

Ultra-Lightweight Cement

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1.0 Abstract

The objective of this project is to develop an improved ultra-lightweight cement using ultralight hollow glass spheres (ULHS). Work reported herein addresses Task 1: Assess Ultra-Lightweight Cementing Problems, Task 2: Review Russian Ultra-Lightweight Cement Literature, and Task 3: Test Ultra-Lightweight Cements. Results reported this quarter include a review and summary surface pipe and intermediate casing cementing conditions historically encountered in the United States and establishment of average design conditions for ULHS cements. Russian literature concerning development and use of ultra-lightweight cements employing either nitrogen or ULHS was reviewed, and a summary is presented. Quality control testing of materials used to formulate ULHS cements in the laboratory was conducted to establish baseline material performance standards. A testing protocol was developed employing standard procedures as well as procedures tailored to evaluate ULHS. This protocol is presented and discussed. Finally, results of initial testing of ULHS cements is presented along with analysis to establish cement performance design criteria to be used during the remainder of the project.

2.0 Table of Contents

Disclaimer

1.0 Abstract

2.0 Table of contents

3.0 List of graphical materials

4.0 Introduction

5.0 Executive summary

6.0 Experimental

7.0 Results and discussion

8.0 Conclusions

9.0 References

10.0 List of acronyms and abbreviations

11.0 Appendices

3.0 List of Graphical Materials

3.1 Tables

Table 7.1	Summary of casing conditions in USA
Table 7.2	Cement physical requirements for quality-control testing program
Table 7.3	Percent calcium chloride for low-temperature compressive strengths
Table 7.4	Quality-control testing of cements
Table 7.5	Glass bead specifications
Table 7.6	3000 psi ULHS with Class A cement at 13.0 lb/gal
Table 7.7	3000 psi ULHS with Class A cement at 10.0 lb/gal
Table 7.8	3000 psi ULHS with lightweight cement at 11.5 lb/gal
Table 7.9	3000 psi ULHS with lightweight cement at 10.0 lb/gal
Table 7.10	3000 psi ULHS with Class A cement + 1.0% dispersant at 13.0 lb/gal
Table 7.11	3000 psi ULHS with Class A cement + 1.0% dispersant at 10.0 lb/gal
Table 7.12	3000 psi ULHS with lightweight cement + 1.0% dispersant at 10.0 lb/gal
Table 7.13	Ascending and descending viscometer readings
Table 11.1.1	Mixing procedures of cement and glass beads
Table 11.1.2	Stability test procedures
Table 11.1.3	Calculations for determining density difference due to separation
Table 11.1.4	Density determination using a Pycnometer
Table 11.1.5	Procedure for determining effects of pressure on collapse of glass beads
Table 11.2.1	Surface casing parameters
Table 11.2.2	Intermediate casing parameters

3.2 Figures

- Figure 1 Rheology of cements outlined in Table 7.9. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 2 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.9. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 3 Density changes of cements outlined in Table 7.9
- Figure 4 Rheology of cements outlined in Table 7.10. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 5 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.10. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 6 Density changes of cements outlined in Table 7.10
- Figure 7 Rheology of cements outlined in Table 7.11. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 8 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.11
- Figure 9 Density changes of cements outlined in Table 7.11
- Figure 10 Rheology of cements outlined in Table 7.12. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 11 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.12. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 12 Density changes of cements outlined in Table 7.12
- Figure 13 Rheology of cements outlined in Table 7.13. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 14 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.13. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 15 Density changes of cements outlined in Table 7.13
- Figure 16 Rheology of cements outlined in Table 7.14. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

- Figure 17 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.14. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 18 Density changes of cements outlined in Table 7.14
- Figure 19 Rheology of cements outlined in Table 7.15. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 20 300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.15. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.
- Figure 21 Density changes of cements outlined in Table 7.15
- Figure 22 Effect of high-shear mixing on ULHS cement density
- Figure 23 3,000 psi ULHS specific gravity vs. pressure
- Figure 24 6,000 psi ULHS specific gravity vs. pressure
- Figure 25 10,000 psi ULHS specific gravity vs. pressure

4.0 Introduction

Oilwell cementing involves placing a pumpable slurry of Portland cement, additives, and water into a well bore. The slurry is pumped into the annular space between the borehole and a steel pipe, called a casing, intended to produce a conduit from the reservoir to the surface. The cement sets in place to support the casing in the hole, isolate various formations from one another, and to control fluid movement within the well.

Normal cement fluid density ranges from 14 to 17 lb/gal. Certain conditions can be encountered during the well construction process that necessitate application of cements with much lower density. Lower density is required to limit hydrostatic pressure exerted on formations through which the well bore passes in order to prevent the formation from fracturing and imbibing the well fluid. This phenomenon, named lost circulation, increases time to drill and complete the well and increases construction cost due to expensive remedial treatments. Most common sections of a well in which lost circulation occurs are the upper sections: surface casings and intermediate casings. Since formations covered by these casings are relatively close to the Earth's surface, application temperatures for these low-density cements are relatively low.

The minimum density achievable with conventional cements and additives is roughly 11 lb/gal. At this density, the stability of the slurry and strength of the set cement are only marginally acceptable. The primary density-reducing material in these conventional cements is water. Additional water dilutes the cement, causing low strength. Lower temperature further decreases strength development. Achieving density requirements lower than this threshold or strength requirements greater than minimum necessitate use of ultra-lightweight materials mixed into the slurry.

Ultra-lightweight hollow spheres (ULHS) are excellent as candidate material for producing ultra-lightweight cements. These small, hollow, glass beads effectively encapsulate air in the slurry, thereby lowering the slurry density significantly compared to the addition of water to the slurry.

This project is designed to develop cementing systems using ULHS. The development will be achieved through a carefully designed program of modeling, design, laboratory testing, and field testing.

This phase of the project involves evaluation of conditions requiring ultra-lightweight cement, review of previous investigations conducted in Russia, and preliminary laboratory design testing.

5.0 Executive Summary

The initial laboratory phase of this investigation focused on establishment of test parameters and quality-control procedures. Standard test procedures employed for oilwell cement testing will not always work for ULHS cements. For instance, the high shear delivered by a Waring Blender can physically damage a portion of the spheres, thereby

altering the density from the design requirement. Additionally, the ULHS are subject to failure with application of hydraulic pressure. Therefore, the density of a cement slurry containing ULHS will vary with pressure application. Therefore, test procedures must be modified to avoid or account for this breakage.

Testing methods for mixing without subjecting the ULHS to high shear were developed and evaluated. Additionally, a method of exposing the cement slurries to hydraulic pressure was developed in order to establish specific gravity vs. pressure correlations for the various grades of ULHS.

A project of this magnitude and duration requires a large volume of cement and additives to complete. During the course of the project, several batches of material will probably be utilized in the testing. This requires an extensive material classification and quality control process. Such a process has been established for this project.

Appropriate test criteria for testing ULHS cements under realistic design conditions were developed from historical United States data. These criteria will be used to evaluate appropriate cements throughout the project. Additionally, appropriate criteria for slurry stability and mixability were developed and used to establish ULHS water requirement ranges.

Evaluation of applications of ULHS cements has been initiated. A synopsis of investigations conducted in Russia has been completed. This report reveals that several successful applications have been achieved. Review and analysis of this synopsis is under way.

Problems necessitating use of ULHS are being summarized to establish test and performance evaluation criteria.

6.0 Experimental

Experimental methods employed in this investigation are based on generally-accepted laboratory test procedures for oil well cements. Where applicable, standard methods presented in the API RP 10 B,¹ These tests include: thickening time, compressive strength, rheology, and free fluid.

Non-standard test procedures were necessitated because of the unique nature of the ULHS. The spheres are brittle and can break when mixed in a slurry and subjected to differential pressure or shear. Additionally, the sphere's specific gravity is less than water, so the spheres can float, resulting in solids segregation. These non-standard laboratory methods include slurry mixing, density vs. pressure, and slurry stability.

Non-standard testing procedures are outlined in detail in Appendix 1, Section 11.

7.0 Results and Discussion

7.1 Summary of Casing Conditions in USA

The application of ULHS cements will primarily be in surface and intermediate casing cementation. Average conditions under which these casings are installed were assessed in order to establish representative testing conditions. First, historical review of casing sizes, hole depths, bottomhole static temperature (BHST), and bottomhole circulating temperature (BHCT) was conducted using **Worldwide Cementing Practices**.² The data were tabulated and are presented in Appendix 11.2. Data were then averaged and summarized in Table 7.1. This analysis indicates that the average surface casing size in the US is 8 5/8 inches. Average intermediate casing size is 9 5/8 inches. These average sizes along with average depths and temperatures will be used to calculate representative cement placement times, test temperatures, and volumes.

Table 7.1—Summary of Casing Conditions in USA

Casing	Number of Data Samplings					Avg. Depth (ft)	Avg. BHST (°F)	Avg. BHCT (°F)
	8 5/8 (in.)	9 5/8 (in.)	13 3/8 (in.)	Other	Total			
Surface	64 ^a	37	29	24	182	1,660	96	78
Intermediate	17	34 ^b	—	26	77	8,300	174	128

^aThe average weight was 24 lb/ft

^bThe average weight was 53.5 lb/ft

7.2 Review of Russian Lightweight Cement Literature

A review of literature covering ULHS research conducted by Russian investigators is presented in Appendix 11.3. This review includes compositions of ULHS investigated, physical properties, sources, properties of cement formulated with ULHS, and application conditions. Results of these investigations and applications were generally favorable, indicating both economic and technical benefits of the systems.

Additional evaluation and analysis of the information will be performed and reported in subsequent reports.

7.3 Cement Quality Control Program

An extensive quality-control program was initiated because of the large quantity of cement to be used over the length of this project. Each bucket of cement is labeled with a materials log number and date upon receipt. When a bucket is first opened for use, the date of opening is also being recorded into the materials log. This log number will be referenced on the lab sheets for each test performed. Where applicable, tests according to the API Specification 10A³ are conducted. Additionally, several other tests tailored specifically for the test conditions and materials (rheology and low-temperature compressive strength development) are included in this QC Program.

The Class A and Class H cement performance requirements are presented in API Specification 10. The lightweight cement testing, as it is not referenced in the API Specifications, is conducted according to QC procedures developed by the manufacturer.

This quality-control program is necessary because of the large volume of cement to be used during this DOE project. Initially, the testing lab has received five 5-gallon buckets of API Class A cement (analogous to ASTM Type I cement), ten 5-gallon buckets of API Class H cement, and nineteen 3-gallon buckets of Lightweight Oilwell cement from TXI. Both API Specification tests and Advisory–Board–Member-recommended testing are being performed for the cement quality control program. The physical requirements used for testing each of the cements are those listed in Table 7.2. To accelerate the rate of compressive strength development at low temperature, calcium chloride (CaCl_2) is being used according to Table 7.3 with both classes of cement. Calcium chloride was selected because it is one of the most effective and commonly used cement accelerators.

Table 7.2—Cement Physical Requirements for Quality-Control Testing Program

Cement	Mix Water (%)	Density (lb/gal)	Cement (g)	Water (mL)	Test
Type 1	46	15.7	772	355	API
Lightweight	75	13.2	541	406	TT and CS
Lightweight	105	12.1	426	447	FW
Class H	38	16.5	860	327	API

Table 7.3—Percent CaCl_2 for Low-Temperature Compressive Strengths

Temperature (°F)	CaCl_2 (%)
80	0.0
60	1.0
45	2.0

All of these tests have been run to provide a baseline for each type of cement. This data will provide a comparison when examining other data for this project. The complete set of tests will be conducted periodically throughout the length of DOE Project. Table 7.4 shows the first set of data conducted by the testing lab on the three cements received.

**Table 7.4—Quality Control Testing of Cements
Cement Compositions Specified in Table 7.2**

	Lightweight	Class A	Class H
Free Water (% by vol.)	0.8	0	1.2
Initial Viscosity (Bc)	6	9	12
Spec 5 Thickening Time (hr:min to 100 Bc)	2:20	2:21	1:54
Atmospheric Pressure (psi)			
Compressive Strength (24 hr)			
45°F (2% CaCl₂)	106	471	
60°F (1% CaCl₂)	162	763	
80°F (24 hr)	334	1079	
100°F (8 hr)		482	307
120°F (24 hr)	1009		
Viscometer Readings^a (rpm)			
300	57	80	85
200	50	65	70
100	42	49	53
60	38	40	45
30	33	34	38
6	22	17	14
3	12	10	8

^aAfter 20 minutes conditioning on atmospheric viscometer

7.4 –Design of Cement Slurries Containing Glass Beads

7.4.1 Glass Bead Specifications

The 3M Scotchlite Glass Bubbles K&S Series Product Information sheet provides all of the specifications on this material. The ULHS are hollow, spherical-shaped glass microspheres composed of soda-lime borosilicate. They can be provided in a crush strength range from 250 psi to 10,000 psi. The 3M Scotchlite Glass Bubbles K&S Series Product Information sheet is also the source for Table 7.5.

Table 7.5—Glass Bead Specifications

True Density				Particle Size Distribution (microns, by volume)			Effective Top Size
Bead Application Pressure Rating (psi)	Minimum S.G. (g/cc)	Maximum S.G. (g/cc)	Average S.G. (g/cc)	10th%	50th%	90th%	95th%
3,000	0.34	0.40	0.37	20	40	80	85
6,000	0.43	0.49	0.46	15	40	70	80
10,000	0.57	0.63	0.60	15	30	55	65

Additional specific information can be obtained by calling the 3M Specialty Materials Group at 1-800-367-8905.

7.4.2 Mixing and Settling Data

The next series of tests was designed to determine mixing water requirements for formulating mixable and stable ULHS slurries. Slurry rheology and segregation tests were the basis for this determination. Testing was conducted with a variety of cement compositions with varying 3,000 psi ULHS concentrations.

Rheology testing was analyzed in several different ways and presented in the following figures. The first chart type, *Glass Beads Comparison Rheology Chart*, illustrates the entire viscometer range of results from different concentrations of mix water, with varying concentrations of the ULHS, maintaining constant density. A slurry formulated with normal mix water for base cement has also been included as a baseline reference.

The second chart type, *300 rpm and 200 rpm Glass Beads Comparison Rheology Chart*, illustrates the same information as the chart above it but only of the two rpm results.

The third chart type, *Percent Density Change Charts*, shows the percent change of slurry density with various concentrations of mix water and ULHS. The change in density indicates the extent of separation of the spheres. Procedure is specified in Table 11.1.3.

The mixability limit of a rheology reading less than 300 at 300 rpm and a percent density change less than 5% was used as a standard for analysis of data.

**Table 7.6—3000-psi UHLS with Class A Cement
at 13.0 lb/gal**

Mix Water (gal/sk)	ULHS (% by weight)
4.8	8.26
5.2	7.65
5.4	7.34
5.8	6.72
6	6.42
7	4.87
5.2	Baseline

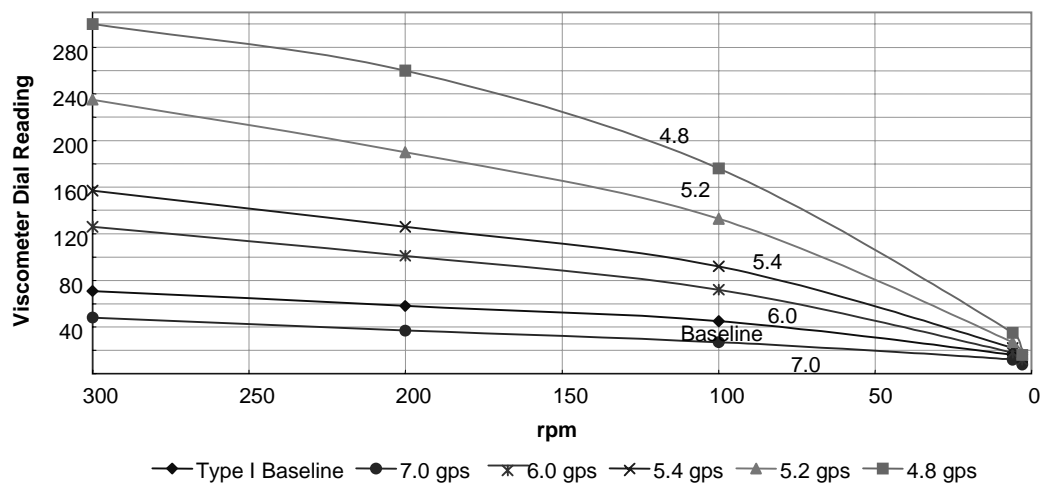


Figure 1—Rheology of cements outlined in Table 7.6. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

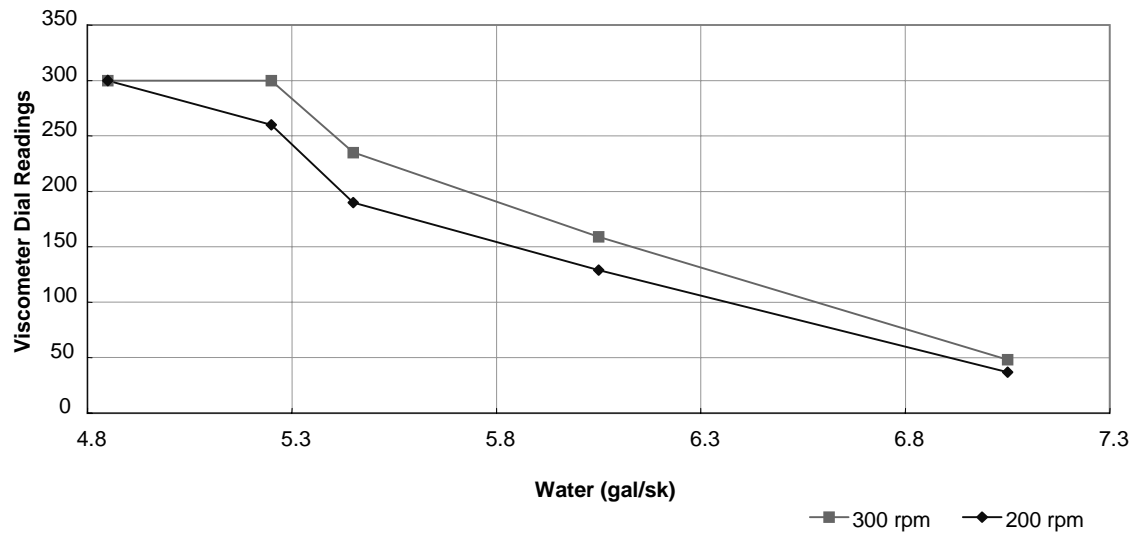


Figure 2—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.6. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

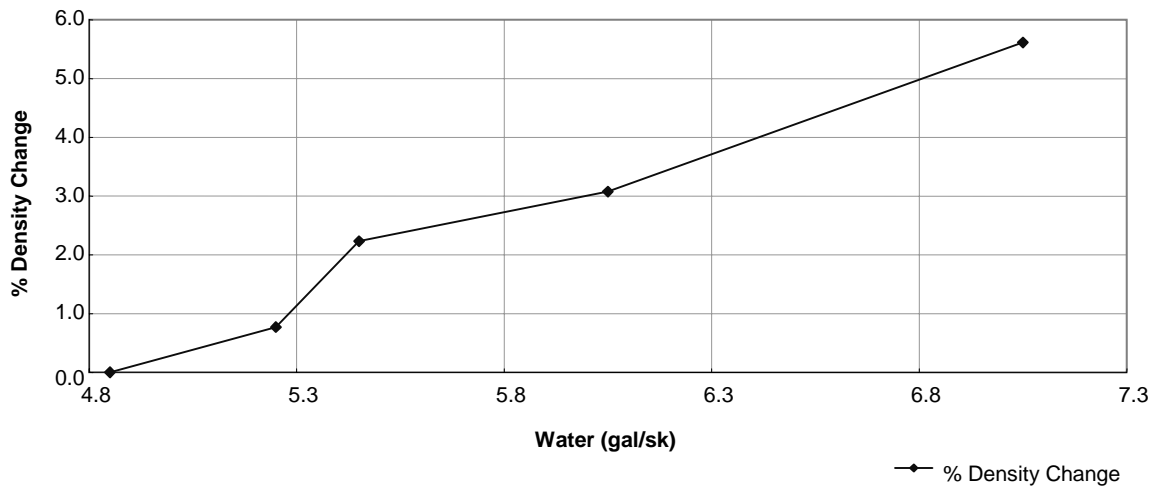


Figure 3—Density changes of cements outlined in Table 7.6

Table 7.6 presents mix water and ULHS requirements for 13.0 lb/gal slurries formulated with Class A cement. Figures 1, 2, and 3 present rheology and settling test data. Using a water requirement of 5.2 gal/sk for the Class A cement, the additional water for the ULHS was in a range of 0.03 gal H₂O/lb to 0.31 gal H₂O/lb.

**Table 7.7—3,000-psi ULHS with Class A Cement
at 10.0 lb/gal**

Mix Water (gal/sk)	ULHS (%)
7.2	21.91
7.6	21.60
8.0	21.27
8.2	21.12
9.0	20.94
9.5	20.10
10.0	19.70
10.5	19.31
11.0	18.92

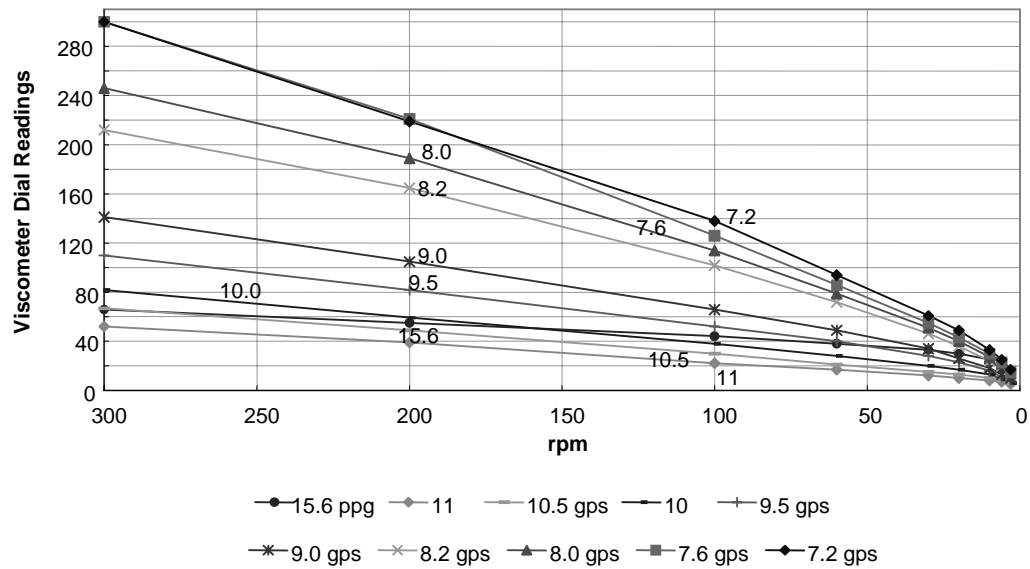


Figure 4— Rheology of cements outlined in Table 7.7. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

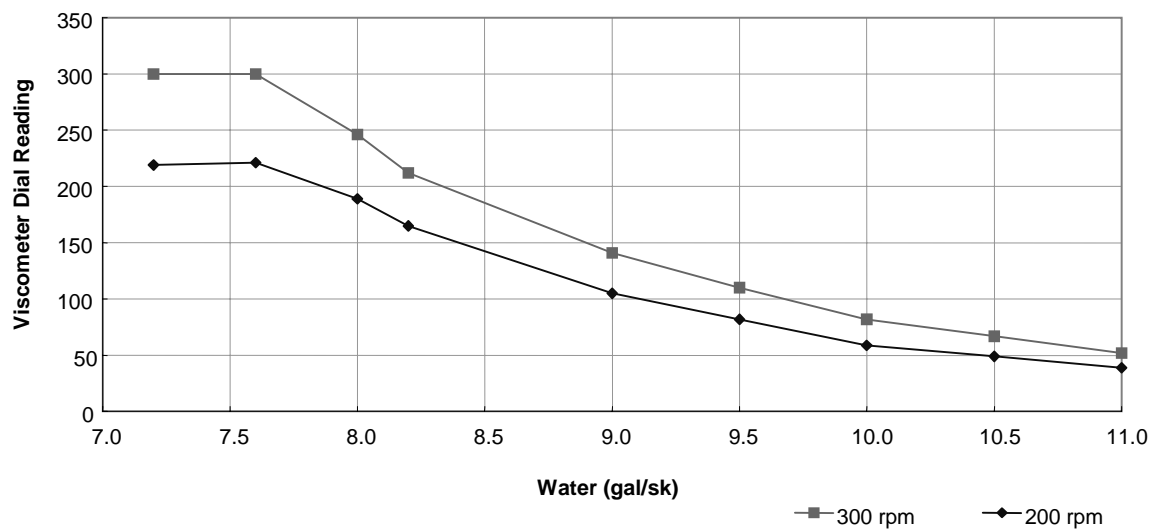


Figure 5—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.7. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

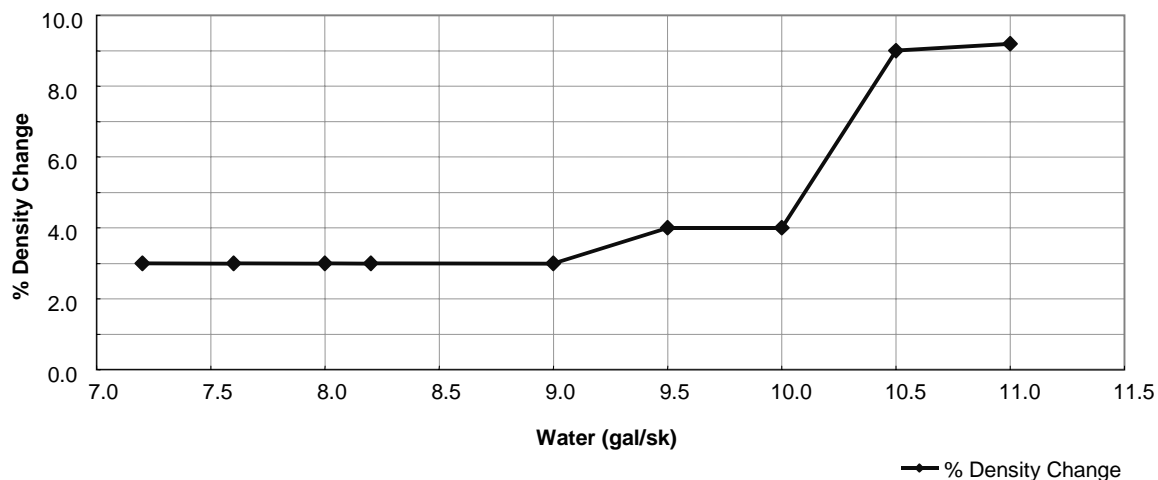


Figure 6—Density changes of cements outlined in Table 7.7

Table 7.7 and Figures 4, 5, and 6 present similar data for 10.0 lb/gal cement slurries formulated with Class A cement. Using a water requirement of 5.2 gal/sk for Class A cement, the additional water for the ULHS was in a range of 0.14 gal H₂O/lb to 0.33 gal H₂O/lb.

**Table 7.8—3,000-psi ULHS with Lightweight Cement
at 11.5 lb/gal**

Mix Water (gal/sk)	ULHS (%)
5.5	9.98
6.0	9.21
7.0	7.67
8.0	6.12
9.0	4.58

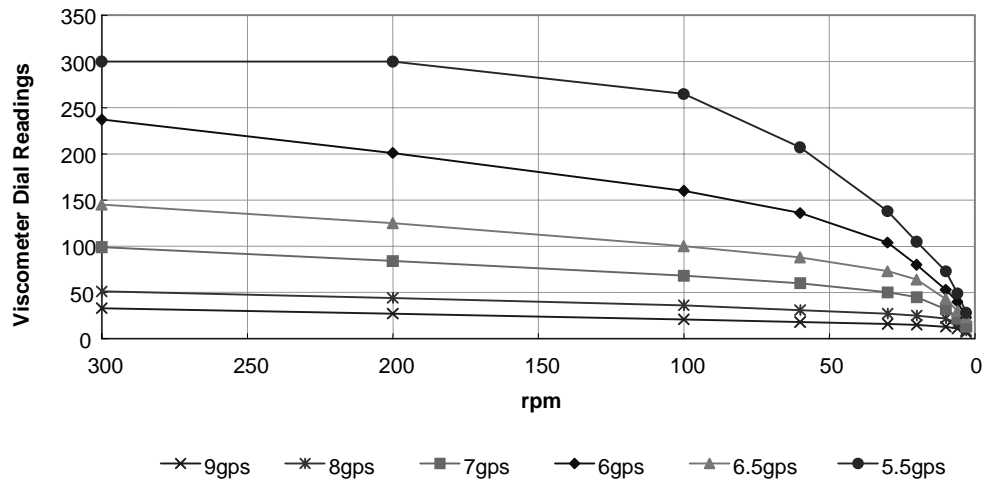


Figure 7—Rheology of cements outlined in Table 7.8. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

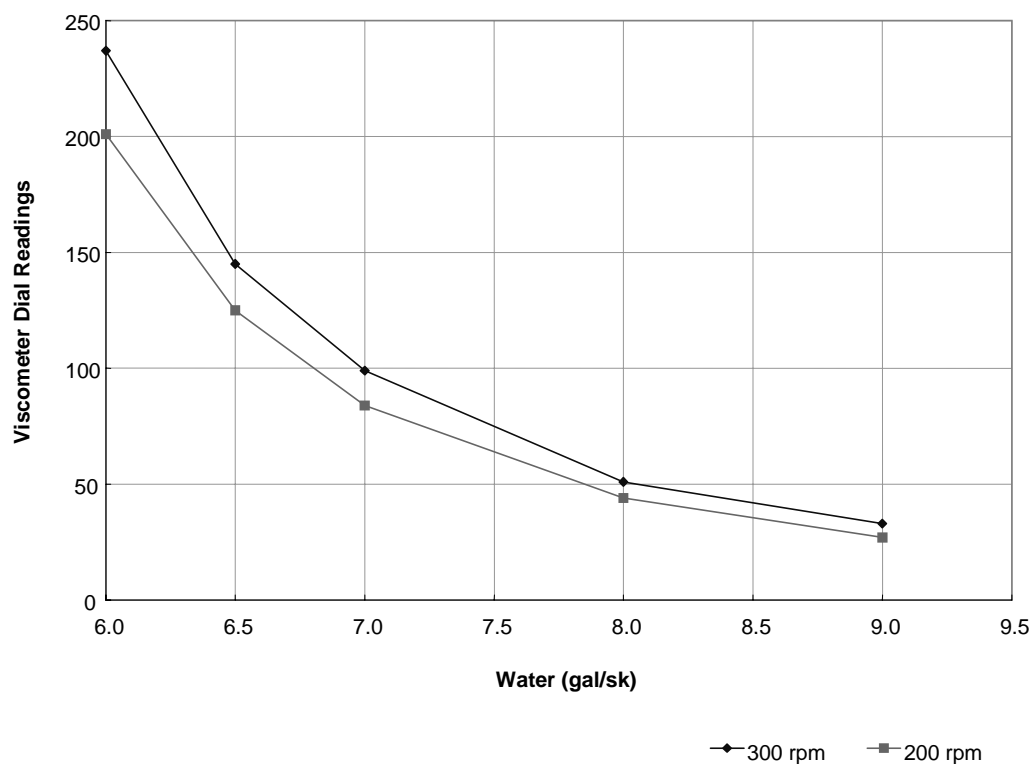


Figure 8—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.8

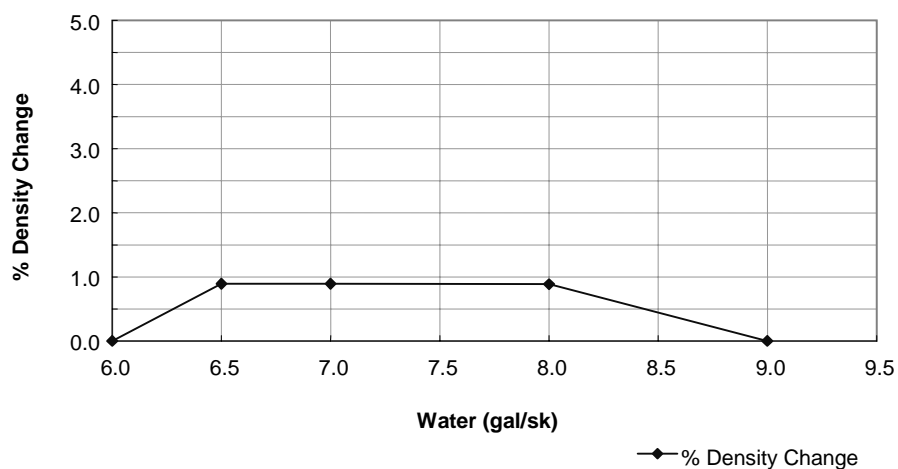


Figure 9—Density changes of cements outlined in Table 7.8

Table 7.8 and Figures 7, 8, and 9 present data for 11.5 lb/gal cements formulated with lightweight cement. Using a water requirement of 7.0 gal/sk for the lightweight cement, the additional water for the 3000-psi glass beads was in a range of 0.14 gal H₂O/lb to 0.58 gal H₂O/lb.

**Table 7.9—3,000-psi ULHS with Lightweight Cement
at 10.0 lb/gal**

Mix Water (gal/sk)	ULHS (%)
6.5	18.96
7	18.46
7.5	17.97
8	17.48
10	15.5
11	14.52

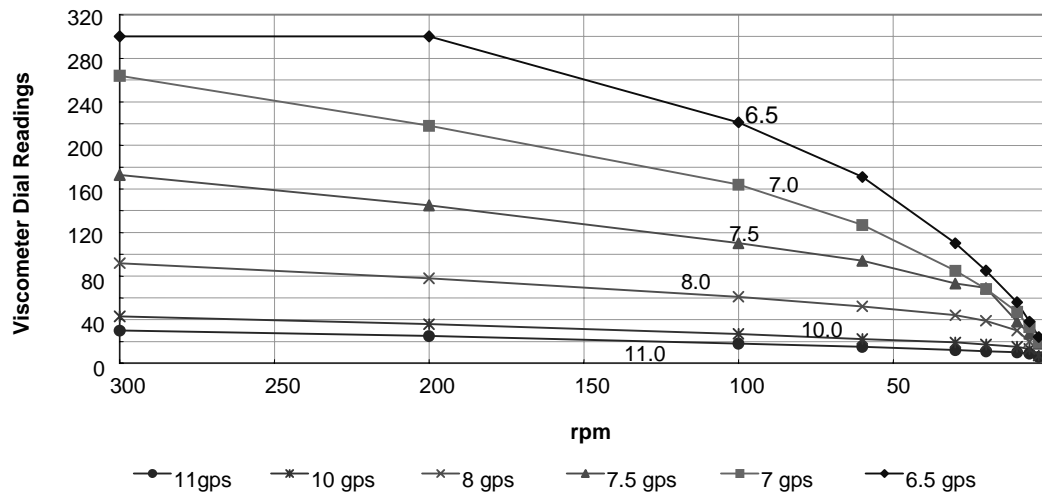


Figure 10—Rheology of cements outlined in Table 7.9. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

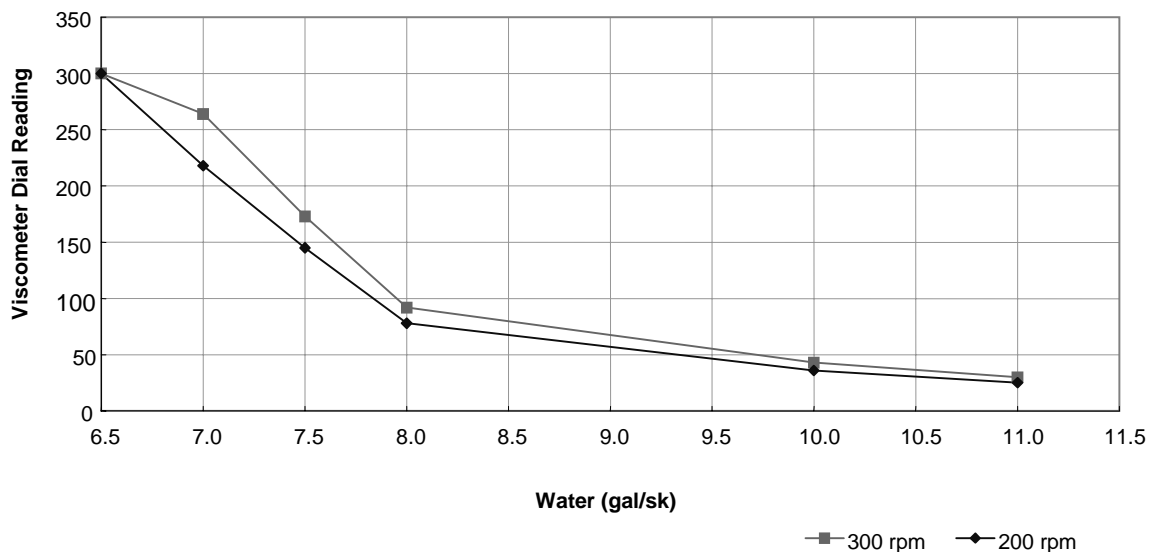


Figure 11—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.9. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

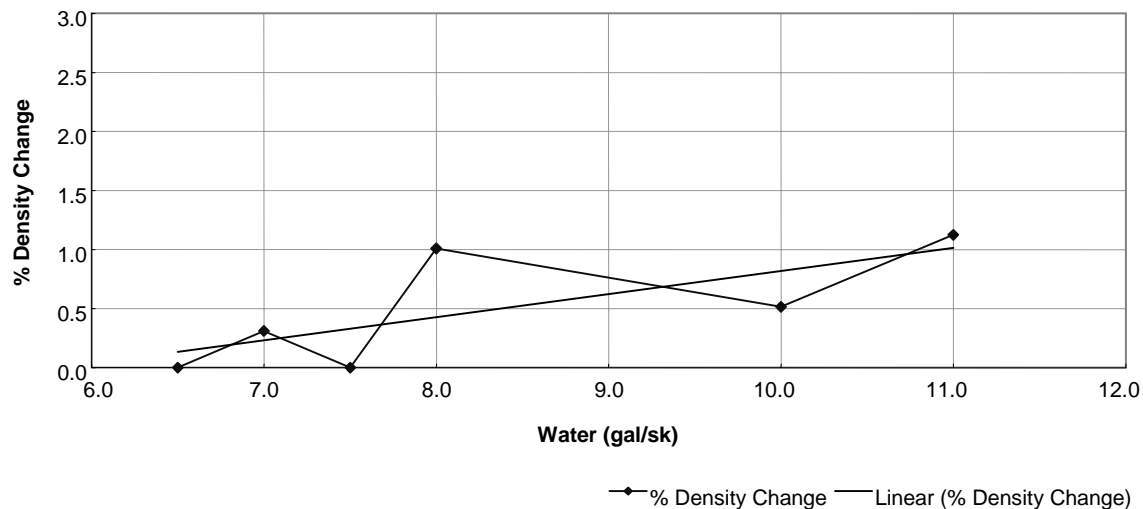


Figure 12—Density changes of cements outlined in Table 7.9

Table 7.9 and Figures 10, 11, and 12 present data for 10.0 lb/gal cements formulated with lightweight cement. Using a water requirement of 7.0 gal/sk for the lightweight cement, the additional water for the 3000-psi ULHS was in a range of 0.14 gal H₂O/lb to 0.58 gal H₂O/lb.

**Table 7.10—3,000-psi ULHS with Class A Cement
Plus 1% Dispersant (bwoc) at 13.0 lb/gal**

Mix Water (gal/sk)	ULHS (%)
4.0	9.00
4.4	8.39
4.8	7.77

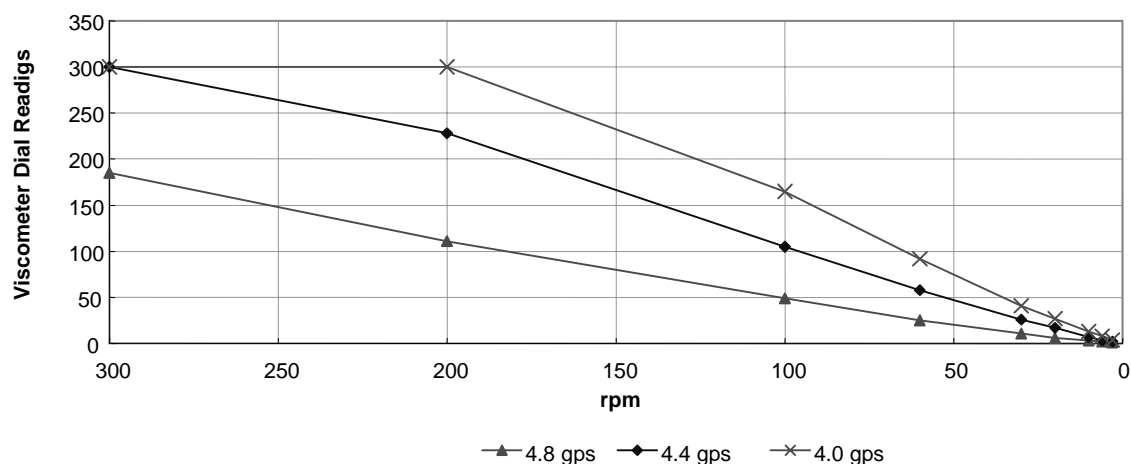


Figure 13—Rheology of cements outlined in Table 7.10. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

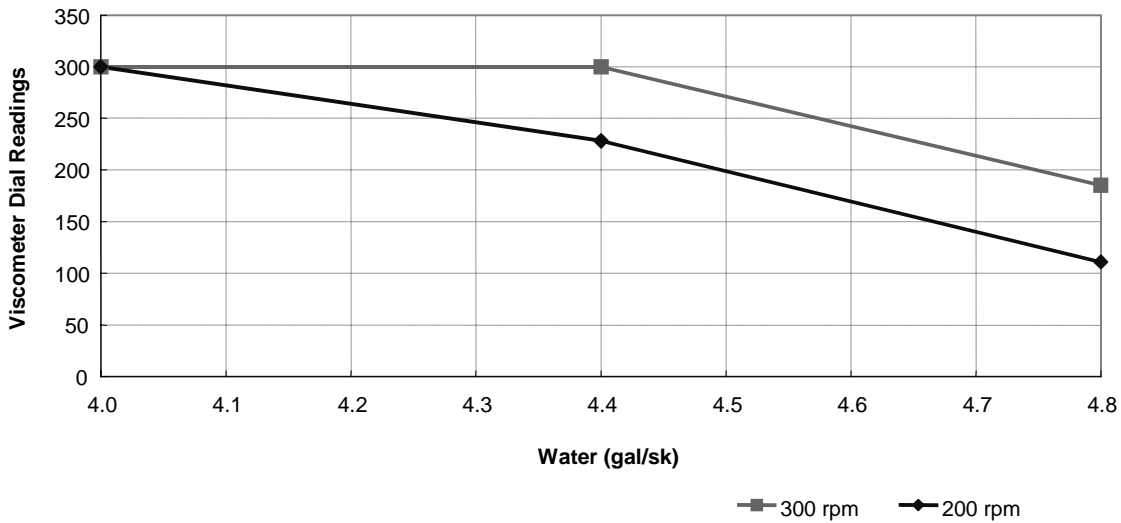


Figure 14—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.10. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

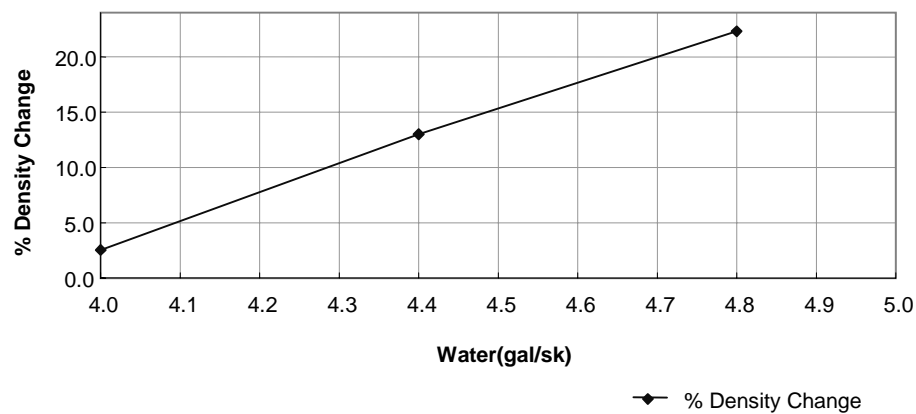


Figure 15—Density changes of cements outlined in Table 7.10

Table 7.10 and Figures 13, 14, and 15 present data for 13.0 lb/gal Class A cement containing a cement dispersant. Using a water requirement of 5.2 gal/sk for the Class A cement, the additional water for the 3000-psi ULHS with dispersant 0.32 gal H₂O/lb.

**Table 7.11—3,000-psi ULHS with Class A Cement
Plus 1% Dispersant at 10.0 lb/gal**

Mix Water (gal/sk)	ULHS (%)
6	22.41
6.5	22.49
7.2	21.94
7.5	21.43

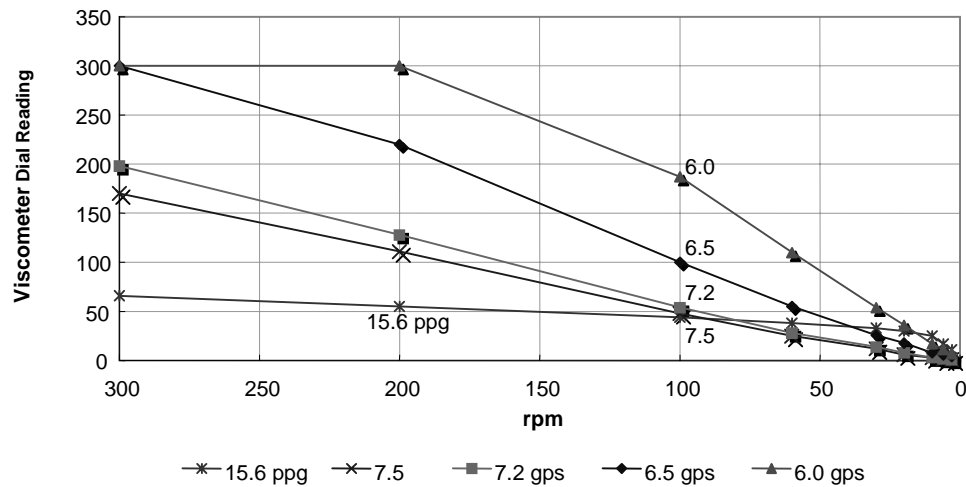


Figure 16—Rheology of cements outlined in Table 7.11. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

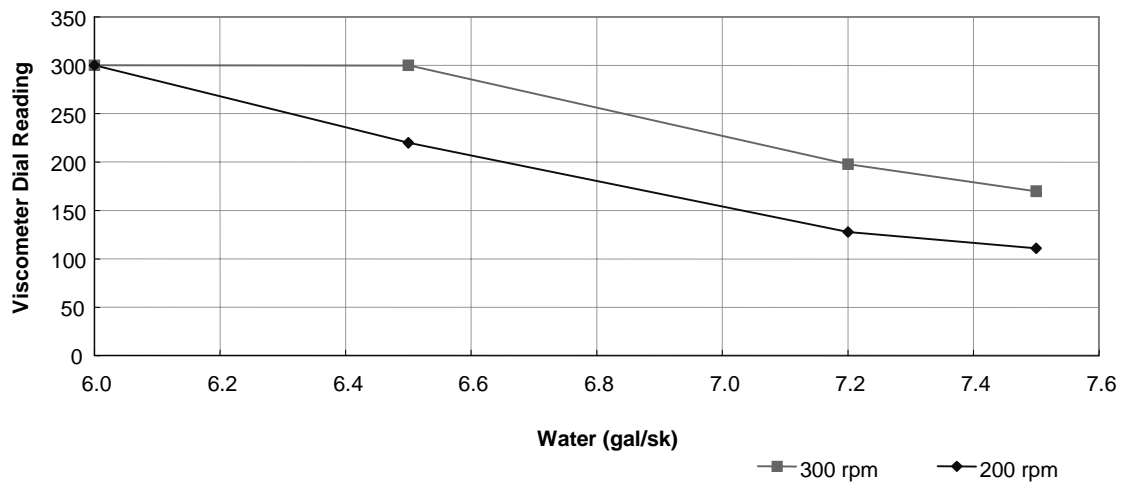


Figure 17—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.11. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

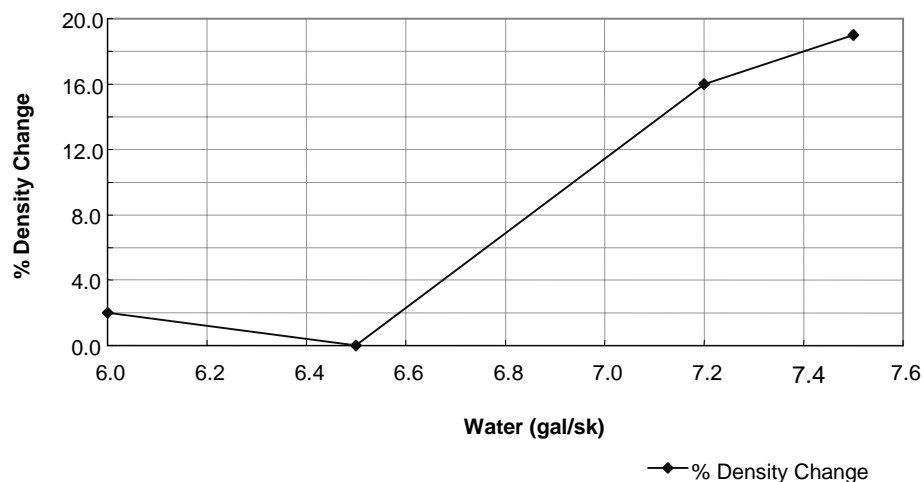


Figure 18—Density changes of cements outlined in Table 7.11

Test data for 10.0 lb/gal Class A cement containing a dispersant is presented in Table 7.14 and Figures 19, 20, and 21. Using a water requirement of 5.2 gal/sk for the Class A cement, the additional water for the ULHS with dispersant was in a range of 0.067 gal H₂O/lb to 0.073 gal H₂O/lb.

**Table 7.12—3,000-psi ULHS with Lightweight Cement
Plus 1% Dispersant at 10.0 lb/gal**

Mix Water (gal/sk)	ULHS (%)
6	19.01
6.5	18.51
7	18.02
7.5	17.53

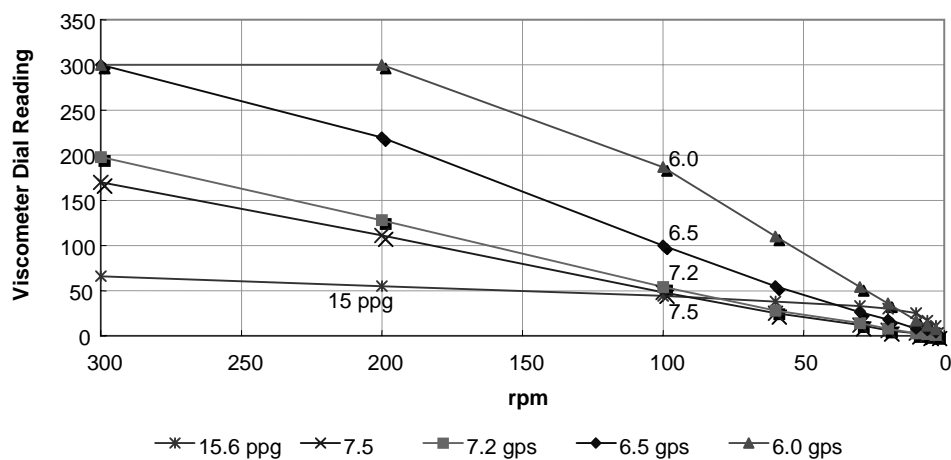


Figure 19—Rheology of cements outlined in Table 7.12. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

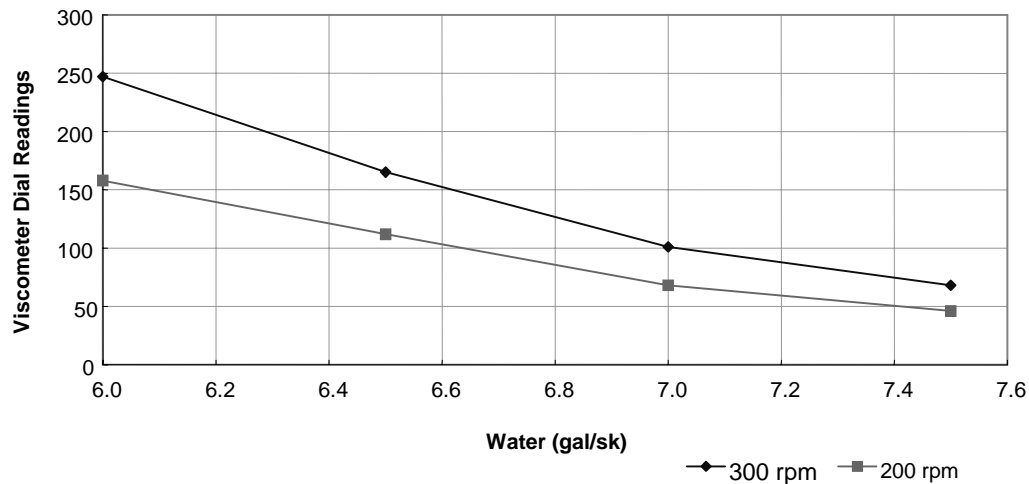


Figure 20—300 rpm and 200 rpm rheology measurements of cements outlined in Table 7.12. Note that the 300 dial reading on the chart is actually a 300 plus (300+) dial reading.

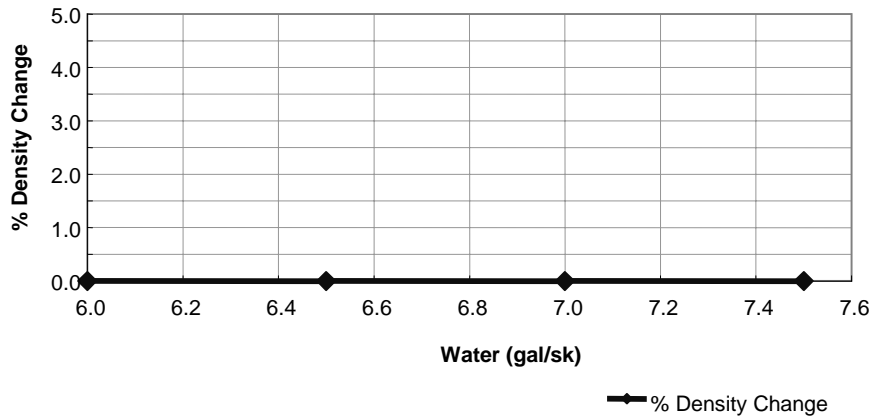


Figure 21—Density changes of cements outlined in Table 7.12

Table 7.11 and Figures 19, 20, and 21 present data for a 10.0 lb/gal lightweight cement containing dispersant. Using a water requirement of 7.0 gal/sk for the lightweight cement, the additional water for the ULHD was in a range of 0.07 gal H₂O/lb to 0.03 gal H₂O/lb. No density change was found throughout the entire test.

The dispersant concentration of 1% was arbitrarily chosen from past experience. However, rheology of the dispersant-containing cements demonstrates erratic behavior that may be indicative of sub-optimum dispersant concentration. The effect of the ULHS on dispersant activity must be further evaluated to resolve this.

Table 7.13—Descending and Ascending Viscometer Readings of Lightweight Cement at 11.5 lb/gal

Rheology (rpm)	5.5	Reverse	6.0	Reverse	6.5	Reverse	7.0	Reverse
300	300	300	237	220	145	146	99	94
200	300	300	201	187	125	126	84	83
100	265	256	160	150	100	101	68	67
60	207	207	136	130	88	85	60	58
30	138	132	104	102	73	69	50	50
20	105	107	80	81	64	63	45	45
10	73	72	53	50	43	43	32	31
6	49	43	40	38	30	28	22	21
3	28	28	23	23	23	23	13	13

The effects of running the viscometer in descending and ascending order are shown in Table 7.13 with three different ULHS and mix water concentrations. This testing was conducted to evaluate the centrifugal effects of the rotational viscometer on the stability of the slurries.

The data indicate that little effect results from testing in descending rotational speed. However, the maximum centrifugal effect would come from running the tests in ascending then descending order. Therefore, the testing will be repeated this way.

7.4.3 Shear Effect on Slurry Density with 3M 3K Glass Beads

Mixing of ULHS with a Waring Blender causes breakage of some spheres due to shearing of the blender blade. This breakage alters the slurry design density. An example of this occurrence, as shown in Figure 22, which presents data on a Class A cement slurry mixed with 3000 psi ULHS mixed with a Waring Blender. The cement and water were first mixed in a Waring Blender. The ULHS were then added while continuously mixing by hand with a spatula. The slurry density was then measured using a pycnometer as outlined in Table 11.1.4. The same slurry was returned to the Waring Blender for 35, 105, 210 seconds to ascertain shearing effect on slurry density from breakage of glass beads.

These data indicate the occurrence of air entrainment since the measured density was 0.4 lb/gal lower than calculated. The data must be repeated with a pressurized mud balance. Additionally, it is proposed to use slurry defoamer in all cements to alleviate the problem.

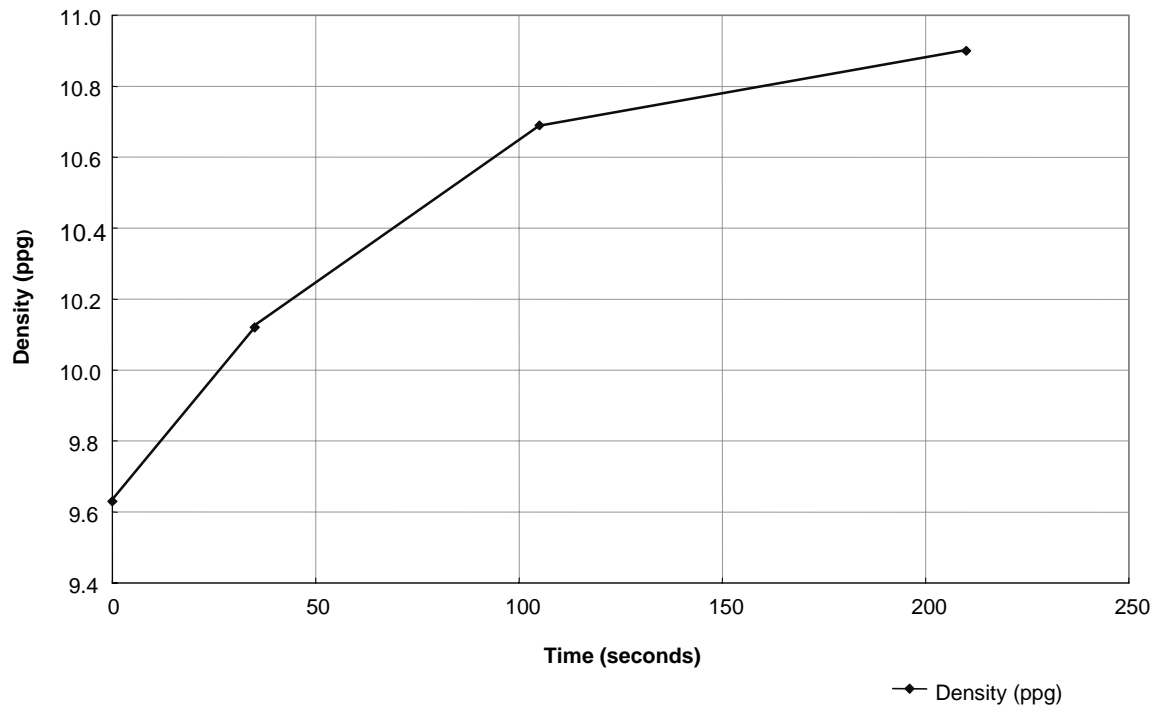


Figure 22—Effect of high-shear mixing on ULHS cement density

7.4.4 Glass Beads Specific Gravity versus Applied Pressure

The following three charts (Figures 26,-27, and 28) are results of slurries with 3,000, 6,000, and 10,000 psi ULHS after being pressurized at several predetermined pressures. These data will be used to calculate effective density lowering capacity of the ULHS vs. pressure.

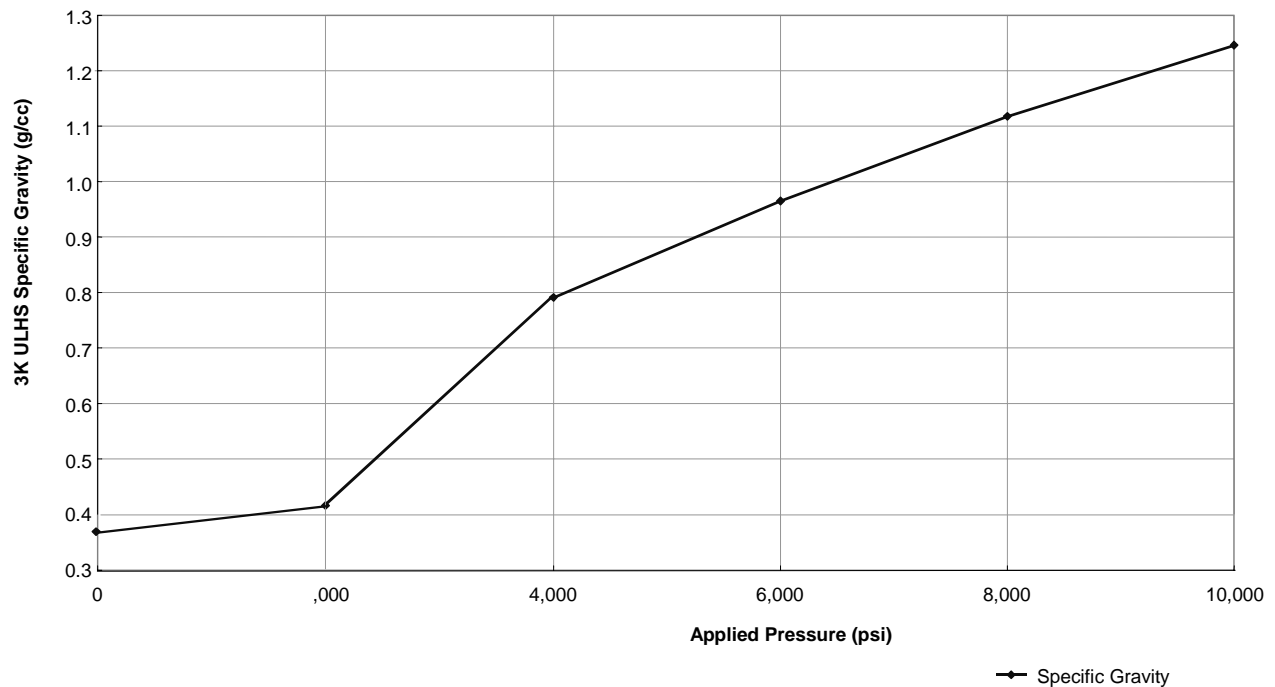


Figure 23—3000 psi ULHS specific gravity vs. pressure

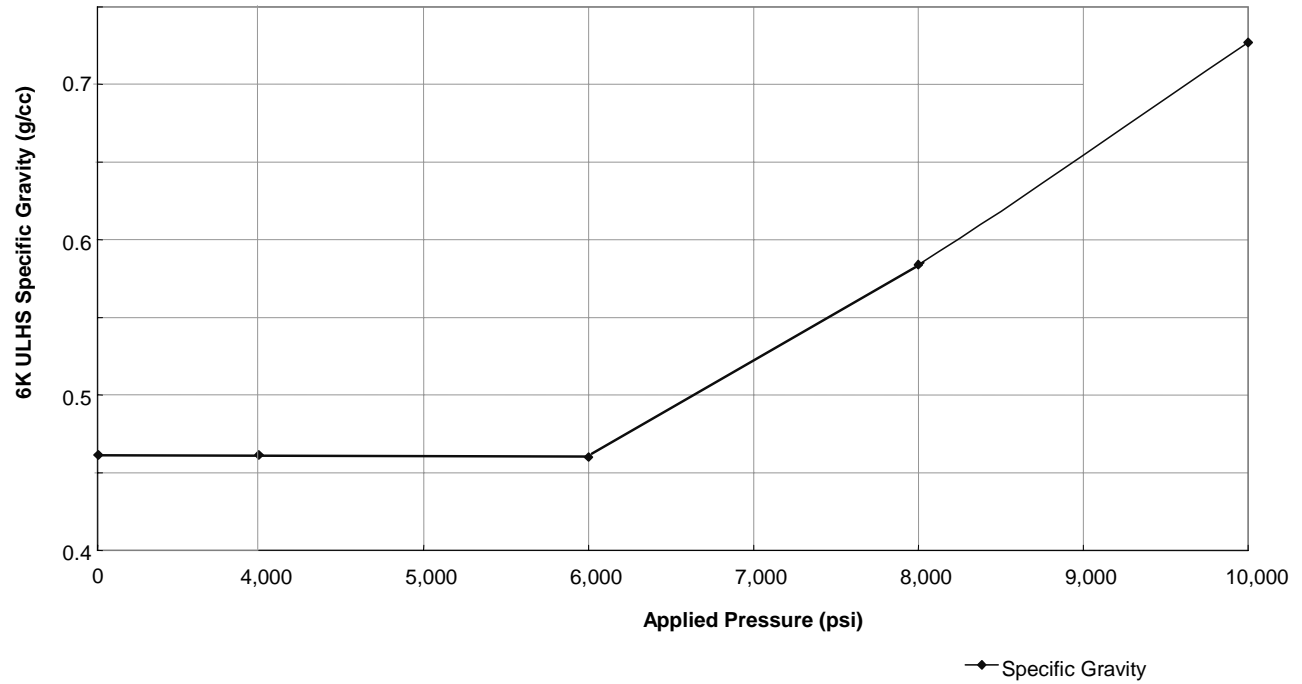


Figure 24—6000 psi ULHS specific gravity vs. pressure

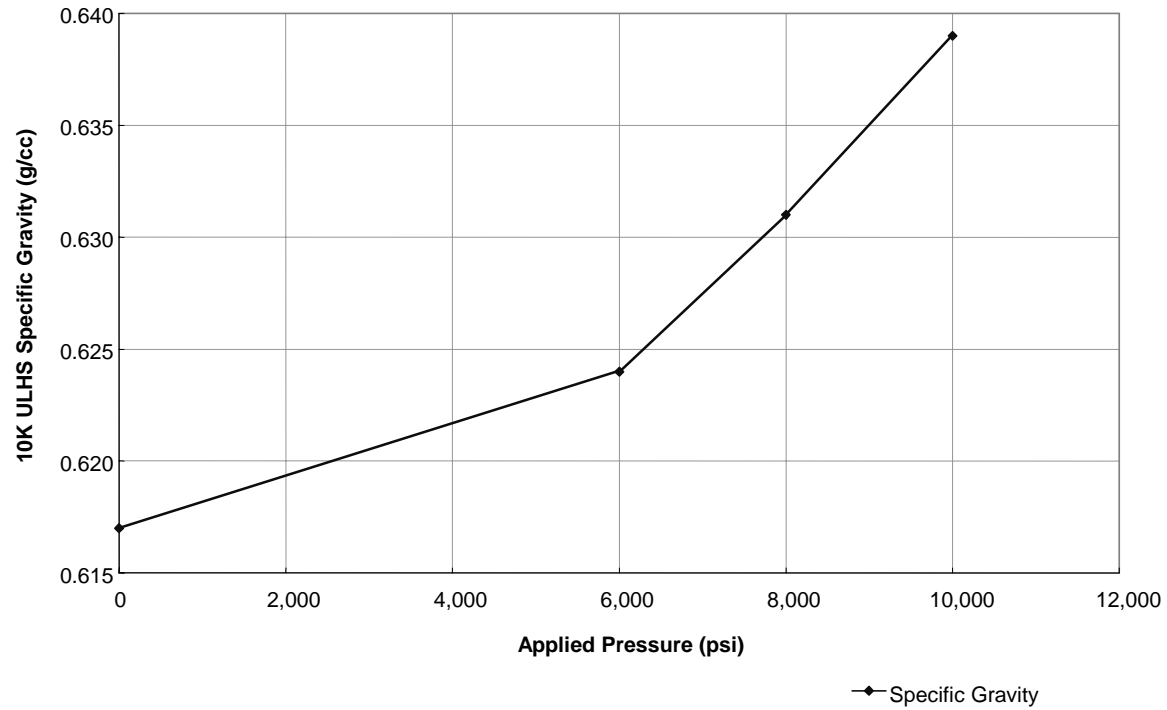


Figure 25—10,000 psi ULHS specific gravity vs. pressure

8.0 Conclusions

Based on initial results presented herein, the following conclusions can be drawn:

Laboratory procedures for cement design tests to establish mixability, slurry stability and separation, effects of pressure, and mixing are established.

Satisfactory quality-control procedures have been established.

Typical design parameters derived from USA historical data were established to evaluate field application of ULHS under realistic conditions.

Physical performance properties of ULHS materials measured over a wide range of application pressures indicate that the materials are functional as light weight additives for typical oilwell cementing conditions.

Air entrainment affects atmospheric density measurement techniques, and a cement defoamer must be employed in laboratory mixing methods.

9.0 References

1. API Recommended Practice 10 B, 22nd Edition, December 1997: 22nd Edition, December 1997: "Recommended Practice for Testing Well Cements," American Petroleum Institute
2. Worldwide Cementing Practices First Edition, American Petroleum Institute, January 1991.
3. API Specification 10 A, 22nd Edition, January 1, 1995: "Specification for Cements and Materials for Well Cementing," American Petroleum Institute.

10.0 List of Acronyms and Abbreviations

lb/gal — pound(s) per gallon
lb/ft — pound(s) per foot
rpm —revolutions per minute
gal/sk — gallon(s) per sack
H₂O/lb — water per pound
gps — gallon(s) per second
g/cc — grams per cubic centimeter
g — gram
cc — cubic centimeter
psi — pound(s) per square inch
UHLS —ultralight hollow glass spheres
API — American Petroleum Institute
avg. — average
BHCT — bottomhole circulating temperature
BHST — bottomhole static temperature
TXI — a cement supplier
CSI — Cementing Solutions, Inc.
QC — quality control
Bc — Bearden units of consistency
AT — atmospheric
3M — Minnesota Mining and Manufacturing
3K — 3,000-psi designation
TT—thickening time test
CS—compressive strength test
FW—free water test

11.0 Appendices

Appendix 11.1

Non-standard Test Procedures Developed for ULHS Cements

Table 11.1.1 Mixing Procedures of Cement and Glass Beads

Procedure 1: Mixing beads without high shear

(Mixing glass beads into a cement slurry using a Waring Blender can break beads, thereby altering the slurry density.)

1. Weigh out the appropriate amounts of the cement sample and additives, water, and glass beads into separate containers.
2. Mix the cement slurry according to Section 5.3.5 of the American Petroleum Institute (API) Recommended Practice for Testing Well Cements, Twenty-Second Edition, December 1997.
3. Pour the slurry into a metal mixing bowl and slowly add the glass beads while continuously mixing by hand with a spatula.

Procedure 2: Mixing beads with high shear

Mix slurry including beads according to API Specification 10. Measure density with pressurized mud balance to assess degree of density change due to breakage.

Table 11.1.2 Procedures for Performing Stability Test

1. Prepare the cement and bead slurry as described in the *Mixing of Cement and 3M Scotchlite Beads* instructions above.
2. Pour 250 mL of the thoroughly mixed slurry into a 250 mL graduated cylinder and seal to prevent evaporation.
3. Stand the graduated cylinder upright in an 80°F water bath with water level equal to height of cement in graduated cylinder for 1 hour.
4. Mark the 250 mL graduated cylinder into three sections (Top, Middle, Bottom).

Top 1/3 Section: 170 mL – 50 mL

Middle 1/3 Section: 80 mL – 170 mL

Bottom 1/3 Section: 0 mL – 80 mL

5. Fill a (30mL) syringe with 1 to 5 mL of the cement and bead mixture to remove any air trapped in the tip of the syringe; then eject slurry leaving the tip filled. Wipe any residue from the outside of the syringe.
6. Tare the washed syringe on a balance.
7. Refill the syringe with a least 10 mL of the cement and bead mixture from the top 1/3 section of the graduated cylinder.
8. Weigh and record the weight and volume of the syringe plus mixture.
9. Calculate the specific gravity of the mixture by dividing the recorded weight of the cement and bead mixture by the volume of mixture measured into the syringe. Compute density by multiplying by the density of water (8.33 lb/gal).

Example:

Syringe plus Cement & Beads – 38.14 g

Volume of Cement & Beads – 30 cc

$$38.14 \text{ g} / 30 \text{ cc} = 1.271 \text{ g/cc}$$

$$1.271 \text{ g/cc} \times 8.33 = 10.59 \text{ lb/gal}$$

10. Repeat steps 6 – 9 with the other two (middle, bottom) 1/3 sections of the graduated cylinder. Use a length of tubing attached to the syringe tip to access the lower portions of the cylinder.

TABLE 11.1.3

Calculations for Determining Density Difference Due to Separation

1. Using the data obtained in the *Procedure for Performing Stability Test* Subtract the top density from the bottom density.
2. Divide this value by the bottom density and multiply by 100.
3. The resulting value is the percent density difference due to glass bubble separation.

Example:

Top Density - 15.0 lb/gal

Bottom Density - 15.5 lb/gal

$$15.5 - 15.0 = 0.5$$

$$(0.5 / 15.5) \times 100 = 3.23\% \text{ density difference}$$

Table 11.1.4 Density Determination using a Pycnometer

1. Assemble and weigh the empty pycnometer.
2. Remove the cap and lid.
3. Fill the cup with distilled or deionized water.
4. Lay the lid on top of the cap. Screw down the cap. Water should run out the hole in the center of the lid. This must occur to assure that the pycnometer is completely filled. With a soft, lint free cloth or wiper, wipe the pycnometer dry. Be careful to avoid touching the wiper directly to the hole in the center of the lid. If water is wicked up, the pycnometer will no longer be completely filled.
5. Re-weigh the assembled pycnometer. Subtract the weight of the empty pycnometer from the weight of the filled pycnometer. The resulting value is the net weight of the water.
6. Disassemble the pycnometer. Pour out the water and completely dry all parts.
7. Fill the pycnometer with the cement and bead mixture. Take care to fill the cup completely to eliminate air pockets by gently tapping the cup on a flat surface. Screw down the cap. The mixture should run out of the hole in the center of the lid. With a lint free cloth or wiper, wipe the pycnometer clean and dry. Avoid touching the wiper directly to the hole in the center of the lid.
8. Weigh the filled and clean pycnometer. Subtract the weight of the empty pycnometer from the weight of the mixture filled pycnometer. This is the net weight of the cement and bead mixture.
9. Divide the net weight of the cement and bead mixture by the net weight of the water. The result is the specific gravity of the sample.
10. Multiply the specific gravity by the density of water (8.33 lb/gal) to determine the density of the mixture. Report the temperature at which the measurements are made in case accounting for thermal expansion is necessary.
11. Thoroughly clean and dry all parts of the pycnometer.

Example:

Pycnometer – 52.0 g

Water – 63.6 g

Cement & Beads – 68.0 g

$63.6\text{ g} - 52\text{ g} = 11.6\text{ g}$

$68.0\text{ g} - 52\text{ g} = 16.0\text{ g}$

$16.0\text{ g} \div 11.6\text{ g} = 1.38$

$1.38 \times 8.33\text{ lb/gal} = 11.49\text{ lb/gal}$

^aNotes:

A pycnometer can yield greater accuracy than other methods described herein.

Since the volume of the pycnometer is constant, determinations made are based only on weight.

Since density varies with temperature, it is important to make the determination of the mixture and water at the same temperature.

^aExcerpts taken from Fisher Scientific Catalog No 03-247 – Instructions # 103234 First Issue: 03/98.

Table 11.1.5 Procedures for Determining Effects of Pressure on Collapse of Glass Beads

1. Weigh out the appropriate amounts of the cement sample, water, and glass beads into separate containers.
1. Mix slurry according to procedure outlined in Appendix 1.
4. Pour slurry into a 1-gallon plastic bag.
5. Close bag airtight, without air in slurry; use heavy-duty tape to seal bag.
6. Place bag into pressurized consistometer (API RP 10 B, Section 9).
7. Pressurize unit to desired pressure and maintain for 10 minutes.
9. Depressurize unit and remove slurry bag.
10. Ascertain that no cement leaked from bag or oil leaked into the bag.
11. Wipe oil from exterior of bag.
14. Open bag and pour slurry to the fill line in an atmospheric consistometer cup.
15. Condition slurry for 20 minutes at room temperature.
16. Record initial and final slurry consistency.
18. Determine density using a pressurized mud balance.

11.2 Appendix 2

Surface and Intermediate casing Analysis

A review of the *Worldwide Cementing Practices*; First Edition, January 1991 was conducted. All the United States of America surface and intermediate casing jobs were tabulated into a list, shown in Tables 11.2.1 and 11.2.2. Analysis of this list provides insight into the application prospect for lightweight slurries.

Table 11.2.1—Surface Casing

Field No.	Csg Size (in.)	Csg. Wt. (lb/ft)	Depth (ft)	BHST (°F)	BHCT (°F)
1	9 5/8	39	140	70	70
2	8 5/8	24	350	75	70
3	9 5/8	39	3,500	120	90
4	20	94	1,135	93	70
5	13 3/8	46	8,750	192	140
6	8 5/8	24	350	75	70
7	13 3/8	72	2,700	40	32
8	13 3/8	72	2,700	40	32
9	13 3/8	72	2,700	40	40
10	9 5/8	47	2,600	40	32
11	9 5/8	39	600	80	80
12	11 3/4	50	1,500	100	90
13	8 5/8	22	825	100	80
14	8 5/8	24	650	87	70
15	8 5/8	24	1,000	85	70
16	7	23	1,353	85	70
17	13 3/8	68	80	80	60
18	13 3/8	68	800	90	70
19	8 5/8	30	2,000	100	80
20	10 3/4	40.5	300	80	70
21	20	94	300	100	80
22	22	92.5	250	95	70
23	13 3/8	54.5	350	85	70
24	9 5/8	36	300	245	175
25	10 3/4	40.5	3,250	150	100
26	8 5/8	24	300	90	70
27	8 5/8	26.5	400	85	70
28	8 5/8	36	800	90	70
29	10 3/4	40.5	1,000	92	70
30	9 5/8	36	400	190	
31	9 5/8	32	550	80	70
32	13 3/8	72	4,500	143	105
33	10 3/4	45.5	2,500	120	85
34	13 3/8	68	1,700	80	70
35	13 3/8	61	40	65	65
36	9 5/8	35.25	300	80	70
37	8 5/8	30	175	70	70
38	9 5/8	39	3,500	120	90
39	13 3/8	46	8,750	192	140
40	8 5/8	24	400	65	65

41	8 5/8	24	375	65	65
42	9 5/8	32	425	60	60
43	8 5/8	22	1,100	110	80
44	8 5/8	22	1,100	110	90
45	9 5/8	38	1,800	120	90
46	10 3/4	40.5	2,500	110	80
47	8 5/8	22	375	90	80
48	8 5/8	22	475	90	70
49	9 5/8	40	2,500	112	80
50	13 3/8	40.5	4,000	124	90
51	13 3/8	68	4,487	125	90
52	13 3/8	46	3,000	115	85
53	8 5/8	22	1,200	115	80
54	16	84	3,500	118	95
55	16	84	1,150	92	70
56	13 3/8	68	1,932	103	80
57	16	84	3,300	100	70
58	13 3/8	68	4,600	140	100
59	13 3/8	72	11,000	220	140
60	10 3/4	40.5	3,000	116	90
61	10 3/4	40.5	2,000	104	80
62	13 3/8	72	3,500	120	90
63	16	84	3,300	125	90
64	13 3/8	72	3,000	116	90
65	20	133	7,400	70	70
66	13 3/8	72	4,000	128	95
67	16	72	4,500	134	95
68	10 3/4	40.5	3,000	116	90
69	11 3/4	40	950	70	70
70	16	75	800	70	70
71	11 3/4	40	325	70	70
72	8 5/8	22	600	80	80
73	9 5/8	38	2,750	120	90
74	8 5/8	24	550	85	70
75	9 5/8	39	3,050	120	90
76	9 5/8	39	3,700	125	95
77	10 3/4	45.75	4,000	130	90
78	9 5/8	39	140	70	70
79	8 5/8	24	350	75	70
80	8 5/8	24	350	75	70
81	8 5/8	36	2,000	90	80
82	8 5/8	40	150	100	80

83	8 5/8	24	950	85	70
84	11 3/4	42	500	75	70
85	13 3/8	48	350	70	70
86	8 5/8	24	90	80	70
87	13 3/8	48	450	80	70
88	9 5/8	38	325	80	70
89	13 3/8	48	350	75	70
90	20	94	625	75	60
91	13 3/8	56	650	75	70
92	8 5/8	24	500	70	70
93	9 5/8	40	3,000	120	90
94	8 5/8	24	200	65	65
95	8 5/8	24	800	70	70
96	8 5/8	22	450	70	70
97	8 5/8	24	850	80	80
98	8 5/8	24	550	75	75
99	13 3/8	68	250	75	75
100	10 3/4	40.5	2,000	90	80
101	8 5/8	22	500	80	80
102	8 5/8	24	900	80	80
103	8 5/8	22	200	65	65
104	8 5/8	22	125	65	65
105	8 5/8	24	1,200	70	70
106	8 5/8	24	105	70	70
107	10 3/4	43	5,300	110	90
108	8 5/8	24	1,000	70	70
109	11 3/4	54	750	80	80
110	9 5/8	36	2,000	90	85
111	9 5/8	36	1,000	80	80
112	9 5/8	36	400	80	70
113	8 5/8	24	600	70	70
114	9 5/8	36	1,900	114	80
115	13 3/8	54.5	350	80	70
116	9 5/8	36	2,000	110	90
117	8 5/8	22	250	90	70
118	13 3/8	68	2,980	116	80
119	8 5/8	24	250	85	70
120	8 5/8	24	400	80	70
121	13 3/8	68	3,250	136	100
122	8 5/8	32	1,500	90	70
123	8 5/8	32	110	80	70
124	8 5/8	24	1,350	100	80

125	8 5/8	24	500	88	70
126	8 5/8	20	150	100	80
127	8 5/8	24	3,000	120	95
128	9 5/8	36	500	85	70
129	8 5/8	24	250	85	70
130	9 5/8	36	2,700	92	85
131	9 5/8	36	2,700	92	85
132	9 5/8	36	800	95	80
133	10 3/4	40.5	2,300	115	80
134	10 3/4	60.7	2,080	105	80
135	8 5/8	28	3,600	142	110
136	13 3/8	72	5,200	90	70
137	11 3/4	42	975	80	70
138	9 5/8	36	500	103	80
139	8 5/8	24	160	95	80
140	8 5/8	24	475	85	70
141	8 5/8	24	400	90	80
142	8 5/8	24	120	80	70
143	13 3/8	68	3,000	125	95
144	10 3/4	45.75	2,000	115	90
145	10 3/	60.7	3,250	100	80
146	8 5/8	24	600	85	70
147	8 5/8	20	320	70	70
148	13 3/8	72	980	70	70
149	9 5/8	40	1,500	103	80
150	9 5/8	36	1,800	95	70
151	8 5/8	24	200	85	70
152	8 5/8	24	150	85	70
153	9 5/8	36	600	80	60
154	8 5/8	32	950	100	80
155	13 3/8	72	4,900	141	100
156	13 3/8	72	4,500	132	95
157	13 3/8	68	4,000	135	105
158	8 5/8	28	1,900	85	70
159	13 3/8	54.5	450	70	60
160	13 3/8	68	3,000	125	90
161	10 3/4	40.5	2,000	110	80
162	9 5/8	43.5	2,000	95	80
163	20	94	2,000	110	90
164	8 5/8	24	3,300	120	90
165	10 3/4	40.5	1,900	105	80
166	13 3/8	72	5,000	120	90

167	13 3/8	68	3,000	125	95
168	13 3/8	54.5	450	69	60
169	8 5/8	24	600	90	80
170	13 3/8	68	6,100	160	120
171	13 3/8	61	40	65	65
172	11 3/4	38	250	70	70
173	8 5/8	24	1,500	70	60
174	9 5/8	36	800	77.5	65
175	10 3/4	40.5	550	75	70
176	9 5/8	36	500	110	90
177	9 5/8	38	500	100	90
178	13 3/8	61	600	110	90
179	12 1/2	36	80	80	80
180	9 5/8	36	1,300	80	80
181	9 5/8	38	500	110	90
182	8 5/8	30	1,000	90	90

Table 11.2.2—Intermediate Casing

Field No.	Csg. Size (in.)	Csg. Wt. (lb/ft)	Depth (ft)	BHST (°F)	BHCT (°F)
1	13 3/8	72	10,500	250	180
2	9 5/8	42.5	17,500	330	265
3	9 5/8	47	9,500	190	120
4	9 5/8	47	9,000	185	120
5	9 5/8	47	8,500	180	120
6	8 5/8	28	3,200	115	90
7	8 5/8	37	1,000	100	80
8	9 5/8	36	1,300	80	60
9	9 5/8	47	7,200	175	130
10	13 3/8	68	3,000	120	95
11	16	75	2,000	110	90
12	9 5/8	36	3,000	120	90
13	9 5/8	53	11,600	230	155
14	7 5/8	31.7	12,400	260	185
15	9 5/8	53.5	5,000	145	100
16	8 5/8	22	2,000	110	80
17	7	24.7	4,700	140	100
18	9 5/8	41.5	17,500	330	255
19	7	20	2,000	80	70
20	9 5/8	53.5	13,400	240	180
21	9 5/8	53.5	11,700	210	140
22	9 5/8	43.5	13,200	242	160
23	11 3/4	65	11,750	206	140
24	10 3/4	45.5	2,500	110	90
25	9 5/8	47	4,751	126	95
26	13 3/8	72	5,650	120	90
27	9 5/8	53.5	7,500	205	140
28	9 5/8	53.5	19,000	315	240
29	9 5/8	53.5	11,950	212	140
30	11 3/4	65	11,500	230	160
31	9 5/8	53.5	13,000	180	125
32	9 5/8	53.5	14,500	254	180
33	9 5/8	53	15,500	280	205
34	8 5/8	28	37,500	85	80
35	10 3/4	51	6,500	120	95
36	8 5/8	28	1,600	70	70
37	7 5/8	35	14,400	297.5	235
38	8 5/8	32	3,000	90	70
39	8 5/8	28	3,050	95	80
40	8 5/8	28	3,000	110	80

41	8 5/8	24	2,200	110	80
42	13 3/8	61	2,900	95	70
43	9 5/8	40	4,300	113	80
44	5 1/2	17	8,000	155	110
45	8 5/8	24	1,000	90	85
46	7 5/8	39	16,000	195	140
47	7 5/8	39	16,500	220	155
48	8 5/8	32	3,000	120	100
49	8 5/8	28	6,000	130	95
50	9 5/8	47	9,207	209	155
51	9 5/8	53.5	10,750	256	195
52	7	24.5	10,850	190	130
53	7	24.5	10,850	190	130
54	7 5/8	29.7	6,500	185	125
55	7 5/8	33.7	11,000	250	190
56	10 3/4	45.75	12,800	160	110
57	8 5/8	32	4,900	110	80
58	9 5/8	53.5	9,500	232	170
59	7 5/8	39	10,425	236	180
60	8 5/8	32	4,500	85	70
61	9 5/8	53.5	9,280	176	125
62	9 5/8	53.5	8,300	185	130
63	9 5/8	43.5	9,700	210	145
64	8 5/8	32	5,000	110	90
65	9 5/8	47	7,200	195	130
66	7 5/8	29.7	8,300	220	165
67	7	35	9,100	220	170
68	13 3/8	68	8,100	200	130
69	7 5/8	26.4	8,400	220	155
70	9 5/8	47	15,000	260	175
71	9 5/8	53.5	10,300	245	190
72	9 5/8	43.5	9,600	250	190
73	8 5/8	22	2,000	110	80
74	8 5/8	24	1,400	70	70
75	7	72	2,300	85	85
76	7	23	3,875	90	80
77	9 5/8	38	4,800	160	115

11.3 Appendix 3

TR00-1 Russian Hollow Microsphere Cements

Russian Hollow Microsphere Cements

TR00-1

By

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1. The Light-Duty Cements and Materials Used for Their Preparation

The traditional components for the light cements are: expanded clay aggregate, expanded perlite sand, filter perlite, burnt diatomite sand, petroleum coke, coal dust, Gilsonite, plaster, asbestos, Kerogen, and clay.

All of these components have large water requirements, and do not allow cement weights less than 1.45 g/cm^3 without changing other cement properties. Some of them (e.g., expanded perlite and sand) fail under pressure and form new surfaces, intensively linking water to the concrete mix, increasing cement density, and increasing circulation loss problems.

The addition of high strength hollow microspheres increases crack resistance, and reduces density and cement strength. The Russians have used hollow spheres made from phenol-formaldehyde and carbamide formaldehyde tars, which have a trademark Plaminol [1, 2].

The hydrophobic microspheres are filled with nitrogen to withstand pressures up to 15 MPa and allow cement weights of 1.20 g/cm^3 . Plaminol limitations are limited hydrostatic collapse strength, reduced cement strength, and high cost. Plaminol microsphere characteristics are shown in Table 1.

TABLE 1. Plaminol Microsphere Characteristics

Plaminol	Trademark (grade) FFP	Trademark (grade) MFP
1. Weight, g/cm^3		
- bulk	0.22-0.27	0.08-0.16
- mean	0.35-0.42	0.04-0.12
2. Dimensions, μm	50-400	50-300
3. Volumetric Compression Strength, MPa	20.0	15.0

The use of glass and ceramic microspheres made in the USA, Japan, Finland, Russia, and France have more potential. The hollow microspheres are produced from a mixture of liquid sodium silicate glass and a foaming agent. Carbonates, bicarbonates, sulphates, nitrates, and acids are used as foaming agents. The mass is dried and crushed after a foaming agent is added. The crushed powder is simultaneously melted and filled with gas bubbles (more often CO_2) during a high-temperature blending and blowing process. There are also other technologies, for example [3].

The glass microspheres have low density, high specific volumetric compression strength, low dielectric permeability in a broad band of frequencies, and good thermal insulation characteristics. There

is no irregular stress distribution around the microspheres as with other irregular fillers such as expanded perlite.

Silicate, carbon, ceramic, and natural crystalline phase volcanic glass microspheres are produced also. The Russian hollow glass microsphere performance is shown in Table 2.

TABLE 2. Russian Hollow Glass Microsphere Characteristics

Grade	Group	Weight		Dimensions			Min 10% destr.	Max	Dielectric	
		True	Volumetric				Strength	Appl. Temp. °C	Properties	
		G/cm³	g/cm³	µm *	µm *	µm *	MPa		ε	tgδ
MC	A1	0.24-0.32	0.13-0.20	156	77	35	2.0	700	-	-
	A2	0.26-0.32	0.14-0.21	119	51	39	2.8			
MC-A9	A1	0.24-0.32	0.14-0.21	148	79	38	3.0	150	1.4-1.6	0.008
	A2	0.26-0.32	0.16-0.21	104	48	27	4.5			
	B1	0.33-0.40	0.20-0.26	102	50	28	4.5			
	B2	0.31-0.36	0.19-0.24	110	59	29	5.0			
MC	B	0.15-0.30	0.08-0.20	159	83	33	0.8	650	1.4	0.002
	1L	0.20-0.24	0.12-0.16	116	64	40	4.5			
MC-VP	2	0.25-0.32	0.13-0.21	122	68	33	6.0	-	1.4	0.006
	1L	0.20-0.24	0.13-0.16	111	63	41	4.5			
MC-VP	2	0.25-0.31	0.16-0.20	128	67	34	6.5	150	1.6	0.006
	3	0.27-0.31	0.17-0.20	105	64	42	9.0			
BK	-	0.25-0.30	0.13-0.18	158	78	39	4.5	1100	1.2	0.0005

* – Typical values

** – Max. diameter for fractions with 90, 50, and 10% microsphere mass on the integral distribution line

*** – For frequency interval 0.1-10 Hz.

Microspheres are delivered in the polyethylene sacks, stacked in cardboard boxes. The boxes can be delivered in piles.

TABLE 2a. Domestic Aluminum Sodium Borosilicate Glass Hollow Microsphere Properties (Manufacturer: "Fiber Glass," Novgorod, "Glass Fibre Plastics," Moscow Area)

Parameter	Microspheres Grade			
	O Group A	O Group B	MCO-O A9 Group A	MCO-O A9 Group B
Weight, g/cm ³ :				
– bulk	0.12-0.16	0.16-0.20	0.12-0.16	0.15-0.20
– mean	0.24-0.30	0.31-0.40	0.24-0.30	0.31-0.40
Wall Thickness, μm	1-2	2-3	1-2	2-3
Thermal Conduction, W/(m°C)	0.06	-	-	0.067
Volumetric Compression Strength MPa	10.0-15.0	12.0-18.0	12.0-15.0	15.0-20.0

Notes: Diameter – up to 200 microns, Volume Space Factor – 0.6

The properties of hollow microspheres made in countries outside of Russia are shown in Tables 3 to 10.

TABLE 3. Hollow Glass Microsphere Properties
Manufacturer: “Emerson and Cuming Inc.” (USA)

Parameter	Grade					
	Sodium borosilicate glass				SI (Silica – 95%)	VT (Silica with finishing agent)
	IG101	IG101D	IG25	R		
Weight, g/cm ³ :						
– bulk	0.19	0.19	0.14	0.17	0.15	0.16
– mean	0.31	0.30	0.24	0.36	0.25	0.27
Dimensions, μm	<200	<150	<175	<200	<175	<175
Volume Space Factor	0.62	0.65	0.61	0.46	0.56	0.60
Wall Thickness, μm	2	1.5	1.5	2	1.5	1.7
Initial Softening Temperature, °C	480	480	480	480	1000	315
Thermal conduction, W/(m °C)	0.06	-	-	-	-	-

TABLE 4. Hollow Glass Microsphere Properties
Manufacturer: “Minnesota Mining Manufacturing Co.” (USA)

Parameter	GRADE							
	B15/ /250*	B20/ /350*	B23/ /500*	B28/ /750*	D35/ /1000*	B38/ /2000*	FT- 102	FTD- 202
Weight, g/cm ³ :								
– bulk	0.12-0.18	0.17-0.23	0.2-0.26	0.2-0.3	0.35	0.38	0.16	0.15
– mean	-	-	-	-	-	-	0.26	0.24
Volumetric Compression Strength, MPa	25.0	35.0	50.0	75.0	100.0	200.0	-	-
Dimensions, μm	-	-	-	-	-	-	<200	<200
Volume Space factor	-	-	-	-	-	-	0.62	0.62
Wall thickness, μm	-	-	-	-	-	-	1.5	1.2
Initial Softening Temperature, °C	-	-	-	-	-	-	1093	1093

* Close to ordinary leaf glass composition and structure

TABLE 5. Ceramic, Corundum, and Rock Hollow Microsphere Properties

Parameter	Manufacturer, Country		
	Seva Denco Norton Co., Japan, USA (Ceramic)	Carborundum Co., USA (Corundum)	Sirasy, Japan (Volcanic Glass, Feldspar and Quartz)
Weight, g/cm ³ :			
– bulk	0.6-0.9	0.25-0.4	0.14-0.32
– mean	-	-	0.39-0.69
Dimensions, μm	100-8000	40-500	30-6000
Volume Space factor			
Wall Thickness, μm	-	2.3-4.0	6-14
Initial Softening Temperature, °C	-		900-1000
Thermal Conduction, W/(m °C)			0.08
Volumetric Compression Strength, MPa	8.6	-	1.5-2.0

TABLE 6. Pearlite, Silicate, and Carbon Hollow Microsphere Properties

Parameter	Grade, Country – Manufacturer		
	Pearlite USA, France	Q-Cel, Silicate USA, Finland	Carbospheres, Carbon USA
Weight, g/cm ³ :			
– bulk	0.062-0.099	0.1	0.12-0.14
– mean	0.17-0.41	0.2	0.20-0.22
Dimensions, μm	75-145	20-200	5-150
Wall Thickness, μm	0.7-1.5	-	1-2
Thermal conduction, W/(m °C)		0.043	
Volumetric compression strength, MPa	-	-	-

TABLE 7. Carbon Hollow Microsphere (Krecaspheres) Properties
Manufacturer: “Kurecha Karaku” (Japan)

Parameter	Grade			
	A-50	A-100	A-200	A-300
Weight, g/cm ³ :				
– bulk	0.1-0.3	0.1-0.3	0.07-0.20	0.05-0.20
– mean	0.15-0.4	0.15-0.40	0.15-0.35	0.10-0.30
Dimensions, μm	45-75	75-150	150-250	250-420
Wall Thickness, μm	1-2	2-3	3-8	6-12

TABLE 8. Hollow and Polymeric Microsphere Properties

Parameter	Ceramic (Aluminum Silicate)	Polymeric (Phenol-Formaldehyde)
	"Drilling Fluids Service" Poland	"PolymerSyntez" Vladimir, Russia
Weight, g/cm ³ : – bulk – mean	0.32-0.45 0.65-0.8	0.35-0.45 0.7-0.9
Dimensions, μm	<500	-
Wall Thickness, μm	1400	-
Thermal Conduction, W/(m °C)	0.06	0.05
Volumetric Compression Strength, MPa	<5	<4

Note: Volume Space factor - 0.6

Ceramic, glass and polymer microsphere chemical compositions are shown in Table 9 [4].

TABLE 9. Hollow Microsphere Typical Chemical Structure

Components	Microsphere Structure %		
	Glass	Ceramic	Polymer
SiO ₂	60-80	55-59	-
Al ₂ O ₃	4-10	27-31	-
Fe ₂ O ₃	-	4.6-5.5	-
K ₂ O	5-16	3.2-3.7	-
CaO	5-25	1.1-1.8	-
MgO	0-15	1.3-1.7	-
SO ₂ /SO ₃	-	0.05-0.1	-
Cl	-	<0.1	-
Na ₂ O	5-16	1.0-2.0	-
MnO ₂	0-10	-	-
B ₂ O ₅	10-20	-	-
P ₂ O ₅	0-5	-	-
Phenol-formaldehyde	-	-	100

Fractional components of Portland cement made with polymer (PM) and ceramic microspheres (CM) are shown in the Table 10 and X-ray patterns (Fig. 1 and Fig. 2).

TABLE 10. Microspheres and Portland Cement Fractional Structure

Particle Dimension μm	Contents, %				
	Cement Grade			Ceramic CMS	Polymeric PMS
	PC	GMS	AGMS		
0-15				-	-
16-30	12.8	22.3	23	-	-
31-45	32.6	40.5	40.6	-	5
46-60	28.1	27.2	25.7	5	10
61-80	15	10	10.7	5	5
81-250	8.8	-	-	78	60
251-500	2.7	-	-	12	20
Mean	2.7	-	-	140.2	110.3
	35.9	25.45	24.98		

AGMS denotes finished MCO-A9 Group B microspheres. Finish agent is a silicone fluid:

γ - aminopropylsilane $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$. Finished agent required quantity is 0.3% from a microsphere mass.

We can see the peaks $(3.52; 3.22; 4.04) \cdot 10^{-10}$ m on the X-ray pattern (Fig. 1), stipulated probably by a sodium borosilicate glass and boroaluminate glass peak $(2.81; 4.29; 3.80) \cdot 10^{-10}$ m. These components add glass corrosion resistance.

Microspheres with metal cover on external and internal surfaces are developed in the USA also as well as sodium borosilicate glass and boroaluminate glass microspheres [5, 6, 7].

The use of microspheres requires the enlarged contents of water, as a rule, with the purpose of a sliding stratum creation [8, 9]. Waterless sodium metasilicate (3%) have to be added for preservation of microspheres wholeness during intermixing.

It is known, the sodium glass has stability to acids, but is liable to attack by alkaline medium, which is present in cement systems.

Under the judgement of the contributors majority, the cement matrix aggression in the relation to the glass with the $\text{Ca}(\text{OH})_2$ content increase [10]. It is recommended to enter: ashes – ablation, puzzolana, pumice, slag, ashes, expanded clay aggregate sand, and expanded clay, i.e., components to bind lime, for reduction of the cement matrix aggression [11,12, 13, 14].

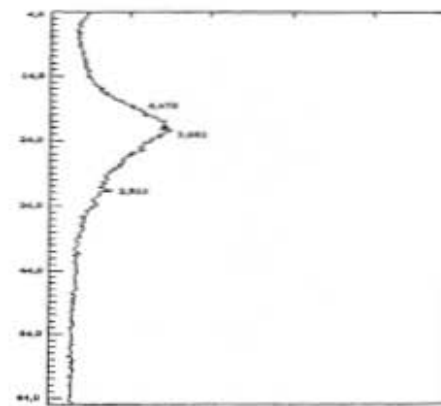


Fig. 1. GMS X-Ray Pattern

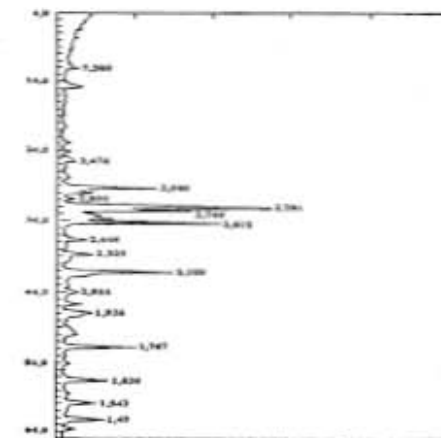


Fig. 2. PC X-Ray Pattern (Manufacturer: Volsky works, Russia)

Leaching takes place on a glass surface during the first stage of cementing. A protective calcium hydrosilicate diffuse layer together with silicon acid forms during the second stage. During the third stage, leaching of surface imperfections takes place along with crystalline hydrate crystallization and growth. This shows that surface protection of the glass microspheres is a necessity.

Silicones or other silicone liquids are used to produce a good cement adhesion with matrix and protect the glass surfaces.

Boron and aluminum silicates are the most chemical strong materials [15]. Difficult-to-dissolve hydroxides and water silicates are generated in protective films on glass surfaces by alkaline earth oxide hydrolysis. Silicon acid gels remain on the surface and slow down silicate glass destruction [15].

Ten years Russian experience has shown that microsphere corrosion does not occur with cements.

The properties of Portland cements (PC) made with polymeric (PMS) and ceramic (CMS) microspheres are shown in Tables 11 and 12.

TABLE 11. Light Cement Parameters

Seq.	Cement Mix		Mean Weight g/cm ³	Fluidity Sm	Circulation P _m ¹⁰⁰ , h-min	Setting Period h-min	
#	% (by mass)					Start	End
1	PC, Water	100 50	1.825	17	1-30	1-55	2-35
2	PC, CMS, Water	100 10 80	1.470	23	2-10	2-30	3-20
3	PC CMS, Water	100 15 90	1.400	25	2-2	2-45	3-40
4	PC, CMS, Water	100 20 105	1.330	25	2-30	3-10	4-15
5	PC, CMS, Water	100 25 115	1.280	25	2-45	3-45	5-15
6	PC, PMS, Water	100 10 75	1.340	24	1-4	2-05	2-55
7	PC, PMS, Water	100 15 85	1.230	24	1-35	2-05	3-20
8	PC, PMS, Water	100 20 95	1.170	24	1-35	1-55	3-35

Notes: Temperature 75°C, atmospheric pressure

TABLE 12. Polymeric and Ceramic Microsphere Cement Properties

Seq. No.	Cement Mix (% by Mass)	Stone Strength, MPa			Body Adhesion Strength MPa
		Bending Strength	Compressive Strength		
			Top	Bottom	
1	PC 100 Water 50	<u>5.25/2.1</u> —	<u>24.93/13.2</u> —	<u>24.93/13.2</u> —	<u>2.96/1.5</u> —
2	PC 100 Water 90 CMS 15	<u>4.46/2.3</u> <u>5.34/2.7</u>	<u>9.90/5.0</u> <u>10.20/5.2</u>	<u>13.20/6.8</u> <u>16.50/8.4</u>	—
3	PC 100 CMS 20 Water 105	<u>2.38/1.2</u> —	<u>6.93/3.5</u> —	<u>12.54/6.29</u> —	—
4	PC 100 CMS 25 Water 115	<u>1.25/0.6</u> —	<u>3.66/1.9</u> —	<u>3.96/2.0</u> —	<u>0.92/0.5</u> —
5	PC 100 PMS 10 Water 75	<u>3.86/2.0</u> <u>3.86/2.0</u>	<u>6.60/3.4</u> <u>7.26/3.7</u>	<u>6.60/3.4</u> <u>10.56/5.3</u>	—
6	PC 100 PMS 15 Water 85	<u>1.19/0.6</u> —	<u>6.27/3.1</u> —	<u>6.6/3.4</u> —	—
7	PC 100 PMS 20 Water 95	<u>0.47/0.25</u> —	<u>2.31/1.3</u> —	<u>2.77/1.9</u> —	<u>1.26/0.6</u> —
Note: 1. Temperature 75°C/22°C, atmospheric pressure. 2. Numerator – grouting mortar is not treated by pressure, denominator – grouting mortar is treated by pressure 30 MPa.					

The effect of pressure on cement weight is shown in Figs. 3 and 4 for light cements containing polymeric and ceramic microspheres.

Рис. 3 Изменение плотности облегченных цементных растворов в зависимости от давления обработки:

1 - 100 % ПЦТ-Д20-100 +
+ 15 % КМС + 90 % воды;
2 - 100 % ПЦТ-Д20-100 +
+ 10 % ПМС + 75 % воды

1

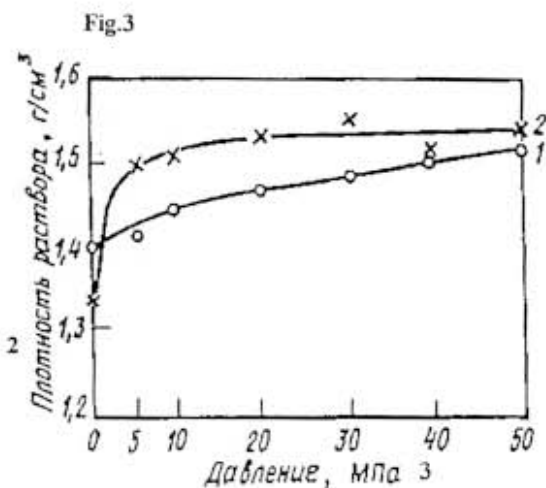


Fig.4

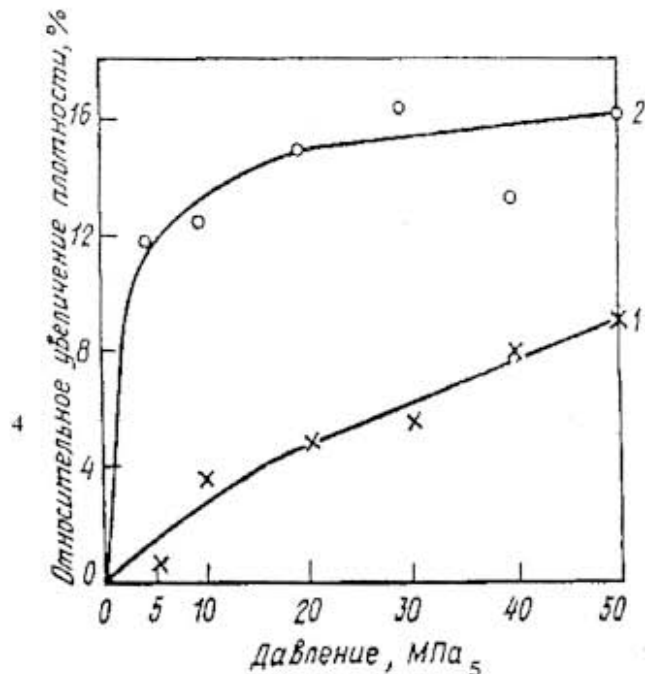


Рис. 4 Влияние величины давления на относительное увеличение плотности облегченных тампонажных растворов (разрушение микросфер) при одинаковой средней плотности, % (по массе).
Условные обозначения см. рис. 4.2

Figs. 3 and 4 captions in English are as follows:

1. Light oil-well cement weight vs. treatment pressure
 - 1) 100% PC-D20-100 + 15% CMS + 10% Water
 - 2) 100%PC-D20-100 + 10% PMS + 75% Water
2. Weight, g/cm³
3. Pressure, MPa
4. Relative weight magnification, %
5. Pressure, MPa
6. Oil-well light relative weight (microspheres failure) magnification vs. pressure

TABLE 13. Cement and Stone Mixture with the Glass Microspheres Components

Composition, %	Setting Period h-min		W/C**	Strength MPa		Dry Mean Weight g/cm ³	Humidity % Mass	Dry Water Absorption %		Cement Martix Volume Fraction
	Start	End		Compres.	Bending			Mass	Volume	
GMS Doping										
GMS,10	3-05	5-50	0.45	14.4	2.68	1.042	8.79	26.52	27.63	0.529
PC, 100										
GMS,20	3-05	6-10	0.645	7.38	2.147	0.762	9.29	35.41	26.27	0.451
PC,100										
GMS,30	3-05	6-30	0.925	5.12	1.317	0.603	9.01	42.26	25.49	0.391
PC,100										
PC from Sebriakovsk Works	3-05	5-50	0.22	51.93	8.833	1.829	7.28	15.47	28.29	1
AGMS Doping										
AGMS,10	3-20	5-20	0.364	16.58	3.82	1.052	7.24	14.31	15.05	0.577
PC,100										
AGMS, 20	3-25	5-40	0.562	10.16	2.65	0.725	7.13	20.84	15.11	0.438
PC,100										
AGMS, 30	3-30	6-10	0.730	6.08	1.84	0.601	8.04	28.14	16.91	0.366
PC, 100										

** Cone spread 115 mm, W/C – Water/Cement Ratio

Note: PC – Portland Cement, GMS – Glass Microspheres, AGMS – Glass Microspheres with aminopropylsilane

The microstructure of cement made with GMS and AGMS microspheres shown in Fig. 5 was obtained using a scanning electronic microscope CAMSKAN (UK).

The cement weight as a function of glass microspheres mass fraction is shown in Fig. 6 and as a function of water/cement ratio (W/C) in Fig. 7. The impact of microspheres fraction on the cement strength is shown in Fig. 8.

The permeability and adhesive bond strength of cements containing glass microspheres are shown in Table 14, and the rheological properties are shown in the Fig. 9.

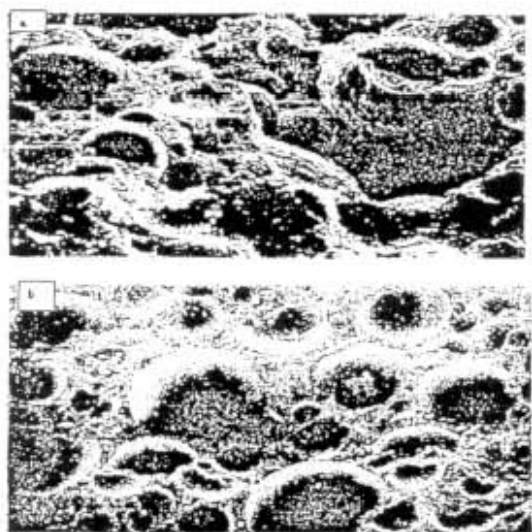


Рис. 5. Микроструктура цементной затравки: (а) – с ГМС, (б) – с АГМС x 400. Рис. 5.

Fig. 5 caption:

1. Fig. 5. Plugging cement microstructure: (a) – with GMS, (b) – with AGMS x 400

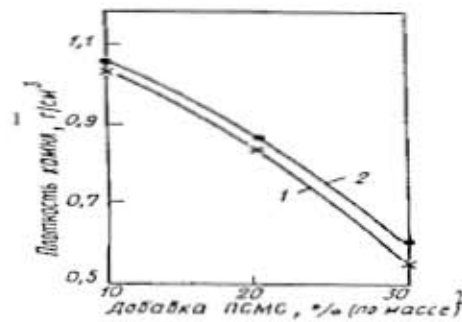


Рис. 6. Зависимость средней плотности облегченного цементного тампонажного камня от содержания микросфер: 1, 2 — в возрасте 28 и 180 сут соответственно

Fig. 6

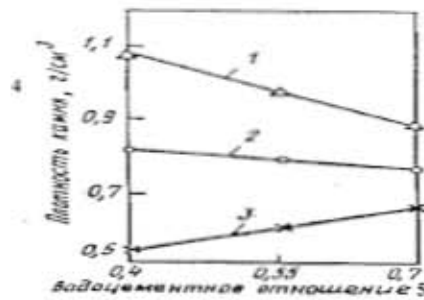


Рис. 7. Зависимость средней плотности облегченного цементного тампонажного камня от В/Ц: 1, 2, 3 — с добавкой ПСМС в количестве 10, 20 и 30 % (по массе) соответственно

Fig. 7

Fig. 6 and Fig. 7 captions (English):

1. Plugging cement weight
2. GMS mass fraction, %
3. Mean plugging cement weight vs. microspheres mass fraction
 - 1) — 28 days cement age
 - 2) — 180 days cement age
4. Plugging cement mean weight
5. Water/cement ratio
6. Mean plugging cement weight vs. water/cement ratio
 - 1) — 10% GMS mass fraction
 - 2) — 20% GMS mass fraction
 - 3) — 30% GMS mass fraction

Fig.8

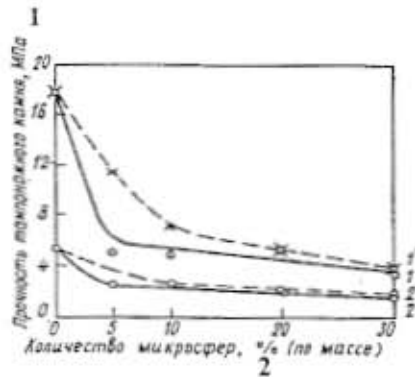


Рис. 8. Зависимость прочности облегченного цементного камня от расхода микросфер: 1, 1' — прочность при сжатии; 2, 2' — прочность при изгибе; 1, 2 — с ПСМС; 1', 2' — с АПСМС

Fig.9

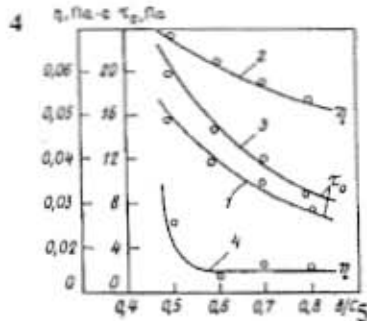


Рис. 9. Зависимость реологических свойств различных растворов от водорасового отношения: 1, 2 — облегченные растворы с добавкой микросфер; 3, 4 — раствор из портландцемента; τ_0 — динамическое напряжение сдвига; η — пластическая вязкость

Fig. 8 and Fig. 9 captions (English):

1. Oil-well cement strength
2. Microspheres mass fraction, %
3. Light oil-well cement strength vs MS mass fraction
 - 1,1' — compression strength
 - 2,2' — bending strength
 - 1,2 — GMS cement
 - 1',2' — AGMS cement
4. η , Pa·Sec., τ_0 , Pa
5. W/C — water/cement ratio
6. Rheological characteristics vs. water/cement ratio
 - 1,2 — light cement with microspheres
 - 3,4 — cement mix
 - τ_0 — yield point
 - η — plastic viscosity

**TABLE 14. Adhesive Bond Between Plugging Cement and Glass or String Metal.
(Plugging Cement Permeability)**

Mix #	Mass Fractions, %			W/C	Permeability $10^{-3} \mu\text{m}^2$	Bond Strength MPa	
	PCT	GMS	AGMS			Glass	Metal
1	100	-	10	0.44	0.0023/0.0038	0.43/0.22	1.71/0.88
2	100	10	-	0.75	0.029/0.05	0.57/0.3	1.25/0.65
3	100	-	-	0.50	0.0041/0.008	0.40/0.25	2.38/1.25

Notes: 1. Conditions of plugging cement setting: temperature 75°C/22°C, atmospheric pressure.
2. Numerator – parameters at the temperature of 75°C

As stated above, one of the lightweight fillers is filter pearlite. VolgogradNIPINeft (Lukoil Oil Research Institute) found that filter pearlite collapsed at pressures of 30 MPa. Filter pearlite is a waste of expanded pearlite production technology and has low cost.

Filter pearlite's specific surface is 3000 cm²/g, average size of particles is 29.22 μm , and the density is 2.19 g/cm³.

Chemical composition:

component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	PPP
fraction, %	74	13	0.8	3.5	4	3/4

Caustic magnesite (CMA) and superplasticizer (SP) are used as additives to improve cement characteristics. Mathematical planning matrixes and filter pearlite cement characteristics are presented in Tables 15 and 16.

The component CMA ensures a volume increase during the solidification and improves bond strength with the casing and borehole walls. Superplasticizer (SP) reduces cement water requirements by 20-25% and ensures low porosity decrease.

TABLE 15. Mathematical Planning Matrix, Cement, and Stone Properties

Mix #	Factors (cement mass fraction, %)		Efficiency functions									
			W/C	P _p g/cm ³	p ¹⁰⁰ _h	Humidity, %		R, MPa		R _{bs} MPa	P ₀ g/cm ³	B _M %
	FP	SP				mass	vol.	bend	comp			
1.	30	1.5	1.25	1.33	1.25	4.92	5.42	2.55	7.14	0.85	0.93	32.8
2.	30	0	1.6	1.32	0.85	2.83	4.33	1.4	2.31	0.12	0.72	59.0
3.	0	1.5	0.26	2.86	0.75	0.93	1.92	9.2	43.3	3.1	1.93	9.16
4.	0	0	0.5	1.81	1.0	1.83	2.92	5.9	17.9	1.54	1.54	20.6
5.	30	0.75	1.25	1.38	1.25	5.25	6.0	2.9	6.18	0.81	1.04	21.9
6.	0	0.75	0.26	2.09	0.75	1.17	2.0	11.0	46.0	3.4	2.01	5.0
7.	15	1.5	0.72	1.56	0.92	3.33	6.25	4.4	11.0	2.02	1.11	15.7
8.	15	0	1.0	1.45	0.65	2.92	3.75	2.7	2.56	0.65	1.20	18.6
9.	15	0.75	0.73	1.57	0.75	3.33	6.25	3.8	7.1	1.94	1.33	11.4
10.	15	0.75	0.73	1.56	0.74	3.3	6.15	3.7	7.0	1.9	1.32	11.2
11.	15	0.75	0.73	1.56	0.75	3.32	6.2	3.8	7.1	1.92	1.32	11.3

Convention: $\frac{p100}{m}$ – circulation; R – strength, R_{bs} – bond strength between steel casing and cement stone; P₀ – means dry stone density; P_p – cement solution density; B_M – water requirements (% of dry stone mass), FP – filter pearlite; SP – superplasticizer

Table 16. Mathematical Planning Matrix, Additive Cement Solution and Cement Stone Properties (Additions: Filter Pearlite and Caustic Magnesite)

Mix #	Factors (Cement Mass Fraction, %)			Efficiency functions									
				W/C	P _p g/cm ³	p _m ¹⁰⁰ h	Humidity, %		R, MPa		R _b MPa	P ₀ g/cm ³	B _m %
	FP	SP	CMA				Mass	vol	bend	Comp			
1'	30	1.5	15	1.3	1.35	1.75	3.08	4.83	2.1	4.72	1.04	1.03	62.3
2'	0	1.5	15	0.41	1.92	0.75	2.16	2.75	5.4	19.9	3.71	1.85	21.1
3'	30	0	15	1.55	1.38	1.33	2.67	3.75	1.9	3.25	0.52	0.94	62.5
4'	0	0	15	0.56	1.83	0.75	1.92	2.58	3.5	11.2	1.68	1.63	27.0
5'	30	1.5	5	1.25	1.38	1.0	2.25	3.68	2.1	5.88	0.52	0.98	63.6
6'	0	1.5	5	0.34	1.88	0.75	1.68	3.68	4.5	11.3	2.55	1.8	20.3
7'	30	0	5	1.6	1.33	0.75	1.25	4.08	1.5	2.88	0.23	0.95	78.2
8'	0	0	5	0.5	1.84	0.7	1.0	2.0	5.1	14.1	1.6	1.58	26.6
9'	30	0.75	10	1.35	1.37	0.75	1.25	4.68	2.3	3.99	0.75	1.06	65.9
10'	0	0.75	10	0.42	1.84	1.0	1.75	2.75	5.0	13.6	2.66	1.87	22.4
11'	15	1.5	10	0.9	1.49	1.1	1.5	3.5	3.4	10.1	1.42	1.16	17.8
12'	15	0	10	1.0	1.5	0.68	1.5	2.5	2.25	4.77	0.72	1.3	47.8
13'	15	0.75	15	0.95	1.55	1.0	1.68	4.0	2.2	5.04	1.18	1.4	43.3
14'	15	0.75	5	0.87	1.44	1.68	2.0	3.68	2.25	6.93	1.62	1.3	44.4
15'	15	0.75	10	0.88	1.48	1.16	1.92	3.68	2.5	6.82	1.04	1.37	42.4
16'	15	0.75	10	0.88	1.49	1.16	1.9	3.65	2.6	6.83	1.1	1.35	42.6
17'	15	0.75	10	0.88	1.48	1.2	01.93	3.68	2.6	6.8	1.05	1.35	42.7
Please see Table 15 convention													

These light cements were first field tested in the JSC "LUKOIL" branch "Nizhnevolzhskneft" oilfields (Volgograd region) where there were used to overcome low formation pressures and lost circulation problems. The tests were conducted in the permafrost zones of the Yamal peninsula mainly by Tumenbargas, a branch of the RAO "GAZPROM."

Wells and cement weights are listed in Table 17.

TABLE 17. Oil-Well Light Cement Industrial Oilfield Introduction

Well number, oilfield	Casing MD m	TOC m	Mean Cement Weight g/cm ³
EPS – Expanded Pearlite Sand, Nizhnia Volga			
9 Pamiatnaj	2627	wellhead	1.39
10 Pamiatnaj	2633	"	1.40
11 Pamiatnaj	2477	"	1.40
135 Pamiatnaj	2663	"	1.40
137 Pamiatnaj	2592	"	1.38
139 Pamiatnaj	2563	"	1.39
195 Sasovskaj	2556	"	1.40
67 Dobrinskaj	2611	"	1.40
68 Dobrinskaj	2738	"	1.42
136 Pamiatnaj	2688	"	1.40
6 Chernuschinskaj	3017	"	1.40
9 Chernuschinskaj	2805	"	1.40
FP – Filter Pearlite, Nizhnia Volga			
78 Tersinskaj	2383	"	1.38
377 Pologaj	2106	"	1.40
372 Pologaj	2103	"	1.40
2 Demidivskaj	2643	"	1.43
329 Pologaj	2100	"	1.40
44 Maily-Haranskaj	3100	"	1.36
42 Maily-Haranskaj	3100	"	1.36
26 Ovrazhnaj	2641	"	1.39
81 N-Korobovskaj	2439	"	1.40
17 Kluchevskaj	2966	"	1.36
71 Tereninskaj	2380	"	1.38
AGMS – Finishing Hollow Glass Microspheres, Nizhnia Volga			
108 Sasovskaj	2520	"	1.38
13 Pamiatnaj	2592	"	1.36
141 Pamiatno-Sasovskaj	2595	"	1.38
143 Pamiatno-Sasovskaj	2604	"	1.36
29 Chernuschinskaj	2982	"	1.40
7 Chernuschinskaj	3022	"	1.40
8 Chernuschinskaj	2929	"	1.40
14 Chernuschinskaj	3070	"	1.40
ASHM – Aluminium Silicate Ceramic Hollow Glass Microspheres, Zapolairnaj			
244	3200	"	1.36
1022	1400	"	1.50
1023	1405	"	1.52
1043	1436	"	1.50
1044	1432	"	1.50
1116	1415	"	1.50
1141	1355	"	1.52
1142	1428	"	1.50
1146	1411	"	1.47
1153	1420	"	1.50
1156	1350	"	1.50
ASHM – Aluminium Silicate Ceramic Hollow Glass Microspheres, Ubileinoe			
272	1228	"	1.35
ASHM – Aluminium Silicate Ceramic Hollow Glass Microspheres, Urengoijskoe			
741	-	-	1.50
2361	2799	2806-1300	1.50
8337	-	-	1.35
8338	1406	-	1.35
10261	1283	Circulation loss	1.50
10262	1362	"	1.40
10263	1329	Wellhead	1.40
10264	1302	"	1.40
AGMS – Finishing Hollow Glass Microspheres, Zapolairnaj			
1021	1441	Underlift	1.50
1025	-	-	1.50
1026	1420	Wellhead	1.50
1040	1399	Partial circulation loss	1.5
1041	1425	Wellhead	1.50
1042	1420	-	1.40

Well number, oilfield	Casing MD m	TOC m	Mean Cement Weight g/cm ³
1045	1350	Wellhead	1.46
1046	1425	"	1.47
1093	1400	"	1.50
1094	1401	"	1.48
1095	1398	"	1.49
1101	1419	"	1.50
1111	1420	"	1.50
1112	1425	Underlift	1.50
1114	1407	Wellhead	1.51
1115	1431	"	1.50
1143	1440	"	1.50
1144	1406	"	1.50
1145	1410	Full circulation loss	1.50
1154	1417	Wellhead	1.48
1155	1418	"	1.45
AGMS – Finishing Hollow Glass Microspheres, Urengoi			
2359	2792	-	1.50
AGMS – Finishing Hollow Glass Microspheres, Komsomolskoe			
1321	1089	Wellhead	1.50
1322	1084	"	1.50
106-H	1030	"	1.40
AGMS – Finishing Hollow Glass Microspheres, Bovanenkovskoe			
6502	450	Conductor	1.50
HMS- High-Strength Hollow Glass Microspheres, Urengoi			
2359	2792	-	1.50
AGMS – Finishing Hollow Glass Microspheres, Komsomolskoe			
1321	1089	Wellhead	1.50
1322	1084	"	1.50
106-H	1030	"	1.40
AGMS – Finishing Hollow Glass Microspheres, Bovanenkovskoe			
6502	450	Conductor	1.50
HMS – High-Strength Hollow Glass Microspheres, Urengoi			
738	3612	Wellhead	1.40
8408	2883	Underlift	1.40
201336	3279	Wellhead	1.40
HMS – High-Strength Hollow Glass Microspheres, Peszovskoe			
208	3500	1 stage before casing shoe	1.50

Convention: EPS – expanded perlite sand, FP – filter perlite, GMS – hollow glass microspheres, AGMS – finishing hollow glass microspheres, ASHM – aluminium silicate ceramic HGMS, HMS – high-strength HGMS

The industrial oilfield testing confirmed the economic and technical benefits of the light-weight microspheres cements.

Aluminum silicate hollow microspheres (ASHM) were used to reduce costs. ASHM are the production wastes of the Kamensk-Schahtinskaj PowerStation. They consist of hollow spherical elements with aluminum silicate shells with the following properties: diameter – from 5 up to 100 microns, wall thickness – 2-15 microns, density – 0.3-0.4 g/cc, melting temperature – 1200-1300°C, hydrostatic collapse strength – 35.0-40.0 MPa (5075 to 5800 psi). ASHM inside gas phase consists of a mixture of nitrogen and CO₂.

For deeper wells, when the strength requests exceed 50 MPa (7250 psi), high-strength microspheres (HMS) manufactured by "Fiberglass," Andreevka City, Moscow region were used.

Aluminum oxide hollow microspheres from (corundum) are also produced in Russia. The main application of these microspheres is in high-temperature applications, and the greatest benefit is obtained when the corundum microspheres are used as a powder. High melting temperature, low thermal conduction, and small microsphere densities are used to form ultra lightweight refractories with a minimum binder quantity, for long operation at temperatures up to 1800°C.

The main characteristics of these aluminum oxide microspheres are shown in Table 18.

Table 18. Aluminium Oxide Microspheres Characteristics

Grade	Chemical Composition mass %	Volume Density g/cm ³	Dimensions, μm*			Melting Temp. °C	Dielectric Properties***	
			d90**	d50**	d10**		ε	tgδ
T	Al ₂ O ₃ 99.7	0.29-0.40	230	137	76	1800	2.4	0.0003

* Typical significances

** Maximal particle size for the fractions with 90, 50, and 10% microspheres weight-part concentration correspond to integral percentile curve

*** For a frequent interval of 0.1-10 Hz

These aluminum oxide microspheres are also used to manufacture new tool-class, high-porous grinding wheels and for metal working. The corundum microspheres increase grinding tool capacity 2.5 to 8 times when grinding composite alloying steels and permanent magnets and provide excellent processing quality. The important advantage of the aluminum oxide microsphere wheels is the high ecological processing cleanness compared to traditional high porous wheels.

Aluminum oxide microspheres have low dielectric permeability and their small dielectric losses ensure their effective application in composite materials for HF – SHF radio engineering and electronics engineering. These materials are used in the production of foil-clad dielectric, printed boards. An important advantage of aluminum oxide microspheres is their high stability in humid environments, ensuring high operational stability.

Neviansky cement works (Sverdlovsk region – Southern Ural) started using aluminum oxide microspheres in light-weight cement in 1998. Portland cement is manufactured from the power station's waste. These power stations are working on Ekibastus coal, cleared from organic impurities. In accordance with preliminary information, the microspheres density is ~0.4 g/cm³. In Table 19, the properties of light-weight cements containing aluminum oxide microspheres used in the Sverdlovsk region are compared with other lightening components. Their application differs from glass, since cement thickening agents are used to prevent the microspheres from floating upward.

**Table 19. Oil-Well Cement with Aluminum Oxide Microsphere Properties
at the Temperature of 20°C**

Oil-well Cement	Weight g/cm	Fluidity sm	Water/ Solid Fraction Ratio %	Setting period		Water Sediment %	Thickening Time h-min	Strength In 48 hours	
				Start h-min	End h-min			Bend MPa	Comp
1. At the All-Union state standard 1581- 91 request	1.35-1.65	18-22	0.6-1.3	>2 h	<18 h	<3		0.7	
2. Vermiculite-cement based on the CaCl ₂ solution	1.5	24	0.8	4 h 55 min	9 h 35 min		>3 h	0.7	
3. Gel Cement	1.5	20	0.8	13 h 20 min	16 h 40 min	0		0.7	
4. Glass microsphere additive	1.5	25	0.8	8 h 20 min	10 h 40 min	1		1.6	5
5. Aluminum silicate microspheres	1.5	24	0.8	9 h 25 min	11 h 45 min	0	3 h 10 min	2	6
7. Aluminum silicate MS + powder Bentonite	1.5	22	0.8	8 h 15 min	9 h 00 min	0		2.2	8.7
7. Aluminum silicate microspheres	1.3	21	0.6	10 h 45 min	13 h 15 min	1		1.3	4
8. Aluminum silicate MS + powder Bentonite	1.31	25	0.65	12 h 40 min	16 h 20 min	0	6 h 20 min	1.2	3.12
	1.4	25	0.6	10 h 35 min	13 h 10 min	0	6 h 20 min	1.6	4.47
	1.43	30	0.9	10 h 50 min	2 h 15 min	0	7 h 50 min	1.48	3

These aluminum oxide microspheres are manufactured by the company OOO “Bentonite of Ural” together with the company OAO “Neviansky Cementnik” under industrial conditions based on the oil-well Portland cement PC-DO-50, manufactured by “Neviansky Cement Works.”

Despite limited oilfield experience with light-weight cements (0.7 g/cm³ and less), the data in Tables 13 and 15 and in Figs. 6 and 7 as well as expert consensus and separate laboratory experiments, confirm the ability to produce effective light-weight oilfield cements with densities of 0.7 g/cm³ using microspheres. Design of these light-weight cements must consider cement strength, gas permeability, and cement properties for specific application conditions.

Conversion Chart:

1 MPa = 145 psi
1 meter = 3.28 feet
1 g/cc = 8.34 lb/gal

1.1 MICROSPHERE MANUFACTURERS IN RUSSIA AND POLAND

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4. JSC [Polymersintez]
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5. Poland Drilling Mud Service
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