Ultra-Lightweight Cement

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Disclaimer

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.

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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 to limit hydrostatic pressure on the formation, and 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, a portion of the mix water must be replaced with ultra-lightweight materials.

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 (ASR) 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 formulations are being tested.

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

Executive Summary

Laboratory testing during the thirteenth quarter focused on evaluation of the alkali-silica reaction of eight different cement compositions, four of which contain ULHS. This report provides a progress summary of ASR testing. The original laboratory procedure for measuring set cement expansion resulted in unacceptable erosion of the test specimens. In subsequent tests, a different expansion procedure was implemented and an alternate curing method for cements formulated with TXI Lightweight cement was employed to prevent sample failure caused by thermal shock.

The results obtained with the modified procedure showed improvement over data obtained with the original procedure, but data for some compositions were still questionable. Additional modifications of test procedures for compositions containing TXI Lightweight cement were implemented.

Alkali-Silica Reaction (ASR) Data Summary

Approval was granted 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 oilwell cements, and conduct long-term tests to verify whether 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. ULHS slurries with similar bead concentrations and a density of 9.0 lb/gal were used.

The results are presented in Tables 2 through 7. Test specimens of several compositions were recast via a modified procedure to ensure proper curing. Revised test methods are outlined in the ASR Test Protocol section of this report.

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

*All additives are %BWOC

Table 2—Compressive Strength at 174°F, Class H Slurries Normalized to 24-Hour Values

Slurry	24 hr	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	2.05	3.22	2.68	4.37	4.08
3	1.00	0.93	1.78	1.37	1.60	1.19	1.23	2.43	2.13
5	1.00	0.86	1.14	2.30	1.91	3.00	2.46	2.48	2.95
7	1.00	0.95	1.86	1.57	1.40	1.55	1.22	2.09	2.34

*Average of three replicates

Table 3—Compressive Strength at 174°F, TXI Lightweight Slurries Normalized to 24-Hour Values

Slurry	24 hr	7 days	14 days	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
2	1	1.23	1.13	0.79	1.18	1.62	1.74	1.78	1.73
4	1.00	0.83	0.74	0.88	1.02	1.28	1.51	1.40	1.40
6	1.00	1.28	1.00	1.35	1.27	1.07	1.67	1.38	1.33
8	1.00	0.81	0.93	0.93	0.92	1.34	1.70	1.57	1.76

*Average of three replicates

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 4—Tensile Strength at 174°F, Class H Slurries Normalized to 24-Hour Values

Slurry	24 hr	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	0.72	0.75	0.68	1.12	0.84
3	1.00	0.58	0.89	0.64	0.68	0.82	0.75	1.01	0.84
5	1.00	0.59	0.57	0.58	.60	0.88	0.70	0.87	0.99
7	1.00	0.68	1.23	0.83	0.66	0.54	0.63	0.65	1.03

*Average of six replicates

Table 5—Tensile Strength at 174°F, TXI Lightweight Slurries Normalized to 24-Hour Values

Slurry	24 hr	7 days	14 days	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
2	1.00	0.77	0.74	0.92	0.66	0.72	0.42	0.34	0.34
4	1.00	0.79	0.99	1.25	1.15	1.21	1.05	1.07	1.19
6	1.00	0.67	0.68	0.79	0.65	0.60	0.27	0.35	0.21
8	1.00	0.70	1.24	1.55	0.81	0.92	1.62	0.74	0.69

*Average of six replicates

Table 6—Percentage of Linear Expansion at 174°F, Class H Slurries

Slurry	24 hr	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	-0.06	-0.05	-0.04	-0.04
3	0	0.01	0.02	0.38	0.40	0.39	0.38	0.60	0.61
5	0	-0.02	-0.01	0.06	0.06	0.02	0.06	0.07	0.07
7	0	-0.05	-0.04	0.31	0.30	0.30	0.30	0.35	0.33

*Average of six replicates

Table 7—Percentage of Linear Expansion at 174°F, TXI Lightweight Slurries

Slurry	24 hr	7 days	14 days	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
2	0.15	0.19	0.19	0.2	0.31	0.34	0.37	0.40	0.41
4	0.04	0.06	0.06	0.04	0.1	0.12	0.13	0.12	0.14
6	0.14	0.17	0.17	0.17	0.24	0.26	0.32	0.36	0.42
8	0.02	0.04	0.04	0.04	0.06	0.08	0.06	0.07	0.10

*Average of two replicates

Conclusions

1. The testing regime is complete.
2. Compressive strength results indicate no major adverse effect from curing in the caustic curing medium.
3. Tensile strengths of slurry composition numbers 1, 2, 3, 6 and 8 show a decrease over time. Slurry composition numbers 5 and 7 decrease early on but increase back to a baseline value by the end of the testing period. Slurry composition number 4 had an increase in tensile strength over time.
4. Expansion occurs in all compositions except in slurry composition number 1.

Appendix A—Alkali-Silica Reactivity (ASR) Lightweight Testing

Testing Procedures

A ***compressive strength*** test was performed using modified API procedures. Specimens were poured into cylindrical molds and compressive strengths were measured. A compressive strength measurement is performed at 24 hours, 7 days, 28 days, 2 months, 4 months, and every consecutive month for the duration of the project. For statistical purposes, three replicates of each slurry are made.

A variation of Splitting Tensile Strength of Cylindrical Concrete Specimens (ASTM C496-90) was used to determine a change in the ***tensile strength*** of the specimens to determine if ASR may occur in cement containing ULHS. A tensile strength measurement is performed at 24 hours, 7 days, 28 days, 2 months, 4 months, and every consecutive month for the duration of the project. For statistical purposes, six replicates of each slurry are made.

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 Class H 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 Test Methods for Determination of Shrinkage and Expansion of Oilfield Cement Formulations (ISO-WD-10426-5) was used to test ***expansion in TXI Lightweight 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, two replicates of each slurry are made.

Testing Conditions

- Slurries were tested for a minimum of 200 days.
- Curing temperature was 174°F.**

***NOTE: To help prevent thermal shock of the lightweight cement, which can cause a variance in test data, TXI lightweight specimens are ramped from room temperature to 174°F in a freshwater bath prior to being placed in a lime-saturated bath.*

Mixing Procedures

Prepare slurry designs that do not contain ULHS according to Appendix A of API RP 10B.

Prepare slurries containing ULHS as follows.

1. Weigh appropriate amounts of the cement sample, additives, water, and ULHS into separate containers.
2. Mix the cement slurry containing all additives except ULHS 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 the slurry in a 1000 ml Waring blender and mix at 4,000 rpm for 15 seconds.

Alkali-Silica Reactivity (ASR) Testing for Expansion of TXI Lightweight Slurries

The testing method used for measuring expansion of TXI Lightweight specimens is similar to that described in ISO/WD 10426-5, Test Methods for Determination of Shrinkage and Expansion of Oilwell Cement Formulations. For this testing, the slurry is placed in annular ring molds.

Test Apparatus

The annular expansion ring mold is a device suitable for measuring expansion properties of a cement formulation. It consists of five separate parts (Figures A-1 and A-2):

- base
- top lid
- internal ring
- external expandable ring with gage studs
- set bolt (holds the mold together)

The outside diameter of the inner ring is 50.8mm (2 in.), and the inside diameter of the outer expansion ring is 88.9mm (3.5 in.).

Preparation of Mold and Specimens

The mold is prepared according to ISO/WD 10426-5.3.1. The specimen is prepared according to ISO/WD 10426-5.3.2.

Curing Procedures

To help prevent thermal shock of the lightweight cement, which can cause a variance in test data, all TXI lightweight specimens are cured using a temperature ramp method. All samples are placed in a freshwater bath at room temperature (approximately 80°F). Then, a bath heater is turned on and temperature is ramped to 174°F at a rate of 2°F /min. After the bath has reached 174°F, samples are placed in a lime-saturated bath at 174°F.

Test Measurement

Immediately after the mold is filled with slurry and before the specimen is cured in a lime-saturated bath, an initial measurement is taken. A micrometer with a precision of 0.01 in. is used to measure the distance between the two steel gage studs.

After the specimen is cured, a second measurement is taken in the same manner as the initial measurement. This measurement must be performed immediately after the specimen is removed from the 174ºF bath to prevent erroneous measurement due to excessive cooling.

Calculate the expansion as follows:

$\%_{dc} = (d_f - d_i) \times 9.095$

Where

$\%_{dc}$ = dimensional change of the cement sample (expressed as a percentage)
d_f = final distance measured after curing (expressed in inches)
d_i = initial distance measured before curing (expressed in inches)

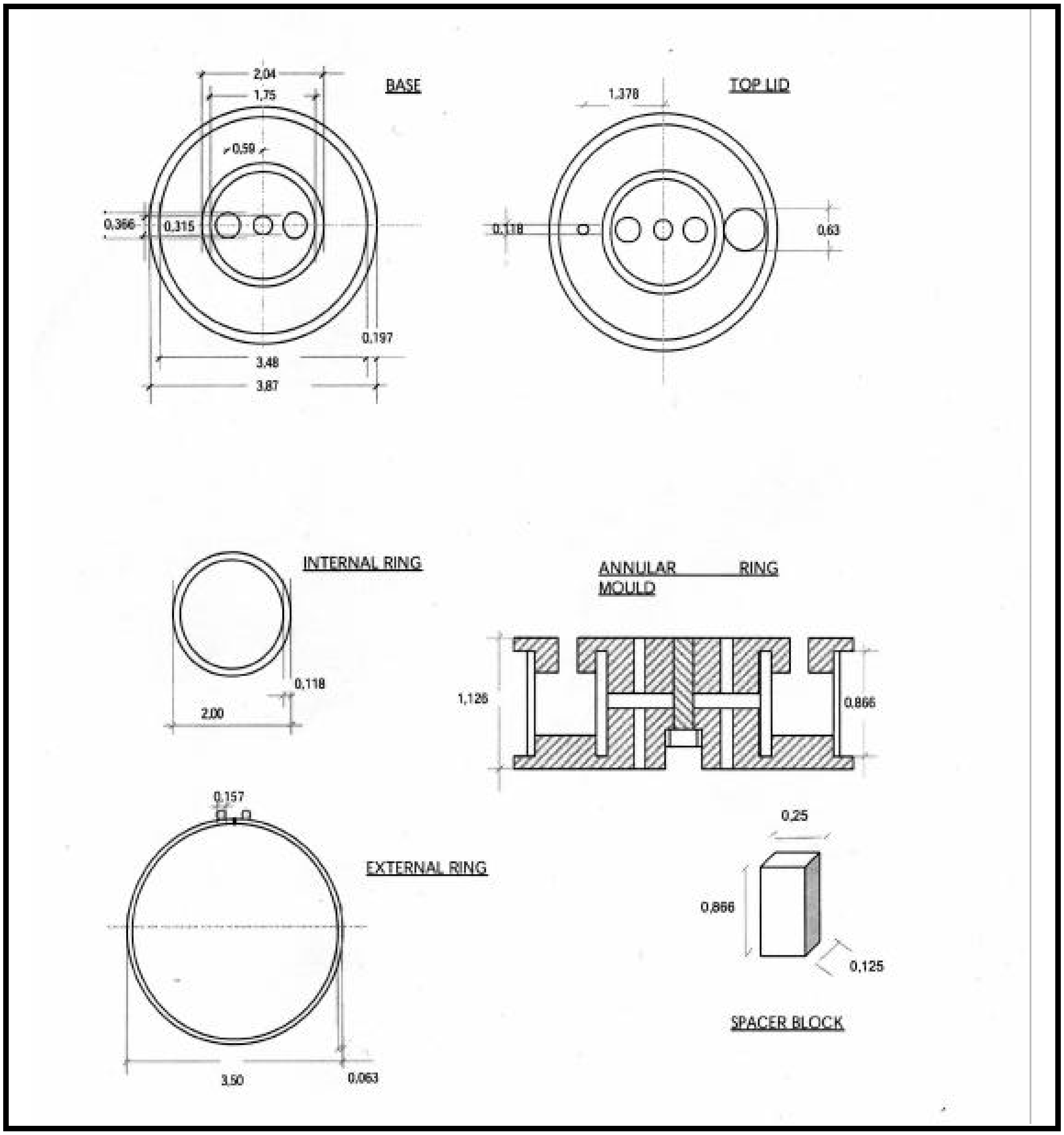
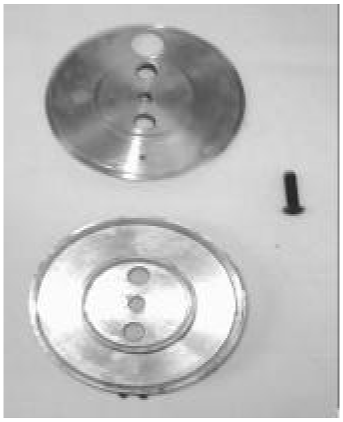


Figure A-1—Test specimen mold schematic

 (a)

 (b)

Figure A-2—Annular ring mold

Alkali-Silica Reactivity (ASR) Testing for Expansion of Class H Slurries

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 Class H 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.

Test Apparatus

Molds for test specimens used in determining the length change of cement pastes and mortars produce 1×1×11 ¼-in. prisms with a 10-in. gage length (see Figure A-3). The gage length is the nominal length between the innermost ends of the gage studs.

Curing Procedures

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. The 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 scriber, 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 ±°F (23.0 ± 0.5°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 Measurement

When the specimens are 24 ± ½ 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 A-4 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 A-4) 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 length.
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 length. 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, %
Lx = comparator reading of specimen at *x* age minus comparator reading of reference bar at *x* age;
Li = initial comparator reading of specimen minus comparator reading of reference bar at that same time
G = nominal gage length, 10 in.

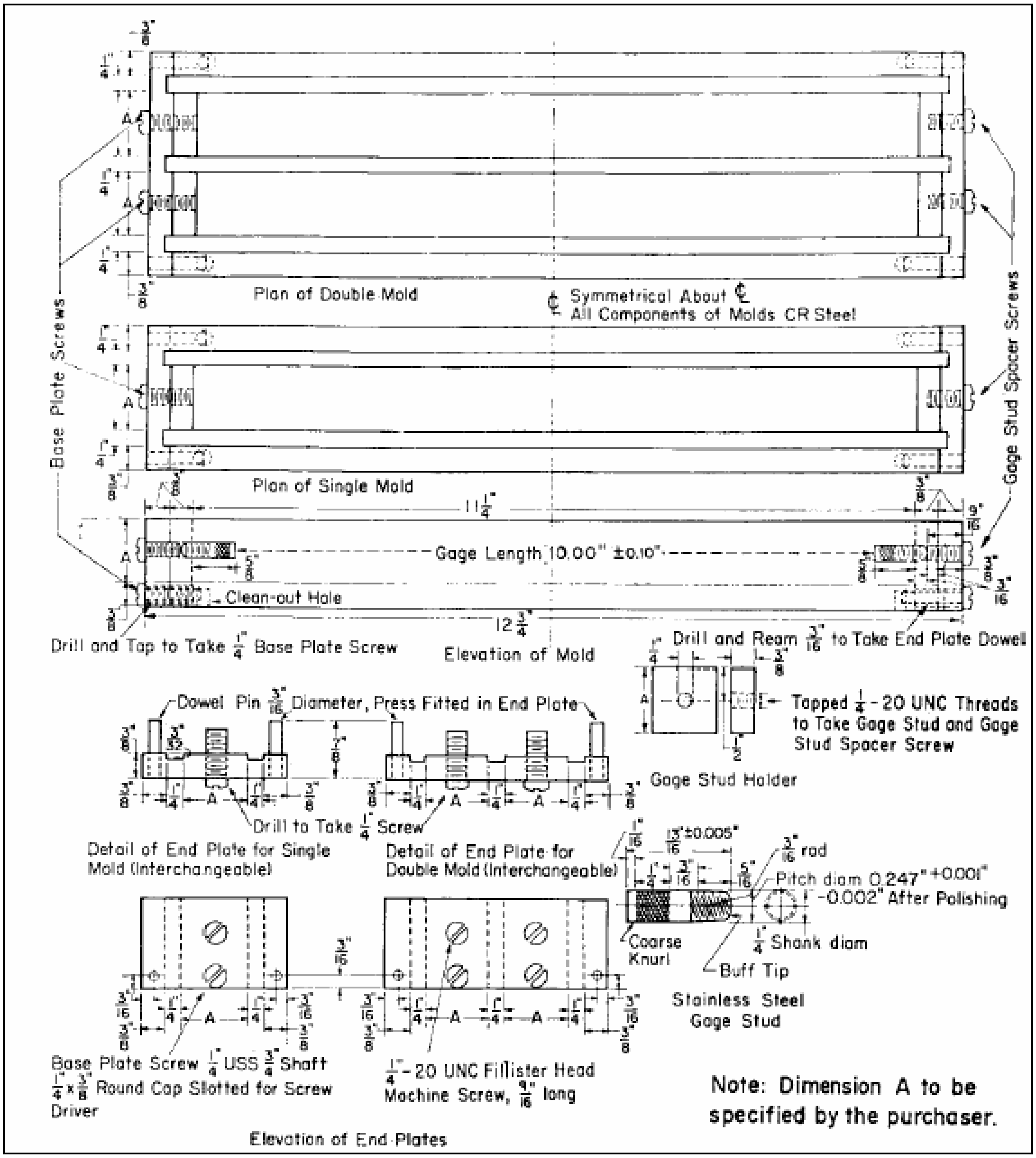
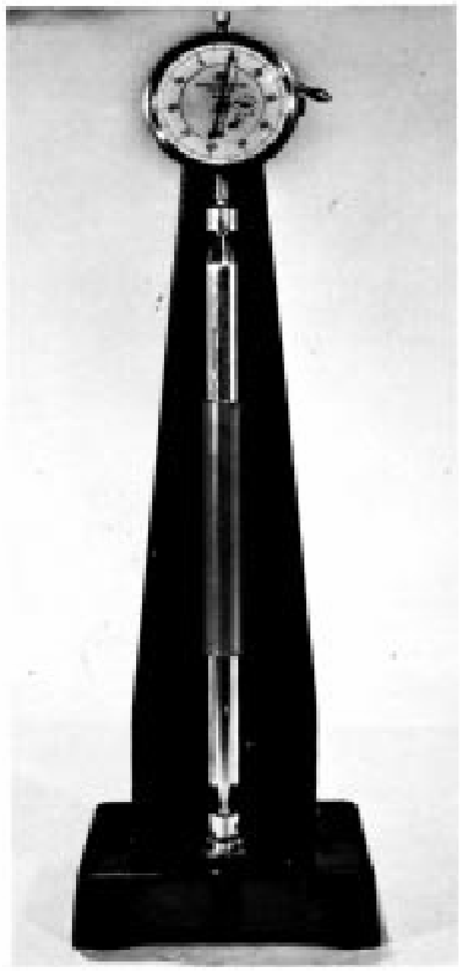


Figure A-3—Expansion test specimen mold schematics



Type of Suitable Apparatus for Measurement of Length Changes

Figure A-4—Reference bar

Alkali-Silica Reactivity (ASR) Testing for Tensile Strength

The testing method used is similar to that described in ASTM C496-90 (Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens). For this testing, the slurry is cured in a 1.5 x 5-in. plastic mold to make three 1 x 1.5 inch specimens.

Curing Procedures

Cure each test specimen in a 174°F circulating water bath containing lime-saturated curing water, as described in the procedure below. Specimens remain confined in plastic molds until they are cut for strength determination.

1. Place the slurry in a mold, filling to approximately one-half of the mold depth, and puddle it.
2. Pour the slurry to the top of mold and puddle it.

3. Mark specimen molds for identification or positioning as required on brass plates inscribed with the slurry design.

Important—Monitor and adjust 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

Tensile strengths are determined at the Westport Technology Center. The cylindrical specimens are cured at Cementing Solutions, Inc. Following curing, a ¼-in. section is cut from each end of the specimen and discarded. Three 1-in.sections are cut and identified as top, middle, and bottom. The sections are then submerged in water for transport to Westport.

Testing is performed within 24 hours once the specimens are received at Westport.

Tensile strength measurements are performed at Westport according to ASTM standard C-496-2. Force is applied by constant displacement of the bottom plate at a rate of 1 mm every 10 minutes. The change in the specimen diameter can be calculated from the test plate displacement. The use of two pieces of plywood as described in ASTM designation C496-90-4.3 is not applied to this measurement.

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

T(psi) = (2*F) / (PI*L*D)

Where

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

Fig. A-5 shows a general schematic of how each specimen is oriented on its side during testing.

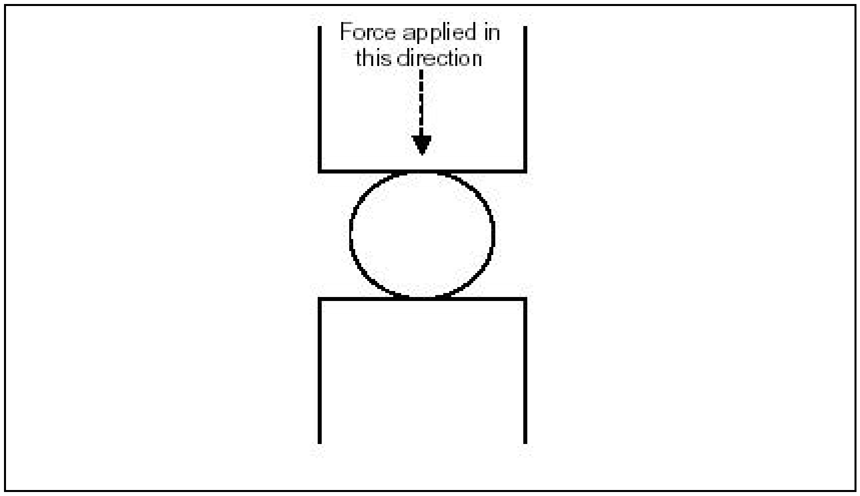


Figure A-5—Tensile strength crush diagram

Alkali-Silica Reactivity (ASR) Testing for Compressive Strength

Compressive strength testing is performed using modified API procedures. For this testing, the slurry is placed in a 1.5 x 5-in. plastic, cylindrical mold.

Curing Procedures

Cure each test specimen in a 174°F circulating water bath containing lime-saturated curing water, as described in the procedure below. Specimens remain confined in plastic molds until they are cut for strength determination.

1. Place the slurry in a mold, filling to approximately one-half of the mold depth, and puddle it.
2. Pour the slurry to the top of mold and puddle it.
3. Mark specimen molds for identification or positioning as required on brass plates inscribed with the slurry design.

Important—Monitor and adjust 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

After curing, three 1-in. by 1.5-in. diameter cylinders are cut from each specimen. A ¼-in. section is cut from the ends of each specimen and discarded. Each section is identified as top, middle, and bottom.

Each sample is then placed in turn in a Carver press (hydraulic) for compressive strength measurements. Force is applied in accordance with API Recommended Practice 10B Section 7.5.6.1**.** A digital pressure gauge records the specimen's failure in pounds per square inch (psi).

Calculate the compressive strength as follows:

$$Cs = F / SA$$

Where

Cs	= compressive strength
F	= force
SA	= surface area

Fig.A-6 shows a general schematic of orientation of specimens during testing.

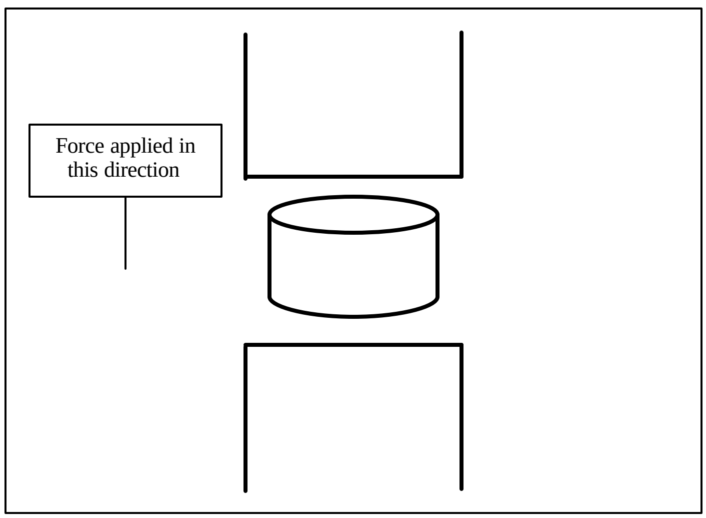


Figure A-6—Compressive strength crush diagram

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
$CaCl_2$—chemical formula for calcium chloride
cp—centipoise
gal—gallon
H_2O—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. ISO 10426-1:2000, Petroleum and natural gas industries—Cements and materials for well cementing—Part 1: Specification.
3. "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.

4. “Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens,” ASTM C496-96, Annual Book of ASTM Standards Vol. 04.02.
5. ISO 10426-5, Cements and materials for well cementing - Part 5: Test methods for determination of shrinkage and expansion of well cement formulations at atmospheric pressure.