EVALUATING THE PERFORMANCE OF CEMENT SLURRY PROPERTIES AT LOW TEMPERATURE

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ABSTRACT:

Shallow wells with low temperature profile bring about extensive long thickening time and low early compressive strength development. This results to waiting on cement (WOC) time and posses enormous cost to rig time and drilling operations. This research work is aimed at formulating cement slurry to shorten the thickening time and give early strength development, thereby reducing the WOC and adding value to drilling operations.

Test results from the study indicated that slurry formulations at low temperatures with sea water and calcium chloride will help to shorten the thickening time and enhance early strength development. Test results at same temperature with slurry formulations without calcium chloride compared with those with calcium chloride indicated a significant difference of over 50% in thickening time variations. The findings, therefore, will be useful for researchers and Operators in the Oil industry to enable them design cement slurries for enhanced performance at low temperature wells.

Keywords: Cement slurry, low temperature, thickening time, compressive strength, accelerators

INTRODUCTION:

CEMENT HYDRATION AND REACTION KINETICS

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: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, and H = H_2O[1]. The reactions used in our cement microstructure models are summarized in figure-1.

Calcium Silicates

On reaction with water, C_3S produces C-S-H and calcium hydroxide, CH, (also known as Portlandite). The simplified reaction of (C_3S) with water may be expressed as[2]

$$2Ca_3OSiO_4 + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \quad \ldots\ldots 1$$

This is a relatively fast reaction, causing setting and strength development in the first few weeks. The kinetics and hydration mechanism for C_2S are similar to those of C_3S except that the rate of reaction is much slower and is mainly responsible for strength growth after one week[2]. The hydration products are the same except that the proportion of calcium hydroxide produced is about one-third of that obtained on

hydration of C_3S. The reaction of (C_2S) which is relatively slow is:

$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2$ 2

Tricalcium Aluminate

Tricalcium aluminate, C_3A, is generally the fastest reacting phase in Portland cement. In fact, gypsum is specifically added to Portland cement to slow down this reaction, thus avoiding 'flash set' of the material. Because the aluminate phase is critical to early hydration properties, it is of great interest in oil well cementing. When gypsum is not present in the system, C_3A reacts with water to form a variety of crystalline hydration products, with hydrogarnet, C_3AH6, being the ultimately stable hydration product.

The products formed on reaction of C_3A in the presence of gypsum depend primarily on the availability of sulfate ions from the dissolution of gypsum. C_3A will react with the gypsum to form ettringite, $C_6A_3H_{32}$, whose crystals are often observed to grow as needles within the cement paste.

$Ca_3(AlO_3)_2 + 3CaSO_4 + 32H_2O \rightarrow Ca_6(AlO_3)_2(SO_4)_3.32H_2O$.....3

The ettringite subsequently reacts slowly with further tricalcium aluminate to form "monosulfate"

$Ca_6(AlO_3)_2(SO_4)_3.32H_2O + Ca_3(AlO_3)_2 + 4H_2O \rightarrow 3Ca_4(AlO_3)_2(SO_4).12H_2O$.....4

This reaction is complete after 1-2 days. When all of the gypsum is consumed, the ettringite may decompose, reacting with more of the C_3A to form the monosulphate phase, C_4AH_{12}. The reactions of the ferrite phase, C_4AF, are the least well understood of those occurring during Portland cement hydration. The ferrite phase is often said to react slowly (in comparison to the other phases) and only contributes to long-term properties of cements (although exceptions to this have been noted in the presence of special additives[3,4]

$2Ca_2AlFeO_5 + CaSO_4 + 16H_2O \rightarrow Ca_4(AlO_3)_2(SO_4).12H_2O + Ca(OH)_2 + 2Fe(OH)_3$ ----------5

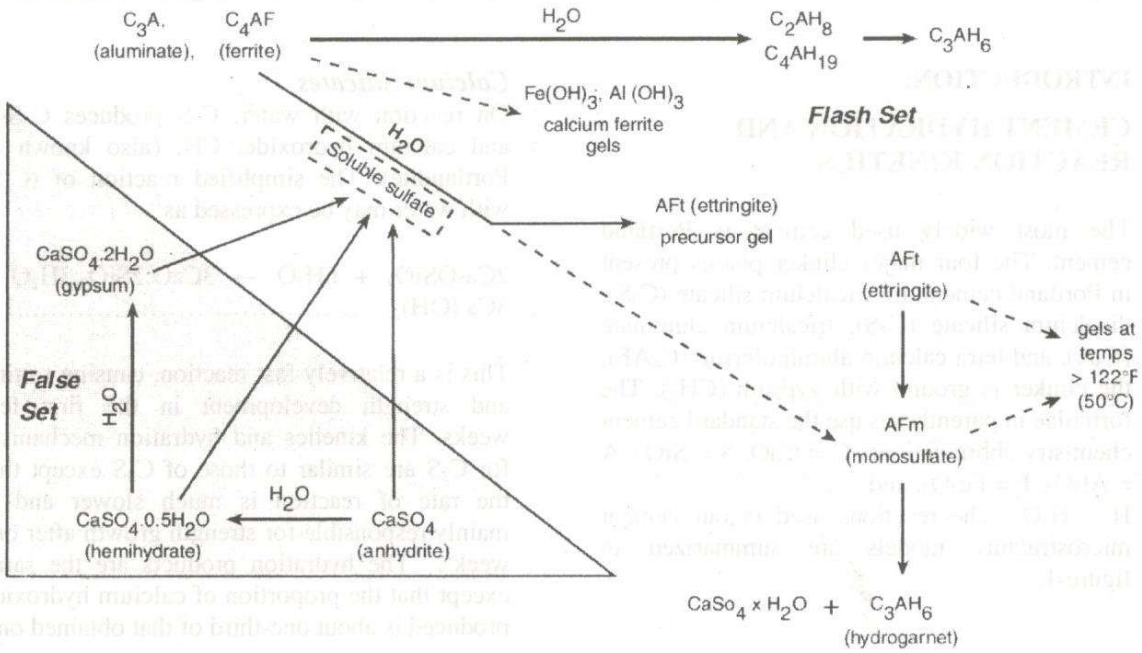

Figure-1: Reaction mechanism for the different phases[1]

Evolution of hydrating cement

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 process can be broken down into five stages. The major activity during each stage is described qualitatively as follows[5].

Stage 1 - Rapid heat generation (15 min.) -- on mixing with water, calcium and hydroxide ions are released from the surface of the C_3S; pH rises to a very alkaline solution. When the calcium and hydroxide reach critical concentrations, crystallization of CH and C-S-H begins. Early chemical reactions are temperature dependent.

Stage 2 - Dormant period - causes cement to remain plastic (2-4 hours). The reaction slows. CH crystallizes from the solution; C-S-H develops on the surface of the C_3S and forms a coating. As the thickness increases, the time it takes water to penetrate the coating increases, thus the rate of reaction becomes diffusion controlled.

Stage 3 - Acceleration period - Critical concentration of ions is reached and silicate hydrates rapidly, maximum rate occurs at this stage. Final set has passed and early hardening begins (4-8 hours).

Stage 4 - Deceleration - rate of reaction slows; completely diffusion dependent reaction.

Stage 5 - Steady state - constant rate of reaction (12-24 hours). Temperature has little effect on hydration at this point.

Accelerators

The term "accelerator" indicates a speeding up or shortening of the reaction time required for cement slurry to become a hardened mass. This indicates a reduction in thickening time and/or an increase in the rate of compressive-strength development of the slurry. This acceleration is accomplished by adding compounds that increase the reactivity of aluminate (substituted -C_3A) or alite (substituted C_3S) phases or both and, in most cases, by using an additive that changes the aqueous phase composition (i.e., pore solution) of the cement slurry. Acceleration is particularly beneficial in cases where a low-density (i.e., high water content) cement slurry is required or in low-temperature formations[7].

The compounds found to be most effective are composed of a cation or anion, or both, that is similar to the components of the cement. The main exception is the chloride anion, which is not a natural component of Portland cement but one that will substitute for the sulfate in the aluminate hydration phases.

Calcium Chloride ($CaCl_2$): Of the chloride salts, $CaCl_2$ is the most widely used and, in most applications, the most economical. The major benefits of $CaCl_2$ are the significant reduction in thickening time achieved and the fact that, regardless of concentration, it always acts as an accelerator. $CaCl_2$ is typically used at concentrations of 1 to 4% by weight of cement (BWOC)[7]

Seawater is a naturally occurring source of alkali chloride salts. Alkali chloride salts include those mentioned above plus magnesium chloride. The equivalent chloride salt content can vary from 2.7% to 3.8% BWOW[8].

RESEARCH METHODOLOGY

A series of tests were performed to evaluate the performance on thickening time, compressive strength and rheological properties. All tests were conducted in line with the specification for materials and testing for Well Cements[9.10.11] .Testing conditions are specified in **Table-1**

Thickening Time

The High Temperature/High Pressure Consistometer (HPHT) made by Fann, rated for operation up to 204°C / 400°F and 30,000 psi was used to measure cement slurry viscosity or consistency under simulated well pressure and temperature conditions as specified[9,10,11]. The test involved mixing the cement slurry according to API procedures, placing the slurry into the slurry cup, and then placing the slurry cup into the Consistometer for testing. The testing pressure and temperature was controlled to simulate the conditions the slurry will encounter in the well. The consistency of the slurry inside the cup was measured by a potentiometer mounted on the shaft of the slurry paddle. As the slurry thickens, the drag on the paddle was transferred to the potentiometer which is calibrated to translate drag or torque into a voltage signal. This signal which represents slurry consistency was displayed and recorded on a strip chart recorder. The test was said to be set when the slurry reached a consistency of 70 Bearden Consistency (BC) units under a dynamic state using the HPHT Consistometer. At this set point it is no longer possible to pump the slurry in the well.

Rheological Testing

The shear stress and shear rate behaviour of slurry at different temperatures was measured in this test.

The cement slurry was conditioned for 20 minutes in an atmospheric consistometer at test temperature before rheological measurements were taken. The viscosity was measured using a rotational Fann Viscometer rated at (115 Volts / 50 Hz, 6 Speed).The test fluid was contained in the annular space or shear gap between the cylinders. The outer cylinder was rotated through precision gearing at known velocities. The viscous drag exerted by the fluid created torque on the inner cylinder or bob. When the torque was transmitted to a precision spring, the spring's deflection was measured and then related to the test conditions. Readings were taken at 300, 200, 100, 6 and 3 rpm respectively and recorded in centipoises (cp)[9,10,11]

Compressive Strength Testing

The pressure it takes to crush the set cement was measured in this test. The cement slurry was poured into Ultra Sonic Cement analyzer (UCA) for non-destructive test. In a non-destructive test, sonic speed is measured through the cement as it sets[9,10,11]. This value is then converted into compressive strength. The UCA cell is equipped with a heating jacket, temperature controller, pressure system, cooling system, transducers and rated at 204°C / 400°F and 30,000 psi. The system measured the strength development by measuring the speed of the Ultra Sonic Signals being sent through the cement while it sets up. The speed of the signals was calculated and correlated to a compressive strength in psi.

Basic Principles for the Evaluation Method

The Power Law model was used to analyze the slurry data as shown below:

The wall shear rate, □ sec^{-1} is given as[12]:

$$\gamma_w := 39.206 \cdot \frac{Q}{d^3} \quad (6)$$

Where Q is the flow rate, gal/min, d = internal diameter of the casing, inch

The wall shear stress, τ_w (lb/ft^2) is given as:

$$\tau_w := \frac{3 \cdot d \cdot \Delta P}{L} \quad (7)$$

Where ΔP is the pressure drop, psi, L is the depth of the well, ft;

A generalized Reynolds Number, N_{Reg}, Dimensionless variable can also be correlated with wall shear rate in the evaluation as follows:

$$N_{Reg} := \frac{928 \cdot \rho \cdot v \cdot d}{\mu_a} \quad (8)$$

Where, v is the average fluid velocity, ft/s; ρ = fluid density, lb_m/gal

Apparent fluid viscosity, cp can be calculated from

$$\mu_a := 47880 K_p \left(\gamma_w\right)^{n-1} \quad (9)$$

where K_p is the consistency index for pipe flow calculations, n is the flow behavior index. These rheology values can be obtained from tables.

The reaction mechanism as shown in figure 1 brought about phase change. Latent heat accompanies phase change with temperature change. This relates to other system properties by thermodynamic equation as follows:[13]

$$\Delta H = T \cdot \Delta V \cdot \frac{dP^{sat}}{dT} \quad (10)$$

Where ΔH is the latent heat, ΔV is the volume change accompanying phase change and P is the vapor pressure.

Table 1: TEST DATA DESIGN SHEET

TEST #		1	2	3	4	5
BHST	°F	106	105	80	80	86
BHCT	°F	86	85	70	70	75
BHP	psi	1200	1200	780	780	780
Heat Up Time	min	17	17	13	13	13
ADDITIVES						
Dyckerhoff cement	%BWOC	100	100	100	100	-
Calcium chloride liquid	**gal/sk**	**-**	**0.20**	**-**	**0.2**	**0.40**
Defoamer	gal/sk	0.02	0.02	0.02	0.02	0.01
Water Type		Sea	Sea	Sea	Sea	Sea
Chloride Content	ppm	17561	17312	17561	16390	17561
Water Requirement	gal/sk	5.2	5.06	5.2	5.06	5.21
Mixing Fluid	gal/sk	5.22	5.28	5.22	5.28	5.22
Yield	cu. ft/sk	1.17	1.18	1.17	1.18	1.17
Slurry Weight	lbs/gal	15.8	15.8	16	15.8	15.80
RESULTS						
Thickening Time						
30BC	hrs:min	**4:57**	**2:10**	**6:40**	**4:12**	**2.15**
50BC	hrs:min	**5:40**	**2:34**	**7:24**	**4:50**	**2.40**
70BC	hrs:min	**6:13**	**2:54**	**8:00**	**5:16**	**3:00**
Rheologies @ 80 °F						
300rpm	cP	48	50	52	44	34
200rpm	cP	39	40	43	39	30
100rpm	cP	31	31	33	31	24
6rpm	cP	16	17	17	17	15
3rpm	cP	12	12	13	14	13
PV	cP	25.5	28.5	28.5	19.5	15
YP	$Lbf/100ft^2$	22.5	21.5	23.5	24.5	19
Rheologies @ 86°F						
300rpm	cP	70	78	72	66	180
200rpm	cP	61	68	59	56	158
100rpm	cP	48	56	45	46	130
6rpm	cP	19	22	17	22	51
3rpm	cP	13	16	11	15	39
PV	cP	33	33	40.5	30	75
YP	$Lbf/100ft^2$	37	45	31.5	36	105
Compressive Strength						
Time to reach (hrs:mins)	50 psi	4:02	3:04	7:12	6:11	2:22
Time to reach (hrs:mins)	500 psi	6:25	5:04	12:05	9:44	5:29
12 Hours	psi	1538	2072	484	773	1437

12 Hours	psi	1538	2072	484		1437
24 Hours	psi	2948	3474	1736	1807	2789

DISCUSSION

Test–1 at 86°F (BHCT), was conducted with sea water alone without calcium chloride. Thickening time at 70 BC was 6:13 (Hrs: Min), time to reach 50psi was 4:02 (Hrs: Min), and time for 500psi was 6:25 (Hrs:Min) and 12 hrs and 24 hrs compressive strength were 1538psi and 2948psi respectively. However, Test– 2 at 85°F (BHCT), was conducted with sea water and 0.20 gal/sk calcium chloride. 70 BC was attained after 2:54 (Hrs: Min), 50psi at 3:04 (Hrs: Min), and 500psi was 5:04 (Hrs: Min) and 12 hrs and 24 hrs compressive strength were 2072psi and 3474psi respectively. This indicated enhanced response in terms of shortening the thickening time and early strength development.

Test - 3, 4 and 5 were conducted at lower temperatures. Test - 3 was done with sea water alone without calcium chloride while Test 4 and 5 were conducted with sea water and calcium chloride, with test 5 having higher concentration of calcium chloride (0.40 gal/sk) against (0.20 gal/sk) for test – 4. Same tendency of shorter thickening time and early strength development was evident with higher calcium chloride concentration. The rheology parameters for the cement slurry adopted from the Power Law can be used to determine pressure loss test. This should be taken as further evaluation of the cement slurry in subsequent studies.

At the University of Texas in Austin, David Fowler and his colleagues are studying concretes bound together by polymers instead of Portland cements. While such polymer concretes burn or loses their shape at high temperatures, they are stronger, more durable and more resistant to acids, salts and water than are Portland cements at room temperature. Moreover, they set remarkably quickly[14]. The thermodynamics relation of the evaluated parameters as shown in equation 10 could determine the effect of temperature on the performance of cement slurry at flow conditions. Further rigorous analysis of this equation is recommended as to ascertain the optimum temperature required for volume of cement slurry needed for a particular pumping pressure.

CONCLUSION

Cement slurry performance could be enhanced for low temperature wells by using sea water and calcium chloride.

The use of sea water and calcium chloride will help to shorten thickening time and give early strength development

The research finding will help add value to Operators in the Oil industry by saving cost arising from shorter thickening time and early strength development if they adopt slurry formulations with sea water and calcium chloride for low temperature wells.

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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 (°F/100ft) = (BHST – 80)/ TVD
   Where Gradient = Change in Temperature per given depth
   BHST = Bottom Hole Static Temperature in °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 Water = $\frac{\text{ml of Fluid} * 100\%}{250}$
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. psi = Pounds per square inch