RHEOLOGICALLY STABLE DELAYED-SET CEMENT SLURRIES: THEIR MODIFICATION AND ACTIVATION ON DEMAND

Ashok K. Santra, B.R. Reddy and Tony Aldrige
Halliburton Energy Services

SUMMARY

It can be beneficial to store generic cement slurries whose set times have been delayed for weeks, modify the bulk slurry properties (such as density), and activate them just prior to conducting a cementing job. Such technology offers distinct advantages in situations in which storage space is at a premium or bulk blending facilities are not located close to the jobsite.

Although this technology has been available for about two decades, its implementation has been plagued with problems involving slurry gelation during storage, settling, free water development, and unpredictable activation. This investigation discusses improvements to the compositions and processes that can render the technology amenable to implementation in a wide variety of applications. The slurries are designed to provide stable rheology up to four weeks by manipulating the particle size distributions. The versatility in slurry design to meet cementing requirements for a variety of well conditions will be demonstrated.

INTRODUCTION

Set-delayed cement compositions[1-6] are often used when an operator finds it desirable to prepare a volume of cement that will remain “pumpable” for a long period of time (e.g., two weeks or more) and that can be selectively activated to set into a hard mass at a desired time. Such a circumstance might include one in which very large volumes of cement are needed (such as in offshore platform grouting) and the equipment required for mixing and pumping the requisite large volumes is very expensive relative to the revenue generated from the cementing operation. Set-delayed compositions would be beneficial as well when a relatively small volume of cement composition is used, such as in small construction jobs or in plugging and squeezing operations.

Operations involving conventional set-delayed cement compositions may encounter a number of difficulties, including:

- A cement composition that thickens or gels with time, increasing the composition’s viscosity and thus impairing its pumpability.
- An activation process that becomes quite complicated, as exemplified by operations wherein the cement composition’s set time is delayed until shortly before use, after which it is over-activated and again retarded.
- The addition of set-activating agents that cause premature localized setting of the cement, e.g., localized regions within the bulk cement slurry wherein the set-activating agent becomes concentrated and causes premature setting of a portion of the bulk cement due to inadequate mixing. This premature, partial setting can lead to pumping problems such as hardened cement particles that damage pump impellers or setting of the bulk cement while it is contained in storage tanks.
- The performance of the set-activating agents commonly used to selectively activate the cement compositions may be unpredictable, causing problems such as (a) premature setting of the cement before placement (the activating agent imparts an unexpectedly strong activating effect), or (b) delayed setting of the cement after placement (the activating agent imparts an unexpectedly weak activating effect), both of which are undesirable.

This paper will discuss how a simplified approach can help overcome these problems.

RESULTS AND DISCUSSION

1. Adjusting the Particle Size Distribution

This approach has been very successful obtaining a steady rheological behavior over several weeks during the storage of delayed-set slurries. In general, conventional oilwell cements will have wider particle size distribution ranging from <5 to >200 microns. However, it is the relatively smaller sized particles (smaller than the mean size) that contribute more to rheological instability, especially over a prolonged time. Ideally, mono-dispersed particles (all same-sized) would be the best choice for controlling their physical and/or chemical properties uniformly and predictably. However, such systems are hardly a reality. In the current delayed set slurry designs, a cationic polymer was used to control the particle size distribution by narrowing it down to improve long-term rheological stability. Figure 1 and Table 1 show the typical particle size distribution for neat Class H cement before and after exposure to the cationic polymer. It is clear from Figure 1, as well as the spread value ("span") in Table 1, that indeed the distribution envelope moves to the right due to the formation of newer, larger particles at the expense of the original smaller particles.

2. Slurry Design

Essential components of the delayed-set slurries are:

- API-class cement
- Water
- Particle size-adjusting agent
- Dispersant
- Suspending aid
- Retarder

Tables 2–4 show some typical slurry designs. In addition, fluid loss control additive, strength retrogression prevention additive, weighting agent or extender, gas migration control additive, etc. can be added to the design as needed. It is also important to note that a suitable mixing sequence has been found to provide superior rheological stability and longer shelf life to these slurries.

3. Rheological Stability

This is one of the most important properties of the delayed-set slurries during their storage period. Figure 2 and Tables 5–6 show typical rheological behavior over entire shelf lives for slurry Designs 1, 2, and 3 respectively. As seen in Figure 2 and Tables 2 and 3, slurries exhibit relatively high viscosity in the first 2–3 days, after which, the viscosity decreases to a more stable state and remains stable until it rises again toward the end of the slurry's shelf life. This early-stage behavior (thinning of viscosity) was observed for a number of slurry designs and is probably due to the time needed for all the chemical interactions to reach an equilibrium, or steady state. Note that all the slurries were subjected to intermittent stirring during storage (once every two days, or more frequently in the beginning and less frequently later, etc.).

4. Activation Process

Various methods were employed for activating the delayed-set slurries in a predictable manner, depending on the (1) stored slurry density, (2) age of the slurry, (3) required slurry density for final placement, and (4) bottomhole circulating temperature (BHCT)/bottomhole static temperature (BHST). Activation methods may have included (a) thermal activation, (b) retardation, and (c) chemical activation. It is important to mention that the stored slurry density must be designed to be higher than that for the final slurry to be pumped downhole. This design provides an opportunity to add extra water with the chemical activator, retarder, or other additives for slurry property control at this stage. This extra water acts as a carrier fluid and can also (a) function as a diluent for even liquid additives, (b) help aid uniform mixing of additives, and (c) minimize localized activation or the formation of hot spots.

Depending on BHCT, typical activation procedures for Slurries 1 and 2 were as shown:

BHCT ≥ 230°F activation

- Depending on BHCT, no activator may be needed for 2–4 hr thickening time
- Conventional retarders may be used in amounts necessary to obtain longer thickening times

BHCT = 230°F activation

- No activator may be needed for 15.8-ppg slurry after diluting stored slurry with water
- 1-gal/sk Silica fume suspension added to obtain 15.0-ppg slurry

BHCT ≤ 190°F activation

- 2-gal/sk Fumed silica suspension + necessary $CaCl_2$ liquid added for 15.0-ppg slurry to activate at 120°F

In Slurry 3, chemical activation was achieved by adding an aqueous solution containing a synergistic combination of an alkanolamine and NaOH in a proper ratio. Figure 3 shows the dependence of thickening time as a function of added NaOH concentration when a constant amount of an alkanolamine (0.07% bwoc) was used. In each case, the final slurry density after adding activators was adjusted to 16.4 ppg and the thickening times were measured at 190°F BHCT and 3,000-psi bottomhole pressure. Interestingly, the plot in Figure 3 shows excellent linear dependence on sodium hydroxide concentration for thickening time adjustment.

5. Compressive Strength Development

Obtaining the desired compressive strength at a desired rate is another key criterion for judging a good delayed-set slurry. Tables 7–8 show compressive strength values obtained for Slurries 2 and 3 respectively at different curing temperatures.

CONCLUSIONS AND RECOMMENDATIONS

Based on this investigation, the following conclusions can be drawn:

- It is possible to design rheologically stable, delayed-set cement slurries by suitably adjusting the particle size distribution of the cement. This method produces slurries that are rheologically stable for 2–3 weeks.
- By designing a slurry density for storage that is higher than the desired slurry placement density and by adding additives as aqueous solutions or organic suspensions at the time of pumping, any problems due to localized activation because of inhomogeneous mixing of activators can be avoided.
- It was also shown that by using either thermal or chemical methods, the delayed-set slurries could be successfully activated over a wide range of BHCT in a single, simple step.
- Good strength development rates and final strength values can be obtained upon activation.
- When using delayed-set slurries, it is possible to prepare pumpable slurries at various densities by adding a suitable density modifier (heavy- or light-weight additive).
- It is strongly recommended that a specific mixing sequence be used for obtaining desired long-term rheological stability of the delayed-set slurries.

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ACKNOWLEDGEMENTS

The authors would like to thank Halliburton management for their support and permission to present this paper.

Table 1
Particle Size Distribution

Indicated Particle Size (microns)	Individual Volume Percent of Particles Having Indicated Particle Size	
	Neat Cement Class H	Cement Class H after Exposure to Particle Size Adjuster
0.667	0.37	0.21
1.04	0.43	0.25
2.05	0.31	0.15
2.98	0.5	0.21
4.02	0.82	0.37
5.03	1.1	0.57
6.78	1.46	0.92
9.86	1.85	1.43
10.62	1.92	1.53
20.84	2.65	2.35
30.29	2.99	2.91
40.86	2.98	3.52
51.15	2.61	3.86
59.41	2.19	3.68
69	1.7	3.18
74.36	1.44	2.82
86.36	0.96	2.02
93.07	0.74	1.59
100.3	0.56	1.25
Median Size	26.35 micron	35.79 micron
Span	2.72 micron	2.38 micron

Table 2
Slurry Design 1 (Density 16.2 ppg)

Material	Amount	Unit
Water	40.36%	bwoc
Cement-G	100%	bwoc
Suspending aid	0.27%	bwoc
Dispersant	0.20%	bwoc
Retarder	1.50%	bwoc
Particle size adjuster	0.38%	bwoc

Table 3

Slurry Design 2 (Density 16.2 ppg)

Material	Amount	Unit
Water	51.50%	bwoc
Cement-G	100%	bwoc
Silica flour	40%	bwoc
Suspending aid	0.27%	bwoc
Dispersant	0.20%	bwoc
Retarder	0.75%	bwoc
Particle size adjuster	0.38%	bwoc

Table 4

Slurry Design 3 (Density 17 ppg)

Material	Amount	Unit
Water	34.20%	bwoc
Cement-H	100%	bwoc
Suspending aid	0.27%	bwoc
Dispersant	0.10%	bwoc
Retarder	0.93%	bwoc
Particle size adjuster	0.23%	bwoc

Table 5

Rheology Behavior for Slurry 2 (Density 16.2 ppg)

Days	**Fann 35 Rheometer Settings (RPM)**					
	600	**300**	**200**	**100**	**6**	**3**
4	112	77	56	34	10	8
7	98	76	52	34	13	11
10	130	90	69	47	21	17
14	237	158	138	117	33	29

Table 6

Rheology Behavior for Slurry 3 (Density 17.0 ppg)

Days	**Fann 35 Rheometer Settings (RPM)**					
	600	**300**	**200**	**100**	**6**	**3**
0	346	200	146	80	26	20
1	440	240	170	96	16	10
3	430	236	164	94	14	8
6	414	228	164	92	14	8
8	410	230	164	94	14	8
9	430	246	170	100	16	10
10	444	250	180	116	18	12
12	450	253	184	116	18	12

Table 7
Compressive Strength for Slurry 2

Temperature	**Final Density**	**Compressive Strength (psi)**			
	(ppg)	**12 hr**	**24 hr**	**48 hr**	**72 hr**
230°F	15.8	1,000	1,795	2,500	2,540
230°F	15.0	1,372	1,994	2,200	2,300
120°F	15.5	1,025	1,826	2,550	2,800

Table 8
Compressive Strength for Slurry 3 (Final Density: 16.4 ppg)

Activators		**24-hr Compressive Strength at 190°F and 3,000 psi**
TEA % bwoc	**NaOH % bwoc**	
0.07	0.75	4,750 psi

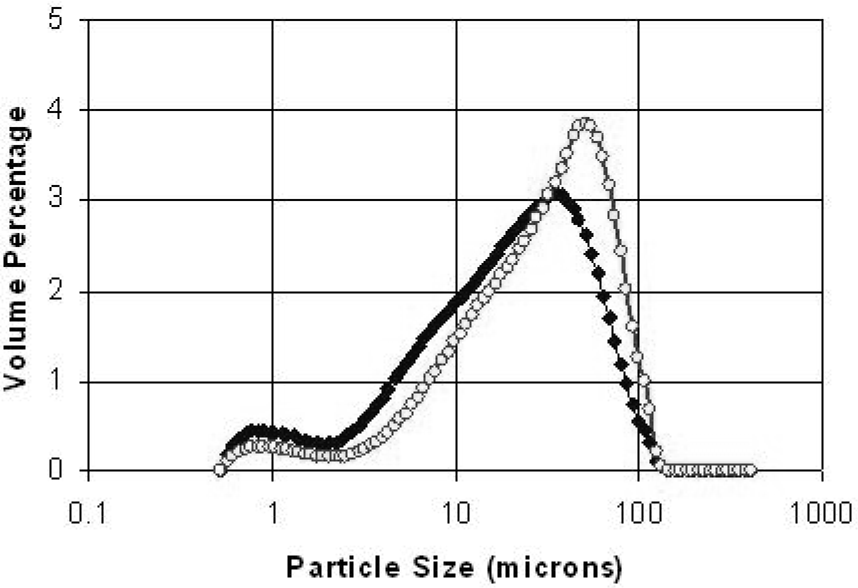

Figure 1 - AbsoluteVvolume; % as Function of Particle Size

◆- Neat Class H
○ - Particle-adjusted Class H

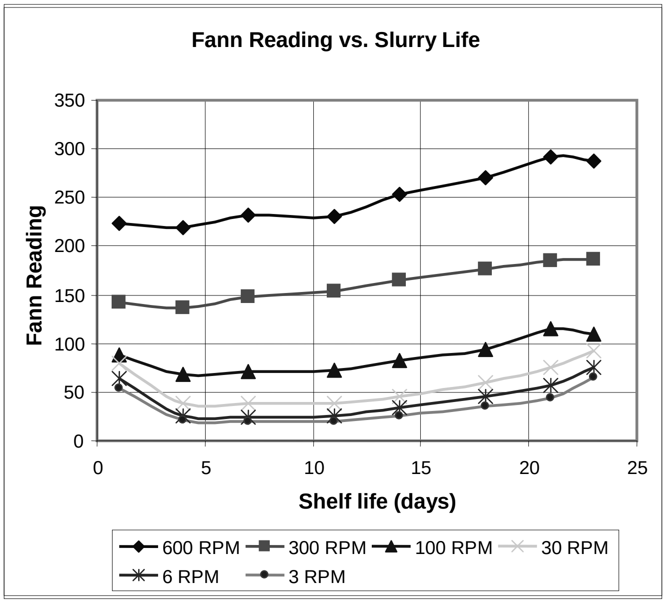

Figure 2 - Rheology Behavior for Slurry 1; Density = 16.2 ppg

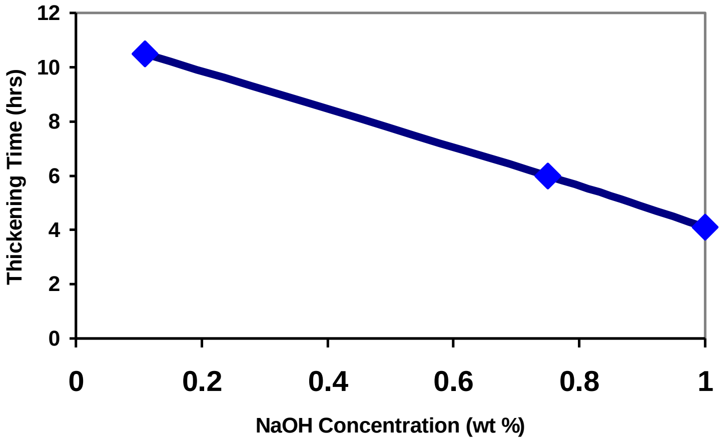

Figure 3 - Thickening Time as Function of %NaOH (at 190°F and 3,000 psi)