THE EFFECTS OF PRESSURE ON THE SET PROPERTIES OF CEMENTS WITH VARIOUS ADDITIVES

ARTHUR S. METCALF and THOMAS D. DRESHER
Dowell Division of Dow Chemical, U.S.A.

ABSTRACT

Limited information is available on the effects of pressure on the set properties of cements with respect to commonly used additives. This report presents compressive strength data on cement systems cured at temperatures of 170° to 260° F and at pressures of 3,000 to 10,200 psi. Of the cement systems studied, those designed for a specific bottom-hole static temperature (BHST) show little change in compressive strength with increased curing pressure at BHST. However, some systems, cured at temperatures lower than BHST, gave increased or decreased compressive strength with increased curing pressure. The use of curing pressures that simulate more closely the pressures actually found in oil or gas wells gives a better understanding of additive performance and a more realistic waiting on cement (WOC) time for cement systems.

INTRODUCTION

Several authors have shown that the effects of curing pressure above 2,000 psi are negligible on the development of 24-hour compressive strengths of *neat cements* at a curing temperature of 200° F.[1,2,3] However, the development of 12-hour compressive strength of oil and gas well cement systems of varying retarder content, cured at different bottom-hole circulating temperatures (BHCT), has been shown to *increase* with *increased* curing pressure.[4]

No other or only limited information is available concerning the effects of curing pressure on the development of compressive strength of cement systems with respect to various additives and combinations of additives. Today in numerous wells, cement systems are placed under varying pressures in excess of 3,000 psi. Therefore, in order to improve the design of cement systems for these wells, an understanding, based on experimentation, of the effects of these higher curing pressures on the performance of additives is needed.

This paper examines the effects of curing pressures of 3,000 psi to 10,200 psi on the 8-, 12-, and 24-hour compressive strengths of cement systems with various additives, cured at 170° to 260° F. The main purpose of this work is to study the compressive strength of cement systems at temperatures and pressures that could exist at the top and bottom of a cement column and under simulated well conditions.

DISCUSSION

The number of various types of additives used in any given cement job is directly related to the depth, temperature, and type of formation encountered in an oil or gas well. With the large variety of additives in existence and the wide range of well conditions possible, some limitations had to be imposed on what was to be studied in this preliminary investigation. The cements examined were limited to a class H, class G, and a 50:50 flyash:class H. The additives examined were limited to a lignosulfonate retarder, a cellulose fluid-loss additive, bentonite, and salt. The well conditions under which samples were cured were based mostly on those possible in a 12,000 ft well.

The specific cement systems examined are listed in Table 1 with the mix water, density, and thickening times. All the cement systems containing additives, except the salt systems, were designed for placement in a 12,000 ft well with a BHST of 260° F. These systems all had 4 to 6 hours thickening time at a BHCT of 197° F. The systems were all cured at 170°, 200°, 230°, and 260° F under various pressures for 24-hour compressive strength determinations, with the lower temperatures used to simulate the tops of various length liner cement jobs. The salt systems

TABLE 1 CEMENT SYSTEMS EXAMINED

System	Water, Gal	Density, lbs/gal	Thickening Time, Hr:Min 118°F	197°F
A - Class H + 35% Silica	4.3	17.3	-	-
B - Class G + 35% Silica	5.0	16.7	-	-
C - Class H + 35% Silica + 0.4% Lignosulfonate Retarder	4.3	17.3	+6:00	5:00
D - Class G + 35% Silica + 0.4% Lignosulfonate Retarder	5.0	16.7	+6:00	4:00
E - Class H	4.3	16.5	2:34	-
F - Class G	5.0	15.8	-	-
G - Class H + 0.4% Lignosulfonate Retarder	4.3	16.3	+6:00	-
H - Class G + 0.4% Lignosulfonate Retarder	5.0	15.8	5:53	-
I - Class H + 3% Salt (BWOW)	4.3	16.5	2:02	-
J - Class H + 10% Salt (BWOW)	4.3	16.5	1:59	-
K - Class H + 18% Salt (BWOW)	4.3	16.5	2:40	1:01
L - Class H + 37% Salt (BWOW)	4.3	16.6	+7:00	-
M - 50:50 Fly Ash:Class H	5.75	14.2	+6:00	-
N - 50:50 Fly Ash:Class H + 0.4% Lignosulfonate Retarder	5.75	14.2	+6:00	4:09
O - Class H + 0.4% Lignosulfonate Retarder + 0.5% Cellulose Fluid-loss Additive + 0.5% Dispersant (Cured at 260°F)	4.3	16.5	+6:00	5:30
P - Class H + 0.4% Lignosulfonate Retarder + 4% Bentonite (Cured at 260°F)	6.7	14.6	+6:00	4:44
Q - Same as P only cured at 200°F	-	-	-	-
R - Same as O only cured at 200°F	-	-	-	-

were examined only at 170°F because this is representative of a temperature at which salt may be used alone. The 30°F intervals in curing temperatures constitute 2,000 ft depth changes in wells with 1.5°F/100 ft depth temperature gradients. Using the "Liner-Cementing Well-Simulation Test" schedules found in API Bulletin RP1OB as a guide, the bottom-hole pressure (BHP) for each depth and temperature was determined. Also, the BHP at depths of ±2,000 ft at each temperature was calculated, Table 2. Using these pressures as a guide, curing pressures of 3,000, 4,800, 6,600, 8,400, and 10,200 psi were selected. These curing pressures in multiples of 600 psi were chosen to correspond with the increments of the pressure gauge of the high-pressure autoclave.

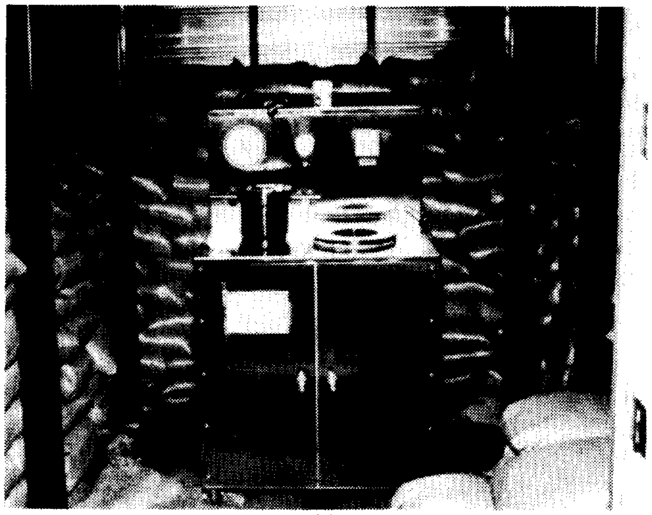
TABLE 2—CALCULATED BOTTOM-HOLE PRESSURE

Depth ft	Mud Density lbs/gal	Surface Pressure psi	Calculated BHP psi
14,000	16	1,750	13,398
12,000	14	1,500	10,236
10,000	12	1,250	7,490
8,000	10	1,000	5,160
6,000	10	750	3,870
4,000	10	500	2,580

PROCEDURE

The procedures used closely followed the guidelines set forth in API Bulletin RP1OB for "Preparation of Slurry" and "Strength Tests." The tests were brought to test temperature following the appropriate temperature schedule listed under "Well-Simulation Test Schedules for Curing Strength Specimens." The pressure was slowly increased over the 4-hour schedule time from an initial pressure of 3,000 psi to the final recorded pressure. Curing pressure was regulated to ± 600 psi at pressures above 3,000 psi.

Specimens were cured in high-temperature, high-pressure autoclaves built by Chandler Engineering of Tulsa, Figure No. 1A, B. These curing chambers have the capability of temperatures to 600°F and pressures to 20,000 psi. The cement samples were cured in a container of water with white mineral oil as the hydraulic fluid.



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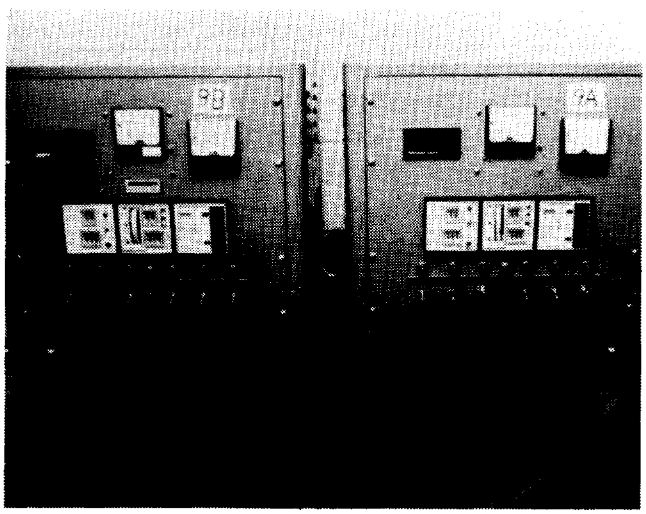

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FIGURE 1A,B—HIGH-TEMPERATURE, HIGH-PRESSURE AUTOCLAVE

DATA

Lignosulfonate Retarder

The results of 24-hour compressive strength tests on class H and class G cements retarded with a lignosulfonate are shown in Figure Nos. 2 through 5. At the BHST of 260°F lignosulfonate-retarded slurries show little change in compressive strength with increased curing pressure. The neat slurries did, however, show a large reduction in compressive strength when the curing pressure was increased from 3,000 psi to 4,800 psi. Lignosulfonate seems to stabilize the compressive strength development over the range of curing pressures examined at this temperature.

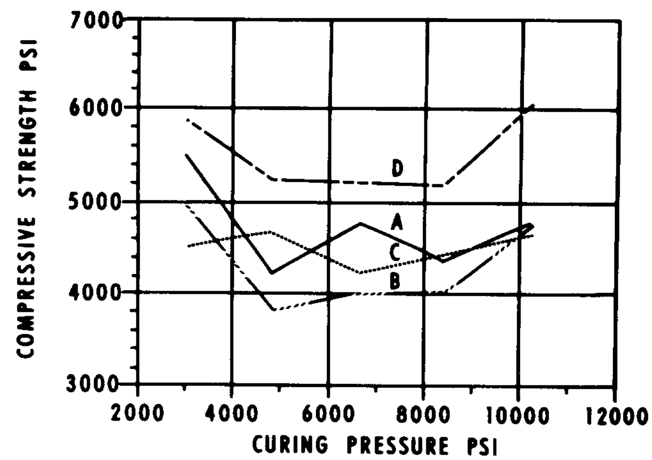

FIGURE 2—24-HOUR COMPRESSIVE STRENGTHS OF LIGNOSULFONATE-RETARDED CLASS G AND CLASS H CEMENT SYSTEMS AT 260°F

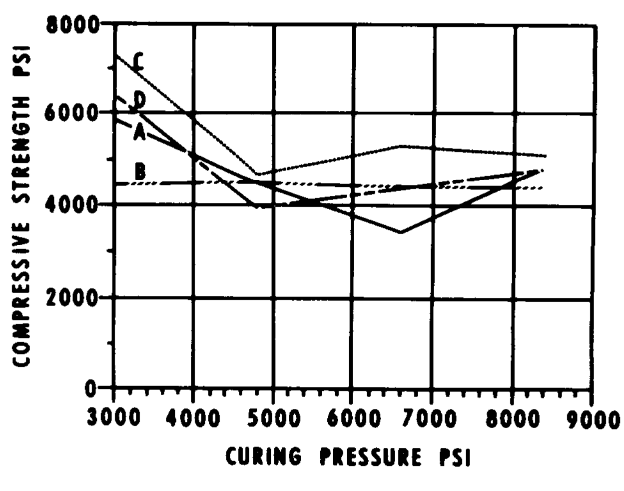

FIGURE 3—24-HOUR COMPRESSIVE STRENGTHS OF LIGNOSULFONATE-RETARDED CLASS G AND CLASS H CEMENT SYSTEMS CURED AT 230°F

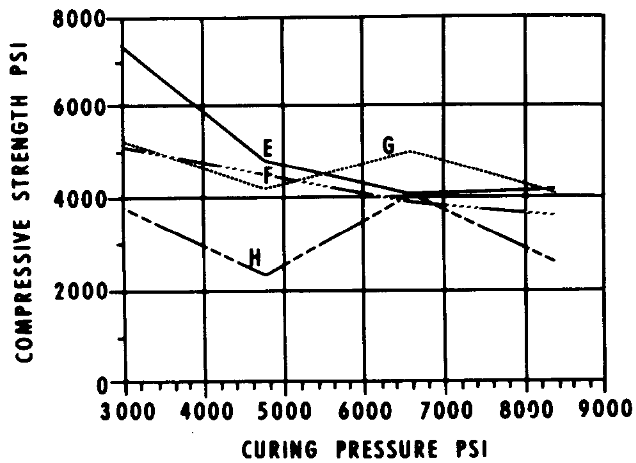

FIGURE 4—24-HOUR COMPRESSIVE STRENGTHS OF LIGNOSULFONATE-RETARDED CLASS G AND CLASS H CEMENT SYSTEMS CURED AT 200°F

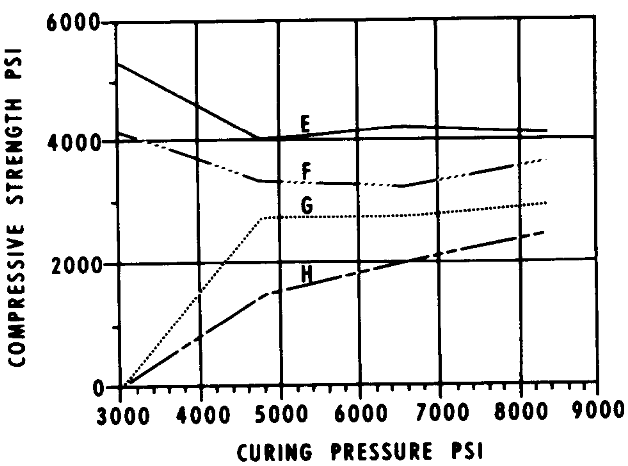

FIGURE 5—24-HOUR COMPRESSIVE STRENGTHS OF LIGNOSULFONATE-RETARDED CLASS G AND CLASS H CEMENT SYSTEMS CURED AT 170°F

Reducing the curing temperature to 230° F brings about some changes in the compressive strength development of lignosulfonate-retarded systems. Class G and class H systems with lignosulfonate show a large reduction in compressive strength in going from 3,000 to 4,800 psi curing pressures. Higher curing pressures, however, show an *improvement* in compressive strength. In comparison, the neat class G system is unaffected by increased curing pressure, while for the neat class H system compressive strength falls off greatly with increased curing pressure. The neat class H system, however, does show an improved compressive strength when cured at 8,400 psi. None of the systems ever showed a compressive strength below 3,000 psi.

At 200° F, lignosulfonate-retarded slurries showed a reduction in compressive strength when cured at 4,800 psi. The strength thereafter fluctuated between 3,000 and 5,000 psi with increased curing pressure, Figure No. 4. Notably, the compressive strength never fell below 2,000 psi for any of the systems. The compressive strengths of neat class G and class H systems decrease with increased curing pressure, showing again the possibility of stabilization by the lignosulfonate.

The extremely large reduction in compressive strength of the neat class H system with change in curing pressure at 200° F led to an X-ray diffraction analysis. The results, recorded in Table 3, showed no positive evidence of curing pressure effects on the chemistry of the cement.

At 170° F the most significant piece of information was obtained. The lignosulfonate systems which are considerably over-retarded, Table 1, at 170° F will not set when cured under 3,000 psi *but will set and*

TABLE 3—X-RAY DIFFRACTION ANALYSIS

System	Curing Temperature	Curing Pressure	Major (25-30%)	Minor (10-30%)	Low (Less than 15%)	Possible Low (less than 15%)
E	200°F	3000 psi* 4800 psi	$Ca(OH)_2$	----	Ca_3SiO_5	Calcite
K	170°F	3000 psi* 6600 psi 8400 psi	----	$Ca(OH)_2$	Ca_3SiO_5	Dolomite, Calcite
M	170°F	3000 psi* 4800 psi	----	----	Quartz, Ca_3SiO_5 $Ca(OH)_2$, $CaO \cdot Al_2O_3$	Calcite

*Within experimental limits of the X-ray equipment, identical patterns were obtained at these curing pressures.

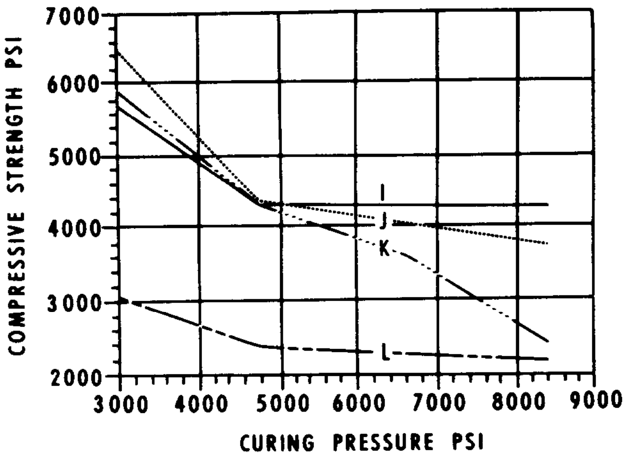

FIGURE 6—24-HOUR COMPRESSIVE STRENGTHS OF CLASS H CEMENT SYSTEMS WITH VARIOUS PERCENTAGES OF SALT CURED AT 170°F

develop excellent compressive strength at higher curing pressures.

Salt

Increased curing pressure reduces the compressive strength of class H cement with various percentages of salt, Figure No. 6. The compressive strength of 3% and 10% salt systems behave identically to that of a neat class H system, Figure No. 5. They both show a large reduction in strength in going from a curing pressure of 3,000 to 4,800 psi and thereafter are unchanged with further increases in curing pressure. The 18% salt system, however, shows a continuous reduction in compressive strength with increased curing pressure. The compressive strength of the 37% salt system shows the least sensitivity to increased curing pressure, but still shows some reduction in strength over the higher curing pressure ranges.

An X-ray diffraction analysis was run on 18% salt systems cured at various pressures. As in the case of the neat class H system, no positive evidence was found to indicate what is being affected by the curing-pressure increases so as to produce the reduction in compressive strength.

Extenders

The compressive strength of the neat 50:50 flyash:class H system shows a somewhat gradual reduction with increased curing pressure as the curing temperature decreases from 260° to 170°F, Figure Nos. 7 through 10. At 260° and 230°F the compressive strength both decreases and increases, depending on the curing pressure. This behavior is very similar to that of a neat class H system at 260° and 230° F, Figure Nos. 2 and 3. This same similarity in compressive strength development of the neat 50:50 and neat class H systems can also be seen at 200° and 170°F, Figure Nos. 4, 5, 9, and 10.

As before in an attempt to determine if any changes in the crystalline products of cement hydration had formed as a result of increased curing pressure, X-ray diffraction analysis was obtained on samples cured at 170°F at both 3,000 and 4,800 psi. The results of this analysis are shown in Table 3 and show no difference in the products of hydration.

The lignosulfonate-retarded 50:50 flyash:class H system shows some reduction in the degree of variance in compressive strength with increased

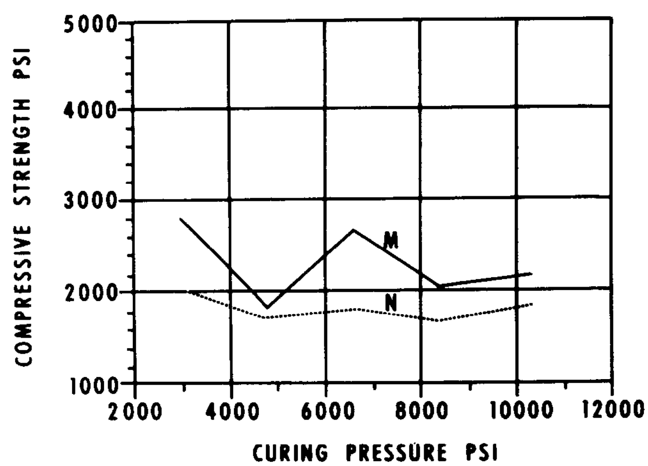

FIGURE 7—24-HOUR COMPRESSIVE STRENGTHS OF 50:50 FLYASH: CLASS H SYSTEMS CURED AT 260°F

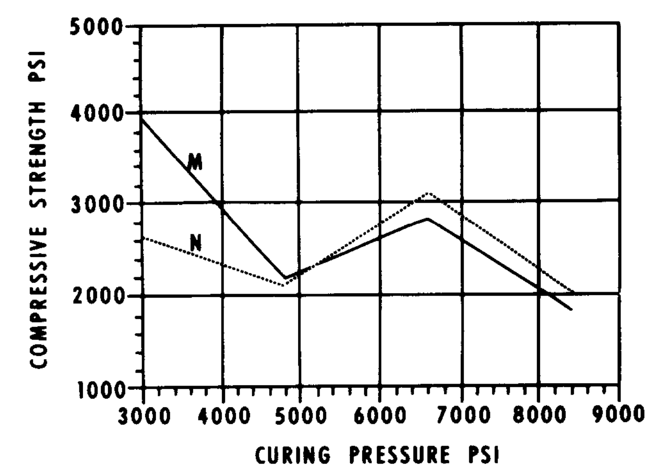

FIGURE 8—24-HOUR COMPRESSIVE STRENGTHS OF 50:50 FLYASH: CLASS H SYSTEMS CURED AT 230°F

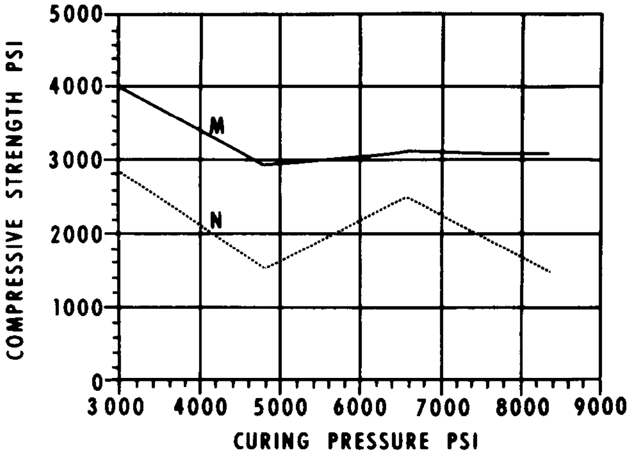

FIGURE 9—24-HOUR COMPRESSIVE STRENGTHS OF 50:50 FLYASH:CLASS H SYSTEMS CURED AT 200°F

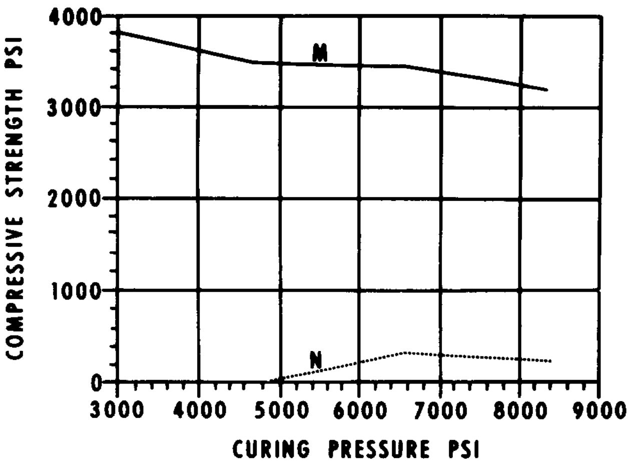

FIGURE 10—24-HOUR COMPRESSIVE STRENGTHS OF 50:50 FLYASH: CLASS H SYSTEMS CURED AT 170°F

pressure at 260°F. The compressive strength at 230°F and 200°F, however, shows only a slight difference from that of the neat 50:50 flyash:class H system. Notably, at 170°F no compressive strength is developed at 3,000 and 4,800 psi, while at 6,600 and 8,400 psi some strength (admittedly low) is obtained.

The gel-extended class H system shows a gradual reduction in compressive strength with increased curing pressure at 260°F, Figure No. 11. However, at 200°F the strength of this same system becomes very sensitive to curing pressure.

Fluid-loss Additives

The compressive strength of a class H system with a cellulose fluid-loss additive is shown in Figure No.

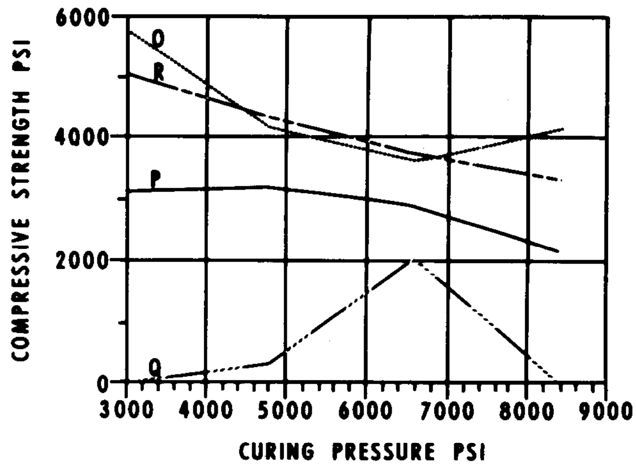

FIGURE 11—24-HOUR COMPRESSIVE STRENGTHS OF CLASS H CEMENT SYSTEMS WITH GEL AND A CELLULOSE FLUID-LOSS ADDITIVE CURED AT 260°F AND 200°F

11. Our test system showed a gradual reduction in strength with increased curing pressure at curing temperatures of both 200° and 260°F. The only noticed exception to this observed trend occurs in the curing pressure range between 6,600 and 8,400 psi, where some compressive strength is regained in the system at 260°F.

TREATMENT DESIGN EXAMPLE

Compressive strengths of a cement system designed for a liner job on a well in southern Louisiana were examined at 3,000 psi and at the approximate calculated pressure at the top of the liner. The bottom of the liner is at a depth of 13,400 ft and the top is at 10,900 ft. The approximate calculated pressures are: top, 10,000 psi; bottom, 13,000 psi. The static temperatures at the top and bottom are 208° and 235°F, respectively. The system designed is a 16.2 lb/gal class H using 0.15% modified sugar retarder to get the desired placement time of about 4 hours at the BHCT of 195°F.

The results of 8-, 12-, and 18-hour compressive strength tests on the system designed are shown in Table 4. It can be seen that a significant improvement in the 8-hour compressive strength was made at 235°F. However, the most significant result was the development of excellent compressive strengths in 8 and 12 hours when cured at 10,200 psi and 195°F in contrast to absolutely no strength in the same time periods cured at 3,000 psi.

This system, when treated under API recommended conditions in a field lab at 3,000 psi at

TABLE 4—TREATMENT DESIGN

Location—Southern Louisiana

Depths—Top: 10,900 ft
Bottom: 13,400 ft

Calculated Pressures—Top (approx.): 10,000 psi
Bottom (approx.): 13,000 psi

Bottom-Hole Circulating Temperature—195° F
Bottom-Hole Static Temperature Top of Liner—208° F
Bottom-Hole Static Temperature Bottom of Liner—235° F

System	Thickening Time at 195° F
Class H + 0.15% Modified Sugar Retarder + 4.52 gal H_2O	4:36

	Compressive Strengths, psi					
Curing Time	8 hour		12 hour		18 hour	
Curing Pressure / Curing Temp	195° F	235° F	195° F	235° F	195° F	235° F
3,000 psi	N.S.	612	N.S.	2,026	N.S.	2,637
10,200 psi	1,850	1,638	1,899	2,115	-	-

the BHCT, showed no strength in 8, 12, and 18 hours. The same tests under pressure conditions simulating those actually found in the well show an 8-hour WOC time to be sufficient for the top and the bottom of the liner.

CONCLUSIONS

The increase in curing pressure from 3,000 psi to a value which more closely simulates the actual downhole conditions of oil and gas wells produces a variance in the compressive strength of cement systems with respect to additives. This effect is not as pronounced as that obtained when the temperature is increased, but is certainly worthy of consideration in the initial design of a cement system. The use of more realistic pressures also has a definite effect on the prediction of the WOC time, especially on cement systems designed for liners. By the testing of cement slurries at actual well pressures, over-retardation at the top and under-retardation at the bottom of a liner can, in many cases, be reduced.

REFERENCES

1. Swayze, M. A. and Mid-Continent District Study Committee on Cementing Practices: "Effects of High Temperatures and Pressures on Strengths of Oil Well Cements," API *Drill. and Prod. Prac.* (1954) 72.
2. Ludwig, N. C. and Pence, S. A.: "Properties of Portland Cement Pastes Cured at Elevated Temperatures and Pressures," *Jour. Am. Concrete Inst.* (Feb. 1956) 673.
3. Bearden, William G.: "Effect of Temperatures and Pressure on Physical Properties of Cements," API *Oil Well Cementing Practices in the United States* (1959) 48.
4. Tragesser, A. F., Jr. and Parker, P. N.: "Using Improved Technology to Obtain Better Cement Jobs on Deep, Hot Liners," *J. Pet. Tech.* (Nov. 1972) 1307-1313.

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