Ultra-Lightweight Cement

Revised Tenth Quarterly Technical Progress Report

January 1 to March 31, 2003

Fred Sabins

Issued June 16, 2003

DOE Award Number
DE-FC26-00NT40919

Submitted by
Cementing Solutions, Inc.
4613 Brookwoods Drive
Houston, TX 77092

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

The objective of this project is to develop an improved ultra-lightweight cement using ultra-lightweight hollow glass spheres (ULHS). This report discusses testing that was performed for analyzing the alkali-silica reactivity of ULHS in cement slurries.

Table of Contents

<i>Introduction</i>	2
<i>Executive Summary</i>	3
<i>Alkali-Silica Reaction (ASR) Data Summary</i>	3
<i>ASR Test Protocol</i>	5
Testing Procedures.....	5
Testing Conditions	6
Mixing Procedures	6
Mold Preparation	6
Curing the Specimens for Compressive and Tensile Strength Testing.....	6
Specimen Preparation for Compressive and Tensile Strength Testing	7
Test Measurement for Compressive Strength.....	7
Test Measurement for Tensile Strength.....	7
<i>Expansion</i>	8
Curing the Specimens	8
Test Apparatus	9
Test Measurement	9
<i>Conclusions</i>	11
<i>List of Acronyms and Abbreviations</i>	12
<i>References</i>	12

Introduction

Oilwell cementing involves placing a pumpable slurry of Portland cement, additives, and water into a wellbore. The slurry is pumped into the annular space between the borehole and a steel pipe (called a casing) that acts as a conduit from the reservoir to the surface. The setting of cement in place serves three important functions: (1) it supports the casing in the hole, (2) it isolates various formations from one another, and (3) it controls fluid movement within the well.

Typically, cement fluid density is anywhere from 12 to 17 lb/gal. Certain conditions that require the application of low-density cements can be encountered during the well construction process. Lower density is required (1) to limit hydrostatic pressure on the formation, and (2) to prevent the formation from fracturing and imbibing the well fluid. This phenomenon, known as lost circulation, increases drilling and completion times and increases construction cost because of the need for expensive remedial treatments. Lost circulation most commonly occurs in the upper sections of the well, where surface and intermediate casings are installed. Because formations covered by these casings are relatively close to the Earth's surface, application temperatures for these low-density cements are low.

The minimum density achievable with conventional cements and additives is approximately 11 lb/gal. At this density, the slurry's stability and set cement's strength and permeability are only marginally acceptable. Adding water to reduce the density of these conventional cements is impractical because additional water dilutes the cement, causing low strength and high permeability. Low temperatures, such as those in the upper well sections, delay strength development. To obtain a lower cement density or greater cement strength, ultra-lightweight materials must be mixed into the slurry.

Ultra-lightweight hollow spheres (ULHS) are excellent candidate materials for producing ultra-lightweight cements. These small hollow glass beads effectively trap air in the slurry, thereby lowering the slurry density without the addition of water. This project is designed to develop cementing systems using ULHS through a carefully designed program of modeling, design, laboratory testing, and field-testing.

The goals of this portion of the project are to study the long-term effects of the alkali-silica reaction in cements and to conduct a comprehensive evaluation of the ULHS from 3M and the potential for this product to be susceptible to ASR. The expansion and tensile and compressive strengths of eight different cement specimens are being tested.

ASR is a potentially damaging phenomenon that occurs in cement materials containing certain types of silica-containing materials and exposed to alkali in a high pH environments. The ASR reaction produces alkali-silicate gel, which swells and disrupts the cement's crystalline lattice. This reaction can cause expansion of the cement and reduced strength.

Executive Summary

Laboratory testing during the tenth quarter focused on evaluation of the alkali-silica reaction of eight different cement compositions, four of which contain ULHS. The original laboratory procedure for measuring set cement expansion resulted in test specimen erosion that was unacceptable. A different expansion procedure is being evaluated

This report provides a progress summary of ASR testing. The testing program initiated in November produced questionable initial results so the procedure was modified slightly and the testing was reinitiated. The results obtained with the modified procedure showed improvement over data obtained with the original procedure, but questionable data were obtained from several of the compositions. Additional modification of test procedures for compositions containing TXI Lightweight cement are being implemented and testing is ongoing.

Alkali-Silica Reaction (ASR) Data Summary

Approval was made for a continuation of the current cooperative agreement with DOE. This agreement consisted of a new task to study the long-term effects of the Alkali-Silica Reaction (ASR) in ULHS cements. The goal of this task is to determine procedures and methods from the construction industry that are applicable to oil well cements, and conduct long-term tests to verify if ASR is occurring and when and how it manifests itself. Compositions to be tested in the ASR evaluation are listed in Table 1.

As a baseline for testing, neat Class H cement with a density of 16.4 lb/gal and TXI Lightweight cement with a density of 13.5 lb/gal is used. Ultra-light hollow sphere (ULHS) slurries with similar bead concentrations and a density of 9.0 lb/gal will also be used. Several 0.5% sodium chloride slurries are used to evaluate accelerated ASR.

The results obtained thus far are presented in Tables 2 through 4. Test specimens of several compositions are being recast via a modified procedure to ensure proper curing. Testing will continue until the project's scheduled ending.

Table 1—Compositions Tested

Slurry Composition Number	Description	Density (lb/gal)	Water Requirement (gal/sk)
1	Class H Cement	16.4	4.30
2	TXI Lightweight Cement	13.5	6.00
3	Class H Cement + 42% 3M Beads	9.0	11.69
4	TXI Lightweight Cement + 37% 3M Beads	9.0	12.63
5	Class H Cement + 0.5% Salt	16.4	4.30
6	TXI Lightweight Cement + 0.5% Salt	13.5	6.00
7	Class H Cement + 42% 3M Beads + 0.5% Salt	9.0	11.81
8	TXI Lightweight Cement + 37% 3M Beads + 0.5% Salt	9.0	12.63

Table 2—Compressive Strength, Normalized to 24-Hour Values

Slurry	24 hours	7 days	14 days	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
1	1.00	1.46	1.48	2.45	X	X	X	X	X
2	*	*	*	*	*	*	*	*	*
3	1.00	0.93	1.78	1.37	X	X	X	X	X
4	*	*	*	*	X	X	X	X	X
5	1.00	0.86	1.14	2.30	X	X	X	X	X
6	*	*	*	*	*	*	*	*	*
7	1.00	0.95	1.86	1.57	X	X	X	X	X
8	*	*	*	*	*	*	*	*	*

*Test not performed pending new test method

X – Test in progress

Compressive strength testing was performed on cylinder molds rather than 2-in. cubes. Therefore, these compressive strength data are normalized to the initial 24-hour reading for each slurry.

**Table 3—Tensile Strength,
Normalized to 24-Hour Values**

Slurry	24 hours	7 days	14 days	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
1	1.00	0.70	0.45	0.70	X	X	X	X	X
2	*	*	*	*	*	*	*	*	*
3	1.00	0.58	0.89	0.64	X	X	X	X	X
4	*	*	*	*	*	*	*	*	*
5	1.00	0.59	0.57	0.58	X	X	X	X	X
6	*	*	*	*	*	*	*	*	*
7	1.00	0.68	1.23	0.83	X	X	X	X	X
8	*	*	*	*	*	*	*	*	*

*Test not performed pending new test method

X – Test in progress

Table 4—% Linear Expansion

Slurry	24 hours	7 days	14 days	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
1	0	0.03	0.03	-0.06	-0.05	X	X	X	X
2	*	*	*	*	*	*	*	*	*
3	0	0.01	0.02	0.38	0.40	X	X	X	X
4	*	*	*	*	*	*	*	*	*
5	0	-0.02	-0.01	0.06	0.06	X	X	X	X
6	*	*	*	*	*	*	*	*	*
7	0	-0.05	-0.04	0.31	0.30	X	X	X	X
8	*	*	*	*	*	*	*	*	*

*Test not performed pending new test method.

X – Test in progress

ASR Test Protocol

Testing Procedures

A variation of the Standard Test Method for Length Change of Hardened Hydraulic-Cement, Mortar, (ASTM C157/C157M-99) was used to test expansion in the slurries. An expansion measurement is taken at 24 hours, 7 days, 14 days, 28 days and every consecutive month for the duration of the project. For statistical purposes, six replicates of each slurry are made.

A variation of Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens (ASTM C496-96) was used to determine a change in the tensile strength of specimens as a result of ASR. For this testing, the slurry is placed in a 1.5 x 5-in. mold sealed at both ends.

A tensile strength measurement is performed at 24 hours (initial reading), 7 days, 28 days, 2 months, 4 months, and 6 months. Data is normalized. For statistical purposes, six replicates of each slurry are made.

A compressive strength test is performed using modified API procedures. Specimens are poured into cylinder molds and compressive strengths are measured on specimens cut from the cylinders. A compressive strength measurement is performed at 24 hours, 7 days, 28 days, 2 months, 4 months, and 6 months. For statistical purposes, 3 replicates of each slurry are made.

Testing Conditions

- Curing Temperature – 174°F
- Slurries tested up to 200 days.

Mixing Procedures

Prepare a ULHS slurry as follows.

1. Weigh the appropriate amounts of the cement sample, additives, water, and ULHS into separate containers.
2. Mix the cement slurry according to Appendix A of API RP 10B.
3. Pour the slurry into a metal mixing bowl and slowly add ULHS while continuously mixing by hand with a spatula. Mix thoroughly.
4. Place this slurry in a Waring blender and mix at 4,000 rpm for 15 seconds.

Mold Preparation

Prepare the molds as follows.

1. Place slurry in a mold, filling to approximately one-half of the mold depth, and puddle it.
2. Stir the remaining slurry by hand and place into additional molds and repuddle it.
3. Seal the molds and place them upright in a heated, circulating water bath at 174°F.

Curing the Specimens for Compressive and Tensile Strength Testing

One of the test slurries (containing six replicates) is prepared each day until all samples for the project have been made. Cure each test specimen in a heated, circulating water bath at 174°F, containing saturated-lime curing water, as described in the procedure below.

1. Remove specimens from the molds at an age of 23 ½ hours. Age of each specimen is measured from the moment when water is added to the cement during the mixing operation.

2. Mark specimens for identification or positioning as required on brass plates inscribed with slurry design.
3. Place the specimens in lime-saturated water maintained at $73.4 \pm ^\circ\text{F}$ ($23.0 \pm 0.5^\circ\text{C}$) for a minimum of 15 min.
4. After specimen identification, specimens for testing at greater than 24 hours are returned to lime saturated water at 174°F .

Specimen Preparation for Compressive and Tensile Strength Testing

After curing, the sample is extracted from the mold and cut into 1-in. $\pm 1/8$ in. sections in length. A $1/4$ -in. section of the top surface of the sample is cut first. Next, the three 1-in. sections to be measured are cut. Each 1-in. $\pm 1/8$ in. section is identified as top, middle, and bottom. The end sample pieces are discarded. The density of each sample is calculated before it is measured for compressive or tensile strength. The density is calculated by suspending the cut-core samples in water and weighing them using a Denver Instruments Lab Balance, model TR-2102.

1. Place the specimens in lime-saturated water maintained at $73.4 \pm ^\circ\text{F}$ ($23.0 \pm 0.5^\circ\text{C}$) for a minimum of 15 min.
2. When the specimens are $24 \pm 1/2$ hours in age, remove them from water storage one at a time, wipe with a damp cloth, and determine compressive strength.
3. After specimen identification, return all specimens for testing at greater than 24 hours to lime-saturated water at 174°F .

Important—Monitor the curing water weekly to ensure that the lime concentration of the saturated aqueous solution is at 1,600 mg/L, ± 300 mg/L.

Test Measurement for Compressive Strength

Each sample is placed in a Carver Press (hydraulic). Force is applied in accordance with API Specification 10B-7.5.6.1. The force at specimen's failure is recorded and is converted to strength in psi.

Test Measurement for Tensile Strength

Tensile strength tests are performed at the Westport Technology Center. The core specimens are cured at CSI and transported to Westport after they have been cured at the desired age. The specimens are delivered submerged in lime-saturated water, and testing is performed within 24 hours.

At Westport, tensile strength testing is performed according to ASTM Standards C496-96. The force is applied by constant displacement of the bottom plate at a rate of 1 mm every 10 minutes.

The maximum reading is noted and used in the following equation:

$$T(\text{psi}) = (2 * F) / (\pi * L * D)$$

Where

T = tensile strength (psi)
F = maximum force recorded (lbf)
PI = 3.14
L = sample length (inch)
D = sample diameter (inch)

Fig. 1 shows a general schematic of how each specimen is oriented on its side during testing.

Figure 1—Tensile strength crush diagram

Expansion

Curing the Specimens

One of the test slurries (containing six replicates) is prepared each day until all samples for the project have been made. Cure each test specimen at 174°F in a heated, circulating water bath containing saturated-lime curing water, as described in the procedure below.

1. Remove specimens from the molds at an age of 23 ½ hours. Age of each specimen is measured from the moment when water is added to the cement during the mixing operation.
2. Etch specimens for identification or positioning as required with a scribe, inscribed with slurry design and expansion bar number on each specimen as it applies.
3. Place the specimens in lime-saturated water maintained at $73.4 \pm 0.5^\circ\text{F}$ ($23.0 \pm 0.5^\circ\text{C}$) for a minimum of 15 min. This helps minimize variation in length measurements due to variation in temperature of the specimens.

Important—Monitor the curing water weekly to ensure that the lime concentration of the saturated aqueous solution is at 1,600 mg/L, +/- 300 mg/L.

Test Apparatus

Molds for test specimens used in determining the length change of cement pastes and mortars produce 1×1×1 ¼-in. prisms with a 10-in. gage length (see Figure 2). The gage length is the nominal length between the innermost ends of the gage studs.

Test Measurement

When the specimens are $24 \pm \frac{1}{2}$ hours in age, remove them from water storage one at a time, wipe with a damp cloth, and immediately take a comparator reading. Then, return each specimen in lime-saturated water at 174°F.

The comparator shown in Figure 3 features a dial micrometer graduated to read in 0.0001-in. units, accurate within 0.0001 in. in any 0.0010-in. range, and within 0.0002 in. in any 0.0100-in. range, and sufficient range (at least 0.3 in.) in the measuring device to allow for small variations in the actual length of specimens.

Reference Bar

Place the reference bar (Figure 3) in the instrument in the same position each time a comparator reading is taken. Check the dial gage setting of the measuring device by taking a comparator reading of the reference bar at least at the beginning and end of a series of specimen readings to span no more than a half-day, provided the apparatus is kept in a room maintained at constant temperature.

To obtain a comparator reading, perform the following steps.

1. Clean the hole in the base of the comparator into which the gage stud on the lower end of the bar fits.
2. Read and record the comparator indication of the length of the reference bar.
3. Take one bar out of curing bath, blot the pins, and place the bar in the comparator, read, and record the indication.
4. Return the bar to curing bath and clean the hole in the base of the comparator.
5. Repeat the procedure with second and subsequent bars until all bars have been read, returned to curing bath, and the readings recorded.
6. After reading the last bar, clean the hole in the comparator base and read and record the reference-bar indication. Blot only around the pins.

Calculate the specimen length change at any age as follows:

$$L = \frac{(L_x - L_i)}{G} \times 100$$

Where:

L = change in length at x age, %

L_x = comparator reading of specimen at x age minus comparator reading of reference bar at x age;

L_i = initial comparator reading of specimen minus comparator reading of reference bar at that same time

G = nominal gage length, 10 in.

Figure 2—Expansion test specimen mold schematics

Figure 3—Reference bar

Conclusions

1. Usable ASR test specimens have been poured.
2. The testing regime is on schedule.
3. Compressive strength results indicate no adverse effect from curing in the caustic curing medium.
4. Tensile strengths of most specimens appear to be decreasing.
5. Expansion is occurring in compositions containing Class H cement and salt.

List of Acronyms and Abbreviations

API—American Petroleum Institute
ASR—alkali-silica reactivity
ASTM—American Society for Testing and Materials
Bc—Bearden units of consistency
BHCT—bottomhole circulating temperature
BHST—bottomhole static temperature
BWOC—by weight of cement
CaCl₂—chemical formula for calcium chloride
cp—centipoise
gal—gallon
H₂O—chemical formula for water
hr—hour
ID—inner diameter
in.—inch
J—Joule
lb—pound
md—millidarcy
min—minute
MMS—Minerals Management Service
OD—outer diameter
psi—pound per square inch
rev—revolution
rpm—revolutions per minute
s—second
sk—sack of cement
QC—quality control
TXI—Texas Industries
TXI LW—manufactured lightweight cement available from TXI
ULHS—ultra-lightweight hollow (glass) spheres
3K—3,000-psi designation
6K—6,000-psi designation

References

1. “Recommended Practices for Testing Well Cements,” API Recommended Practice 10B, 22nd Edition, American Petroleum Institute, Washington, D.C., December 1997.
2. “Standard Test Method for Length Change of Hardened Hydraulic-Cement, Mortar, and Concrete,” ASTM C157/C157M-99, Annual book of ASTM Standards Vol. 04.02.
3. “Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens,” ASTM C496-96, Annual Book of ASTM Standards Vol. 04.02.