example, Tricalcium aluminate (C_3A) hydrates much more rapidly than the other cement components, and Dicalcium silicate (C_2S) hydrates at a much slower rate than Tricalcium silicate (C_3S). In general, the relative hydration rate follows the sequence: $C_3A > C_3S > C_4AF > C_2S$. The development of compressive strength is primarily dictated by the two major cement components, C_3S and C_2S. Tricalcium silicate (C_3S) is the constituent primarily responsible for the development of early (1 to 28 days) compressive strength, while C_2S is responsible for the development of later (28 + day) compressive strength. The hydration rate for cement is also highly dependent on the cement particle size (controlled during the process of grinding the clinker) and the temperature experienced by the slurry during setting. It is possible to control the hydration rate, to some degree, by using accelerating and retarding additives. The hydration of cement is an exothermic process (i.e., heat is liberated during the reactions), and each of the cement components has a characteristic heat of hydration that contributes to the overall heat liberated on hydration.

The overall heat of hydration depends on the relative quantities of each of the constituents in the cement. Ionic composition of the solution also plays a significant role in the hydration process (Figure-2) [4]. Additives that alter the ionic composition significantly alter the hydration process. For example, adding soluble sodium or potassium salts will precipitate calcium hydroxide (CH) from solution and reduce the dormant period.

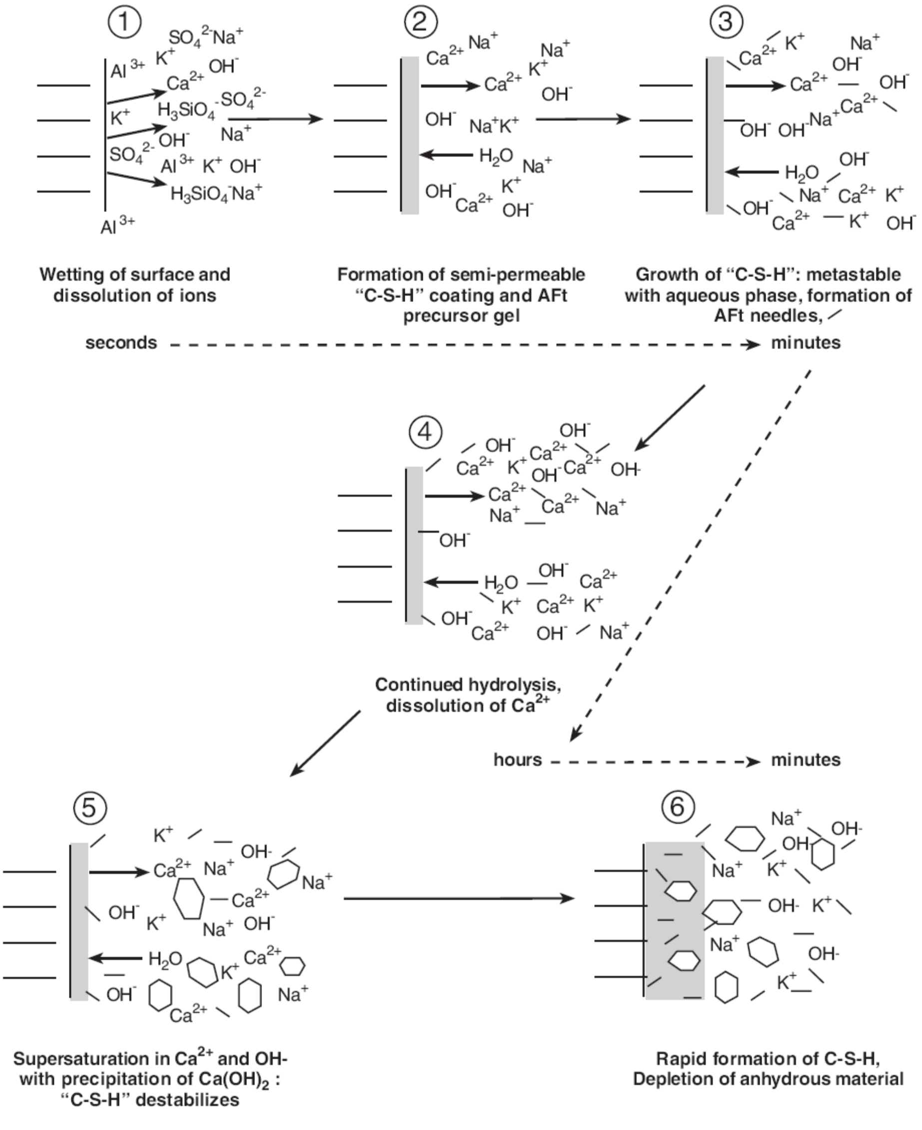

Figure-2. Ionic composition in the hydration process [4].

Cement additives

The rate at which hydration occurs when water is mixed with cement can be altered using chemical additives. The chemicals used to decrease the speed of hydration are called retarders. Those used to increase the speed of hydration are called accelerators. Care should be taken when using retarders as they can affect compressive strength. The most commonly used retarders are cellulose, lignosulfonates and sugar derivatives. These products reduce the rate of hydration by reacting chemically with unhydrated cement components or by forming a physical coat on unhydrated particles thus preventing contact with water

Retarders

The cements commonly used in well applications-API Class A, C, G, and H-as produced in accordance with API Specification 10A [5], do not have a sufficiently long fluid life (thickening time) for use at temperatures above 100°F (38°C) BHCT. For extending the thickening time, additives known as retarders are required. Retarders are used to decrease the set time of cement slurries or to retard the cement setting. They do not decrease the ultimate compressive strength of cement but do slow the rate of strength development. They also lengthen the thickening time. The most common retarders are natural lignosulfonates and sugars. The newest retarders are made from various synthetic compounds. The chemical mechanisms of cement retardation are complex and not well understood. Whereas acceleration is accomplished by modifying the aqueous phase composition, retardation is usually accomplished by modifying the hydration products. On the basis of the theories proposed concerning the mechanisms of the dormant period, an additive that would make the protective layer around the cement grain less permeable and/or poison the growth of the CH nuclei would increase the dormant period. Different mechanisms have been proposed for modifying the protective layer and include adsorption of retarder onto the protective layer, precipitation of retarder with Ca^{2+} and/or OH^- to form an impermeable layer, and adsorption of the retarder onto the nuclei of the hydration products, preventing further growth and transformation into the second hydrate. All or some of these mechanisms may apply in most cases.

Of the chemical compounds identified as retarders, lignosulfonates are the most widely used. A lignosulfonate is a metallic sulfonate salt derived from the lignin recovered from processing wood waste. The resultant aqueous solution of lignosulfonic acid, simple sugars, starches, and natural gums is known as lignin liquor. The composition of the liquor is dependent on the wood source and the reaction conditions. Performance of the liquor as a retarder is dependent upon the proportioning of these compounds, their molecular weights, and the degree of sulfonation. As a result of processing, three grades of lignosulfonate are available for the retardation of cement slurries. Each grade is available as calcium/sodium or sodium salts. The three grades can be described as filtered, purified, and modified.

Numerous studies on the mechanism of retardation using lignosulfonates on both pure phases and cement have been reported [6-10]. The complexities of the hydration, coupled with the different compositions in lignosulfonate, whether filtered, purified or modified, give rise to different and often conflicting opinions. Considering only the purified lignosulfonate, one can reasonably assume the following:

a) Hydration of both aluminate and alite phases are retarded, with the effect being more predominant on the alite phase; and
b) Retardation increases with the increase of the alite/aluminate ratio.

Synthetic retarders

The term synthetic retarder is a misnomer in that the previously discussed retarding compounds are all, in effect, man made. However, the term synthetic retarder has been applied to a family of low-molecular-weight vinyl polymers. These retarders are based on the same functional groups as conventional retarders (i.e., sulfonate, carboxylic, or an aromatic ring). The advantage of synthetic retarders is the ability to control the number and the relative position of the pendent chain containing the functional groups along the polymer backbone.

RESEARCH METHODOLOGY

A series of tests were performed to evaluate the performance on thickening time, compressive strength, free fluid, and rheological properties. All tests were conducted in line with the specification for materials and testing for Well Cements [11, 12]. The testing conditions are specified in (Table-2).

Laboratory testing and equipment:

Thickening time testing

The API thickening time test is the accepted method for measuring how long cement slurry should remain pumpable under simulated down-hole temperature and pressure conditions. The test was performed in a high-pressure/high temperature (HPHT) Consistometer that is usually rated at pressure up to 30,000 psi and temperatures up to 400°F. The test involved mixing the cement slurry according to current API procedures, placing the slurry into the slurry cup, and then placing the slurry cup into the Consistometer for testing [11, 12]. The testing pressure and temperature were controlled to simulate the conditions the slurry will encounter in the well. The test concluded when the slurry reached a consistency considered unpumpable in the well. The time to reach this consistency is called thickening time or pumpable time. The test was said to be set after attaining a consistency of 70 Bearden Consistency (BC) unit under a dynamic state using the HPHT Consistometer.

Fluid loss testing

Fluid loss tests are conducted to establish API procedures to help determine the relative amount of fluid loss that will occur in a given cement slurry. The amount of filtrate lost by the fluid under bottomhole temperature and 1,000 psi differential pressure was measured in this test [11, 12].

Rheology testing

To properly predict the frictional pressures that will occur while pumping the various fluids in the well, the rheological properties of the slurries should be known as a function of temperature.. The shear stress and shear rate behaviour of slurry was measured in this test. The viscosity was measured in centipoises (cp) using a Fan Viscometer.

Compressive strength testing

The pressure it takes to crush the set cement is measured in this test. This test indicates how the cement sheath will withstand the differential pressures in the well. In destructive testing cement slurry is poured into cubical moulds and the cement cubes are then crushed to determine their compressive strength. In a non-destructive test, sonic speed is measured through the cement as it sets. This value is then converted into compressive strength.

Free fluid testing

The purpose of the free water test is to help determine the amount of free fluid that will gather on the top of cement slurry between the time it is placed and the time it gels and sets up. The test involved preconditioning the slurry up to 190^{o}F maximum temperature in an atmospheric Consistometer, is then transferred to a 250ml graduated cylinder and allowed to set static for 2 hours. The slurry was then examined for any free fluid on the top of the cement column. This free fluid was decanted and measured to determine the percent of free water based on the 250ml volume [11, 12].

RESULTS

Table-1. Test data parameters and slurry composition.

TVD = 4213ft; MD = 5500 ft						
Test #		**1**	**2**	**3**	**4**	**5**
BHST	°F	153	153	153	153	153
BHCT	°F	121	121	121	121	121
BHP	psi	2980	2980	2980	2980	2980
Heat up time	min	12	12	12	12	12
Additives						
Dyckerhoff cement **(Retarder)**	%bwoc **gal/sk**	100 **0.01**	100 **0.05**	100 **0.07**	100 **0.09**	100 **0.11**
Defoamer	gal/sk	0.02	0.02	0.02	0.02	0.02
Water type		Drill	Drill	Drill	Drill	Drill
Chloride content	ppm	400	400	400	400	400
Water requirement	gal/sk	5.05	5.02	5	4.98	4.97
Mixing fluid	gal/sk	5.08	5.09	5.09	5.09	5.1
Yield	cu. ft/sk	1.15	1.15	1.15	1.16	1.16
Slurry weight	lbs/gal	15.8	15.8	15.8	15.8	15.8
Test results						
Thickening time						
30Bc	hrs:min	**2:20**	**3:35**	**4:29**	**11:40**	**16:20**
50Bc	hrs:min	**2:33**	**3:47**	**4:49**	**11:52**	**16:35**
70Bc	hrs:min	**2:43**	**3:53**	**5:02**	**12:00**	**16:48**
Rheologies @ 80 °F						
300rpm	cp	64	26	25	25	24
200rpm	cp	54	17	16	15	16

100rpm	cp	35	11	10	9	8
6rpm	cp	17	4	4	3	2
3rpm	cp	12	2	2	2	2
PV	cp	43.5	22.5	22.5	24	24
YP	lbf/100ft^2	20.5	3.5	2.5	1	0
Rheologies @ BHCT						
300rpm	cp	124	88	51	30	20
200rpm	cp	110	79	36	21	14
100rpm	cp	94	67	27	16	8
6rpm	cp	23	24	15	6	2
3rpm	cp	17	16	9	3	2
PV	cp	45	31.5	36	21	18
YP	lbf/100ft^2	79	56.5	15	9	2
Compressive strength						
12 hours	psi	1170	1125	1084	0	0
24 hours	psi	3090	2980	2850	1541	1172
Free fluid @ 45 deg.	%	0.6	1.48	1.78	1.98	2.05

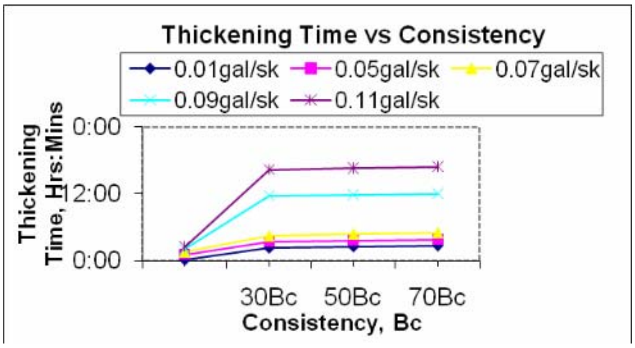

Figure-3. Thickening time at 70 Bc.

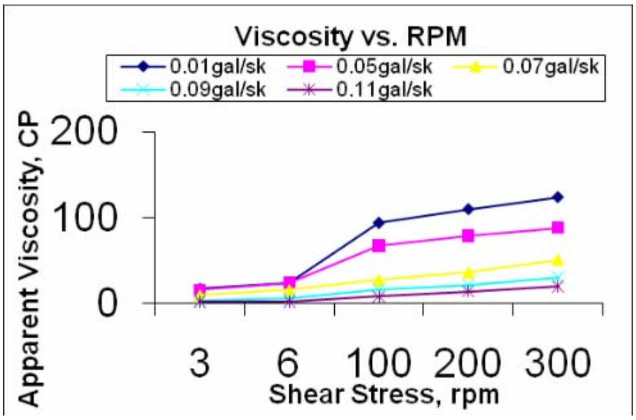

Figure-4. Rheological properties.

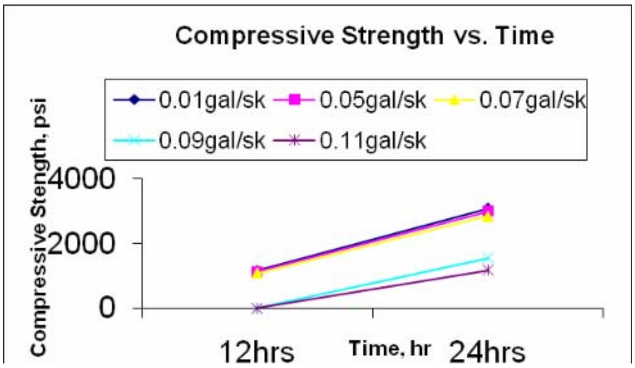

Figure-5. Compressive strength versus time at 24hrs.

DISCUSSION

Thickening time

From (Table-1 and Figure-3), it was seen that thickening time increased with increase in retarder concentration. The intensity of retardation was more pronounced with higher retarder loading. Test results indicated that thickening time at 70 Bc were 2:43 (hrs:min), 3:53 (hrs:min), 5:02 (hrs:min), 12:00 (hrs:min) and 16:48 (hrs:min) for retarder concentrations of (0.01, 0.05, 0.07, 0.09,0.11) gal/sk, respectively.

Rheological values

Test results as indicated from (Table-1 and Figure-4) showed that increasing the retarder concentrations resulted in decrease in rheological values. This shows that in addition to affecting the thickening, it also exhibited dispersing tendencies. The plastic viscosity (PV) and yield point (YP) values for retarder concentrations of (0.01, 0.05, 0.07, 0.09,0.11) gal/sk, respectively were (45 cp and 79 lbf/100ft^2, 31.5 cp and 56.5 lbf/100ft^2, 36 cp and 15 lbf/100ft^2, 21 and 9 lbf/100ft^2, 18 cp and 2 lbf/100ft^2). The lower the YP values, the thinner the slurry and the tendency to settle.

Compressive strength

From (Table-1 and Figure-5), test results indicated that higher concentration values of the retarder affected both the early strength development as well as the strength at 24hrs. The 12hrs and 24hrs compressive strength for retarder concentrations of (0.01, 0.05, 0.07, 0.09, 0.11) gal/sk were (1170 and 3090, 1125 and 2980, 1084 and 2850, 0 and 1541, 0 and 1172) psi, respectively. As could be seen the higher the concentration of retarder, the lower the compressive strength and vice-versa.

Free fluid

Test results from (Table-1) indicated that increasing the retarder concentration resulted to increase in free fluid. This could be attributed to dispersing tendencies observed at higher concentration loading, thereby, affecting the rate of settling of solid particles in the slurry. The free fluid after 2hrs for retarder concentrations of (0.01, 0.05, 0.07, 0.09, 0.11) gal/sk were 0.60%, 1.48%, 1.78%, 1.98% and 2.05%, respectively.

CONCLUSIONS

- Use of retarder in cement slurry design has a synergistic effect on cement properties;
- The intensity of the change depends on the magnitude of the concentration;
- Increasing retarder concentration will affect early strength development and increase on waiting on cement (woc) time and pose additional cost to rig operations
- Slurry design consideration is critical in overall success of drilling and completion operations.

In order to optimize cement slurry design to meet up with design objectives, the choice of optimum retarder concentration is paramount.

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Appendix 1: FORMULA

1. BHP = 0.052 * d * TVD

Where BHP = Bottom Hole Pressure in psi
d = Density of Cement slurry in lb/gal
TVD = True Vertical Depth in ft.

2. Gradient (^{o}F/100ft) = (BHST – 80) / TVD

Where Gradient = Change in Temperature per given depth
BHST = Bottom Hole Static Temperature in ^{o}F
TVD = True Vertical Depth in ft.

3. Fluid Loss at Q_{30mins} = $\frac{Qt * 2 * 5.477}{\sqrt{T}}$

Where Q_{30mins} = Quantity of fluid loss in 30mins.
Qt = Quantity of fluid loss in time #
T = Test Duration

4. Free Fluid = $\frac{\text{ml of Fluid} * 100\%}{250}$

5. Plastic Viscosity (PV) = 1.5 (300rpm-100rpm) reading

6. Yield Point (YP) = 300rpm reading – PV

7. Compressive Strength (Psi) = $\frac{\text{Force (lb)}}{\text{Area}}$

8. Heat- up Rate = $\frac{\text{BHCT - 80}}{\text{Heat up time}}$

9. %bwoc = percentage by weight of cement

10. gal/sk = gallon per sack

11. cu.ft/sk = cubit feet per sack

12. ppm = parts per million

13. Ibs/gal = pounds per gallon

14. MD = measured depth

15. CP = centipoise