AN INVESTIGATION OF THE STATIC-STATE PROPERTIES OF RIGHT-ANGLE-SET CEMENTS

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ABSTRACT

In recent years, the cementing industry has embraced the concept of *right-angle-set* as a desirable feature in the thickening time set profile of oilwell cements. Right-angle-set can be characterized as the rapid thickening of a cement slurry from a stabilized viscosity to a final set of 70-100 Bearden Units of Consistency (Bc). This is a *dynamic-state* phenomenon that usually takes place in the final 30-45 minutes of thickening time. Cement slurries exhibiting right-angle-set thickening time profiles were generally thought of as being preferable over slower "gel" type sets.

However, within the practicalities of field operations, rarely is the cement still being placed while right-angle-set is occurring. More commonly, the cement slurry is mixed and displaced in only a fraction of the designed thickening time. How then does right-angle-set, a *dynamic-state* event late in the pumping history of the slurry, influence the *static-state* properties of the slurry, when placement is completed before the onset of right-angle-set?

Presented are the results of conventional, low shear, and modified-hesitation-squeeze thickening time testing, combined with operating ultrasonic strength analysis, to quantify the differences in right-angle-set slurries as compared to cement designs with slower setting profiles.

INTRODUCTION

How the dynamic viscosity history of a cement slurry influences the physical properties of the cement under static conditions has been a matter of scientific inquiry for a number of years. Investigations into annular gas flow, successful primary cementing, and cement slurry design all took into account possible effects of slurry viscosity history on in-situ cement properties.[1-3]

Additive systems that promoted a rapid transition of a cement slurry from a fully hydraulic fluid to a semi-solid mass with enough gel strength to prevent fluid flow were viewed as a viable means of controlling annular gas. It was suggested[1] that the cement would remain fully fluid (with minimal gel strength) allowing for the full hydrostatic pressure of the column to be transmitted to the gas bearing formation. Once the cement did begin to set, it would do so rapidly as to gain gel strength as quickly as possible. Lowering the time of transition as the cement evolves from a fully hydraulic fluid to a high gel-strength solid would limit its susceptibility to annular gas flow.[1,2] Most of the systems or techniques described also included the use of fluid loss control agents and slurry designs with low free water.

The interrelationship of a cement slurry's viscosity history during thickening time and the subsequent compressive strength development was defined by Hartog et al.[3] in 1983. Their investigation measured the 72-hour compressive strengths of a slurry removed from a consistometer after different shearing periods and at different slurry consistencies. It was shown that the pumping of a "thickened cement" negatively impacts compressive strength development. As a result of their findings, it was recommended that the practical limit of cement "pumpability time" be measured as the time to 40 Bc.

For many field cementing applications, the designed thickening time of the cement falls within the range of 3 - 4 1/2 hours. However, these recommended thickening times are often made without consideration for the actual time needed to mix and displace the cement. More often than not, the slurry is in place well before the cement has reached 40 Bc.

CEMENT VISCOSITY HISTORY

Under normal conditions, a cement slurry reaches a stabilized viscosity shortly after initial placement on the consistometer or once the final temperature and pressure conditions have been reached. The stabilized viscosity is very much dependent on the type of cement, the water content of the slurry, and additive chemistry. The viscosity of a cement then increases with time to 70-100 Bc, a point at which the cement is considered unpumpable.

The viscosity profile of a cement slurry during the course of its thickening time is variable. Certain cement systems exhibit a low viscosity for the majority of their pumping history. As the time of final set approaches, a very rapid increase in consistency from stabilized viscosity to final set occurs in a 30-45 minute time frame. These slurries are said to possess right-angle-set. Other cements have a slower transition from initial (or stabilized) viscosity to final set. The transition time of these cements can range from 45-90 minutes depending on the slurry composition and test temperature. Such slurries are classified as having "gel-type" sets.[2]

CEMENT CHEMISTRY OVERVIEW

The principal components of Portland cement include dicalcium silicate (C_2S), tricalcium silicate (C_3S), tricalcium aluminate (C_3A), and tetracalcium alumino-ferrite (C_4AF). While the hydration of C_3S is often used as a model of Portland cement hydration[4], the C_2S, C_3S, and C_3A phases all have a role in the sequence of hydration events that impact the setting process.

Upon contact with water the C_2S and C_3S react to form calcium silicate hydrate (CSH) gel. The initial surge of reactivity is associated with a large evolution of heat due to the hydration of free lime (CaO).[5] The CSH is coated with a protective, semi-permeable layer which then inhibits further external reactions but allows internal reactions to take place. Having had its external reactivity limited, the cement then goes through a dormant or "induction" phase. The C_3A also enters into the reaction, forming a calcium sulphoaluminate hydrate known as ettringite. Crystals of ettringite coat the C_3A surfaces, minimizing further reactions until the gypsum present in the system is consumed. The ettringite than converts to various calcium aluminate hydrates.[4]

Osmotic pressures within the CSH, the result of the internal reactions, continue to build until the CSH membrane is ruptured. The materials released into the system include $Ca(OH)_2$ and tubular growths of CSH called "fibrils", which form an interlocking network with the other hydration products.[5]

The scenario outlined above is a generalized statement of a very complex chemical reaction. Yet, it can be stated that the viscosity history of a cement slurry is influenced predominantly by the C_3S and C_3A phases. The viscosification that is observed during the course of the thickening time (as portrayed on a consistometer) is the result of the interlocking effect of the hydration products that are consuming and immobilizing internal water. How quickly the viscosification to final set occurs is influenced by the temperature under which the reaction occurs and by additive chemistry. It is thought that certain cement additives may change the micro-structure of the CSH membrane, allowing for an increased amount of internal osmotic pressure to build up during the induction phase of the CSH. A higher release pressure as the reaction product is expelled from the ruptured CSH membrane would create a more extensive network of CSH fibrils over a shorter period of time.

TEST PARAMETERS AND RESULTS

The slurry designs, procedures, and test conditions used in the evaluation of the static-state properties of right-angle-set cements are as follows:

COMPARISON #1

<u>Slurry A:</u> <u>Class H + 0.5% Fluid Loss Additive + 0.5% Dispersant + 40.5% H_2O @ 16.2 Lbm/gal</u>

Fluid Loss at 118°F	:	**68 cm³/30 min**
Rheologies at 118°F	:	**600/128 300/71 200/49** **100/27 6/2.5 3/1.5**
Thickening Time at 118°F (Schedule 4g6, Figure 1)		**3 hrs : 40 min @ 6 Bc** **4 hrs : 00 min to 40 Bc** **4 hrs : 02 min to 70 Bc** **4 hrs : 04 min to 100 Bc**

UCA Compressive Strengths: at 170°F (Operating) — **50 psi in 3 hrs : 58 min**
500 psi in 4 hrs : 50 min
2510 psi in 24 hrs : 00 min

Slurry B: **Class H + 0.2% lignosulfonate retarder + 40.5% H_2O @ 16.2 Lbm/gal**

Fluid Loss at 118°F :	**1000+ cm^3/30 min**
Rheologies at 118°F :	**600/89 300/67 200/58** **100/49 6/15 3/13**
Thickening Time at 118°F (Schedule 4g6, Figure 2)	**3 hrs : 38 min @ 9 Bc** **4 hrs : 07 min to 40 Bc** **4 hrs : 21 min to 70 Bc** **4 hrs : 33 min to 100 Bc**
UCA Compressive strengths at 170°F (Operating)	**50 psi in 1 hr : 45 min** **500 psi in 2 hrs : 42 min** **2775 psi in 24 hrs : 00 min**

TEST PROCEDURES

The compressive strength tests were performed under operating conditions. The samples were prepared as per API Spec. 10[6], placed in a pressurized consistometer, ramped from 80°F to 118°F and 750 to 3900 psi in 20 minutes. After a total time of 2 1/2 hrs (150 min) the sample was removed, placed in a preheated (118°F) UCA cell, and ramped to 170°F in 2 hrs. Curing pressure was 3000 psi.

For the modified-hesitation-squeeze thickening time testing, the slurries were prepared as per API Spec. 10, placed in a pressurized consistometer, ramped from 80 to 118°F and 750 to 3900 psi in 20 minutes. After a total time of 2 1/2 hours (150 min), the motor is turned off for 10 minutes followed by a five-minute on-period. This on-off cycle continues until 100 Bc is reached. Fluid loss and rheological testing were performed as per API.

DISCUSSION OF SLURRY A AND B TEST RESULTS

In this test a slurry featuring right-angle-set is compared to a slurry with a slower setting profile. Slurry A is a Class H cement containing a commonly available fluid loss additive and a standard polynapthalene sulfonate dispersant. The slurry has a 24-minute transition time from a stabilized viscosity to 100 Bc (Figure 1). Slurry B uses the same Class H cement and a lignosulfonate-type retarder to match the thickening time of Slurry A and has a 55-minute transition from a stabilized viscosity to 100 Bc (Figure 2).

As indicated by the test results, when the two slurries are tested on a UCA for compressive strength, after a 2 1/2-hour simulated placement time on a pressurized consistometer, the early strength development of Slurry B proceeds more quickly than that of Slurry A. Slurry B required 1 hour:45 minutes and 2 hours:42 minutes to reach 50 and 500 psi, respectively. Slurry A, however, needed 3 hours:58 minutes to obtain 50 psi and 4 hours:50 minutes to reach 500 psi.

These findings suggest that if cement placement is completed while the slurry is still at a stabilized viscosity level, then early compressive strength development is primarily dependent on slurry composition and independent of the thickening time set profile. Sabins and Sutton[7] reached a broader, yet similar conclusion showing that compressive strength development does not directly relate to the thickening time. (For slurries with thickening times ranging from 3-8 hours).

Modified-hesitation-squeeze thickening time testing was used to simulate the buildup of gel forces of a static cement slurry. The evaluation of Slurries A and B show that after a 2 1/2-hour simulated (dynamic) placement time, the "signature" of the increase in Bearden units of consistency for the two slurries during the on-off cycles is virtually identical (Figures 3 and 4). Both slurries went through eight on-off cycles before reaching 100 Bc. Again, this indicates that the duration and shape of the original thickening time set profile is a dynamic-state event that does not influence the buildup of gel forces (and ultimately compressive strength), once the cement is static.

The effects of shear rate on thickening time profile was also investigated. Figures 5 and 6 show thickening time tests of Slurry A and B that were conducted according to schedule 4g6, but at 75 RPM instead of the standard 150 RPM. The results of the experiment indicates that for the tested slurries and conditions, the set profiles found at 75 RPM bear a close resemblance to those found at 150 RPM with only minor differences in thickening time and set profile.

COMPARISON #2

Slurry C: **Class G + 44% H_2O @ 15.8 Lbm/gal**

Fluid Loss at 100°F	:	**1000+ cm^3/30 min**
Rheologies at 100°F	:	**600/105 300/75 200/66** **100/54 6/17 3/11**

Thickening Time at 100°F (Schedule 3g4, Figure 7)	**1 hrs : 45 min @ 12Bc** **2 hrs : 56 min to 40 Bc** **4 hrs : 05 min to 70 Bc** **4 hrs : 28 min to 100 Bc**
UCA Compressive Strengths at 124°F (Operating)	**50 psi in 1 hr : 05 min** **500 psi in 3 hrs : 13 min** **2180 psi in 24 hrs : 00 min**

Slurry D: **Class G + 1.5 GPS SBR Latex + 0.5% Dispersant + 44% Total Liquid @ 15.8 Lbm/gal**

Fluid Loss at 100°F	:	**106 cm^3/30 min**
Rheologies at 100°F	:	**600/65 300/31 200/22** **100/12 6/2 3/1**
Thickening Time at 100°F (Schedule 3g4, Figure 8)		**3 hrs : 20 min at 8 Bc** **3 hrs : 35 min to 40 Bc** **3 hrs : 54 min to 70 Bc** **4 hrs : 02 min to 100 Bc**
UCA Compressive Strengths at 124°F (Operating)		**50 psi in 2 hrs : 37 min** **500 psi in 3 hrs : 48 min** **2595 psi in 24 hrs : 00 min**

TEST PROCEDURES

The compressive strength tests were performed under operating conditions. The samples were prepared as per API Spec. 10, placed in a pressurized consistometer, ramped from 80°F to 100°F and 500 to 2600 psi in 14 minutes. After a total time of 1 3/4 hrs (105 min), the sample was removed, placed in a preheated (100°F) UCA cell, and ramped to 124°F in 2 hrs. Curing pressure was 3000 psi.

For the modified-hesitation-squeeze thickening time testing, the slurries were prepared as per API, placed in a pressurized consistometer, ramped from 80°F to 100°F and 500 to 2600 psi in 14 minutes. After a total time of 1 3/4 hours (105 min), the motor is turned off for 10 minutes followed by a five-minute on-period. The on-off cycles continue until 100 Bc is reached. Fluid loss and rheological testing were performed according to API procedures.

DISCUSSION OF SLURRY C AND D TEST RESULTS

In this comparison, two Class G-based systems were evaluated. Slurry C is a neat API Class G slurry, while Slurry D is the same Class G containing a styrene-butadiene resin latex (SBR) and dispersant. Conventional thickening time testing of the two slurries showed that the neat Class G cement (Slurry C) had a 2-hour:43-minute transition time from a stabilized viscosity of 12 Bc to a final set of 100 Bc (Figure 7). Slurry D, the latex-modified slurry, had a 42-minute transition time under similar conditions (Figure 8). While a 42-minute transition time from stabilized viscosity to final set is only marginally "right-angle", it is still two hours less transition time than the same cement without the latex and dispersant.

Operating compressive strengths, as determined by UCA, indicates that the neat Class G (Slurry C) requires only 1 hour:5 minutes to achieve 50 psi after a simulated (dynamic) placement time of 1 hour:45 minutes. Under the same conditions, the latex cement (Slurry D) took 2 hours:37 minutes to gain 50 psi compressive strength. The time to 500 psi was 3 hours:13 minutes for the neat Class G and 3 hours:48 minutes for the latex cement. The 24-hour compressive strengths were 2180 psi and 2595 psi for Slurries C and D, respectively. As in the case for the Class H cements, when slurry placement is completed while the Class G slurries are still at a stabilized viscosity, then the early compressive strength development is a function of slurry composition and independent of thickening time set profile.

The modified-hesitation-squeeze thickening time profiles of the two Class G slurries are represented in Figures 9 and 10. As found in the testing of the Class H systems, the two Class G slurries have viscosity "signatures" that are very much alike. The neat Class G required four on-off cycles to obtain 100 Bc consistency, and the latex cement took five on-off cycles to reach 100 Bc. Even though the two slurries have very different thickening time profiles, once the cement is static, the buildup of gel forces proceeds at a similar rate.

This reinforces the notion that dynamic-state properties, such as right-angle-set, do not impact the development of static-state properties, once the cement is quiescent.

CONCLUSIONS

Under the stated test conditions and slurry compositions, the following conclusions can be made.

1. When cement placement is completed while the slurry is still at a stabilized viscosity, then early compressive strength development is primarily dependent on slurry composition and independent of the original thickening time set profile.

2. Modified-hesitation-squeeze thickening time testing shows that the "signature" of the increase in Bearden units of consistency during the on-off cycles is independent of

original thickening time set profile. The duration and shape of the thickening time set profile is a dynamic-state event that does not influence the buildup of gel forces once the slurry is in place.

3. Thickening time set profiles found at 75 RPM consistometer speed bear close resemblance to those found at 150 RPM.

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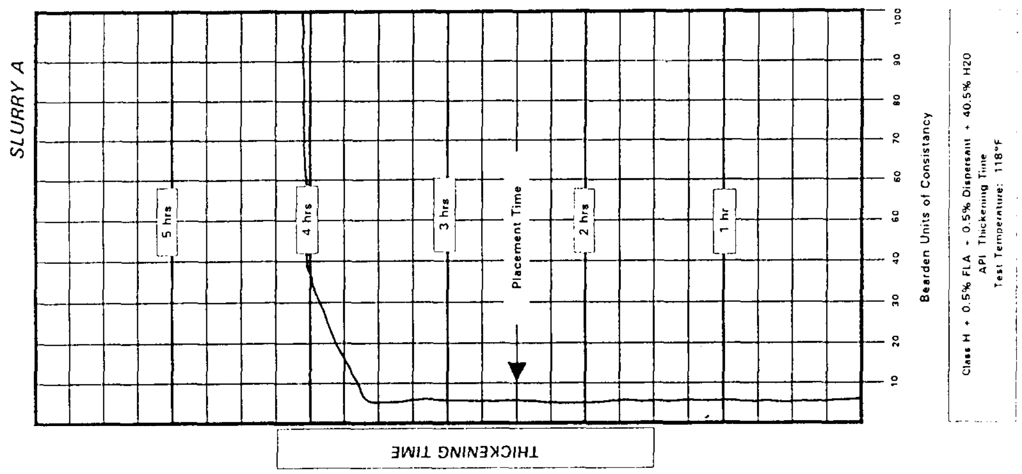
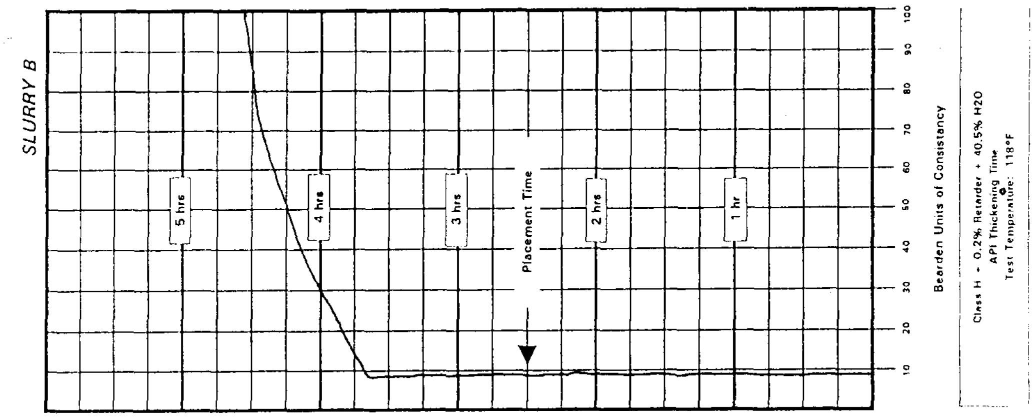


Figure 1



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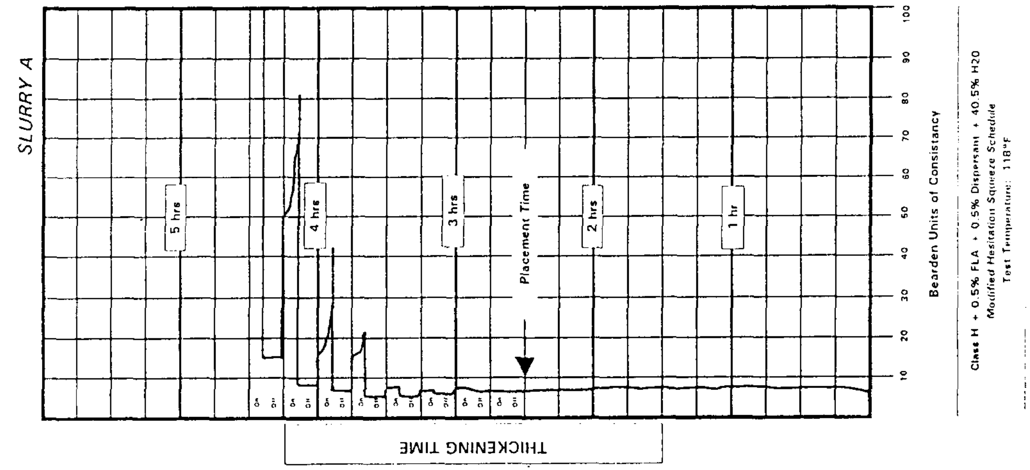

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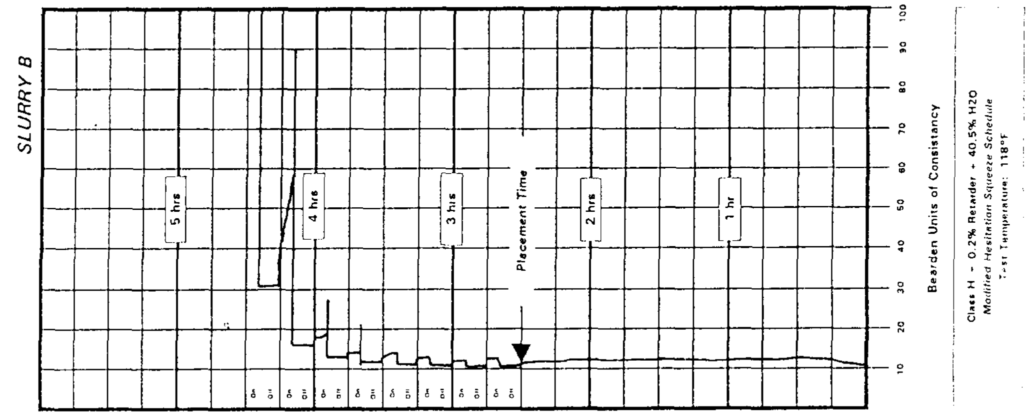

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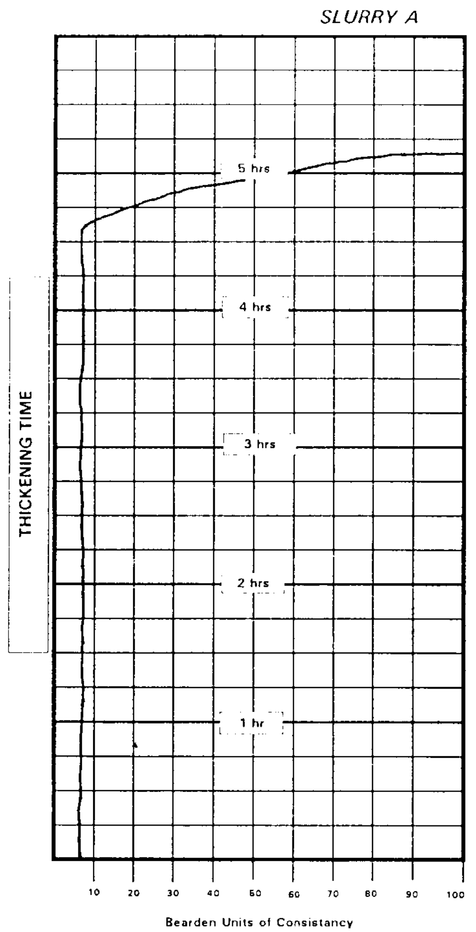
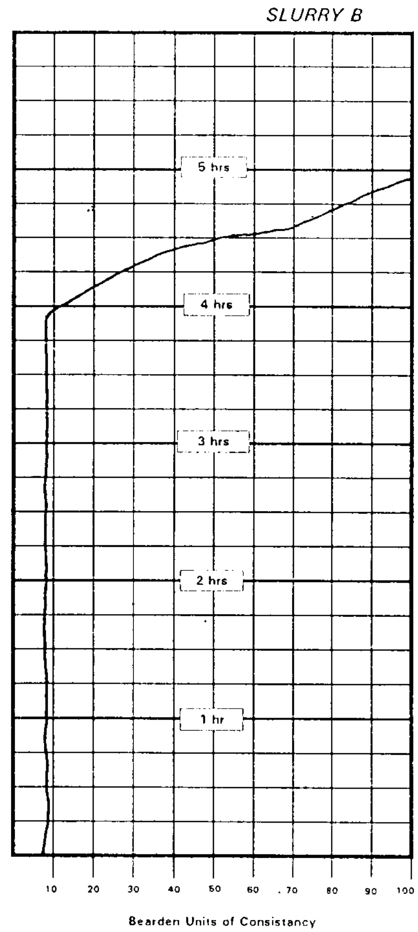


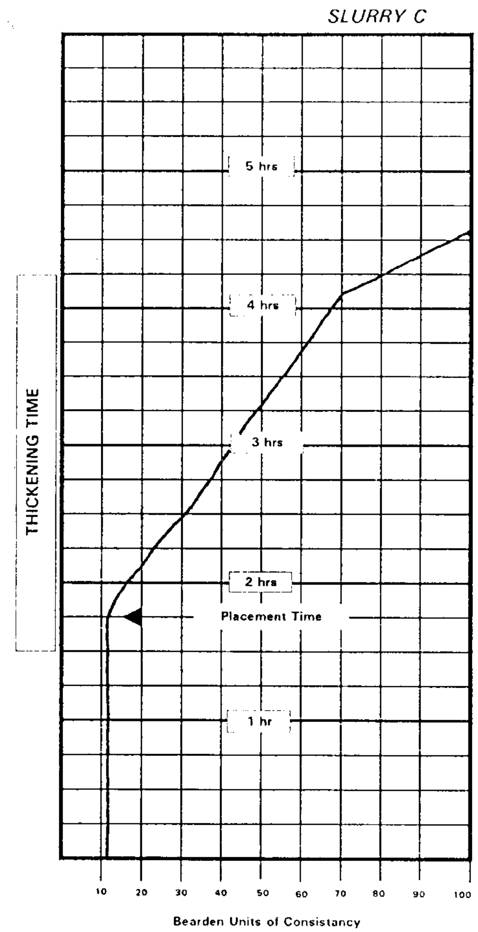
Class H + 0.5% FLA + 0.5% Dispersant + 40.5% H20
75 RPM Thickening Time
Test Temperature: 118°F

Figure 5



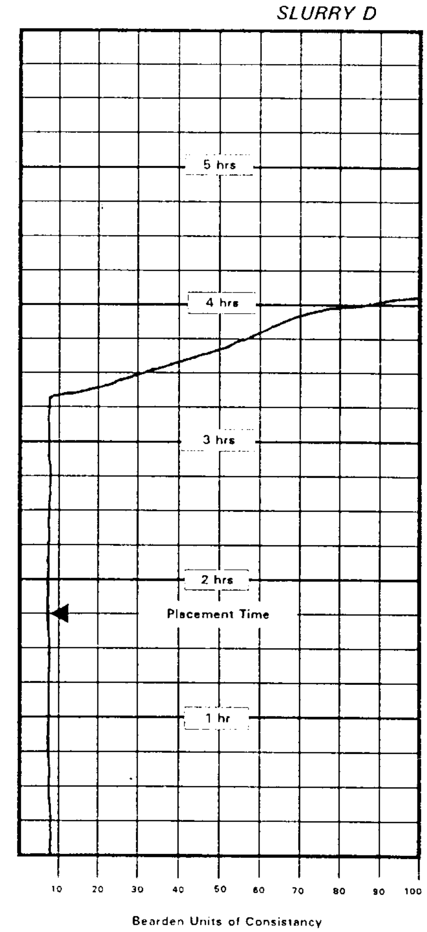
Class H + 0.2% Retarder + 40.5% H20
75 RPM Thickening Time
Test Temperature: 118°F

Figure 6



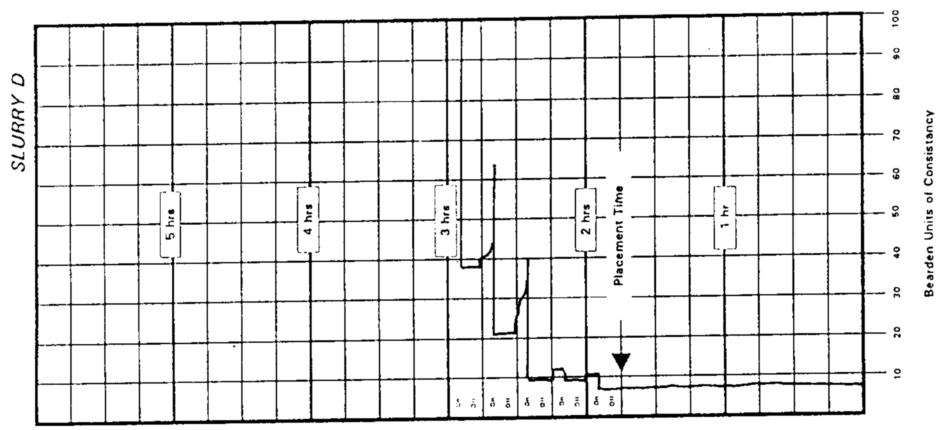
Class G + 44% H20
API Thickening Time
Test Temperature: 100°F

Figure 7



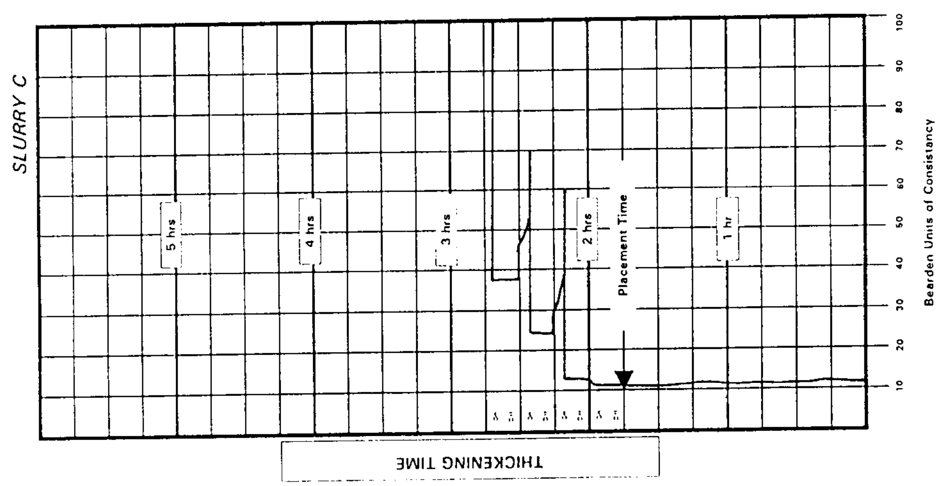
Class G + 1.5% G. S SBR Latex + 0.5% Disperant
+ 44% Total Liquid
API Thickening Time
Test Temperature: 100°F

Figure 8



Class G + 1.5% GPS SBR Latex + 0.5% Dispersant + 44% Liquid
Modified Hesitation Squeeze Schedule
Test Temperature: 100°F

Figure 10



Class G + 44% H2O
Modified Hesitation Squeeze Schedule
Test Temperature: 100°F

Figure 9