PREVENTION OF STRENGTH RETROGRESSION IN HIGH TEMPERATURE WELL CEMENTS

E. B. NELSON
DOWELL Division of Dow Chemical U.S.A.

INTRODUCTION

The decrease of cement strength with increased temperature and age was first reported by oil field related researchers in the early 1950's as a result of the growing trend toward deep well completions.[1] [2] [3] This phenomenon is generally known as "Strength retrogression" and has been an increasingly important problem to consider ever since. Several methods have been employed by service companies to counteract strength retrogression and each will be discussed here in detail.

CEMENT CHEMISTRY REVIEW

For a fuller understanding of strength retrogression and its prevention some familiarity with the chemistry of cement hydration and associated phase equilibria is essential.[4] The following brief resume is submitted.

Portland cement is composed of four major compounds; tricalcium silicate (C_3S)*, dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). The first two compounds, C_3S and C_2S, comprise about 75% of Portland cement by weight, and their related chemistry largely determines the manner in which the cement will perform.

The hydration products of C_2S and C_3S are $Ca(OH)_2$ and C-S-H gel. The C-S-H gel is of a somewhat variable composition but generally has a high C/S ratio (approximate range of 1.3 to 2.4) and has a gel-like structure. It is the principal binder of cement hydrated at ordinary temperature and is the dominant factor governing strength and dimensional stability. The early hydration product of cement even at elevated temperature and pressure is C-S-H gel. It subsequently is subject to metamorphosis at elevated temperature. The alteration products vary depending upon a number of factors. Such alteration is frequently deleterious to strength and permeability. The associated chemistry at elevated temperatures is highly complex and still not fully understood.

In the past, as the temperature of oil wells began to exceed a temperature of about 120°C (247°F) serious strength retrogression difficulties occurred. The corrective for the problem, determined empirically by Memzel in autoclave curing of concrete masonry, was a partial replacement of the cement by

* In the abbreviated formulas, C=CaO, S=SiO_2, F=Fe_2O_3, A=Al_2O_3, N=Na_2O, K=K_2O, and H=H_2O.

ground quartz (silica flour).[5] Later research revealed that the compressive strength vs. silica content correlated closely with the kind of binder formed.[6] Without silica the C-S-H gel transformed into a highly crystallized and dense phase known as "alpha dicalcium silicate hydrate" (α-C_2SH). Porosity increased and strength decreased markedly. The optimum amount of additional silica was determined to be 30-35% corresponding to a gross C/S ratio of about 0.8. The α-C_2SH did not form; instead, the C-S-H gel reacted to form tobermorite, C_5-S_6-H_5, a binder of excellent strength. Most of these studies were conducted at 175°C (347°F) over short periods of time, in the order of 7-24 hours. In prolonged curing, as occurs in production wells, pure tobermorite is stable to about 150°C (302°F). Thus, from a practical standpoint, the chemistry of calcium silicate hydrate phase transformations is basic to the prediction of long term cement behavior under high temperature downhole conditions.

The compositions of the equilibrium calcium silicate hydrate phases depend largely upon the composition of the initial cement-silica blend, temperature, pressure and time of exposure. Production cements generally have a gross composition of 0.6 C/S (or even lower when silicious extenders are used) to about 1.0 C/S.

In order to illustrate the transformations of the cement-silica mixes over a broad temperature range only the tobermorite composition, 0.83 C/S, is considered here.

$$0.83\ C/S \longrightarrow \text{C-S-H gel or tobermorite} \xrightarrow{\simeq 150^\circ C}$$

$$\text{xonotlite } (C_6\text{-}S_6\text{-}H) \text{ plus gyrolite } (C_2\text{-}S_3\text{-}H_2) \xrightarrow{\simeq 250^\circ C}$$

$$\text{xonotlite plus truscottite } (C_2S_4H) \xrightarrow{\simeq 275^\circ C}$$

$$\text{xonotlite plus silica}$$

Obviously each transformation is accompanied by new crystallization. In the event strong intracrystal bonds are present, strength may not be affected in either direction. This is generally the case in the tobermorite to xonotlite plus gyrolite transformation. The subsequent transformations are not yet fully understood.[7] Research on these is currently in progress.

Although chemical reactions and phase transformations are generally acknowledged as the major cause of strength retrogression, evidence also exists that suggests physical changes in the cement, especially relating to the degree of crystallinity, have a profound effect on the integrity of the cement. Some researchers have observed cements that degraded in strength with no apparent chemical changes. For example, J. P. Gallus, et al, reported a cement composition that resulted in the formation of xonotlite.[8] The cement possessed adequate strength initially, but degraded severely with time. X-ray diffraction analysis indicated no change in chemical composition; thus, the strength retrogression may have been due to crystal growth of xonotlite resulting in breakage of the multitude of bonds present when microcrystallinity exists. An analogous though not exactly comparable situation is the devitrification of glass with time resulting in brittleness and low strength. Such behavior is much more difficult to control than bulk chemical changes and a great deal of research is necessary to understand and prevent such crystal growth.

OILFIELD METHODS OF STRENGTH RETROGRESSION PREVENTION

Using the basic chemical background specific practical examples of strength retrogression prevention in oil well cements will be discussed. Hopefully, discussion of the high temperature behavior of various oil field cement formulations and additives in light of the chemical processes involved will lead to a greater understanding of the problem and aid in the design of systems for specific downhole conditions.

In high temperature wells, strength retrogression prevention in primarily achieved by reducing the bulk lime to silica (C/S) ratio in the cement. To accomplish this, silica as α-quartz and/or various silica-rich extenders are used. The most common materials include silica sand (80-200 mesh), silica flour (≈325 mesh), fly ashes, diatomaceous earth, perlite, and bentonite. Results are surprisingly different depending upon which material is employed. Also, specially prepared cements such as API Class J and various lightweight formulations are employed in high temperature cementing.

Although most wells currently encompass lower temperatures, this discussion will focus on the behavior of cement systems in the range 230-320°C (450-600°F). At such temperatures the behavior of cement systems is more pronounced and thus more illustrative. Also, wells in this temperature range will be completed with increasing frequency.

RESULTS

Before discussing the effects of the silica extended cement systems, scrutiny of the performance of neat Portland cement at high temperatures is necessary for comparison. Figure 1 graphically illustrates the compressive strength and permeability behavior of various neat Portland systems.

Curve 1 shows the behavior of a typical neat Class G system with 44 percent water added by weight of cement. Notice the severe strength loss that occurred in less than one month. As time progressed, the strength improved to a reasonable level; however, the permeability was exceedingly high making the cement totally unsuitable. Generally a water permeability of less than 0.1 Md is considered adequate for most cementing applications. System 2 was a slightly heavier Class G system (38% water) that showed slightly improved strength and permeability but was still a very poor cement. System 3, Class H with 32% water, was an abnormally heavy slurry and was barely miscible. Although strength was good due to the density, it was barely suitable as to permeability.

Menzel's conclusion as to the optimum amount of silica addition for stabilization of Portland cement has been largely confirmed by our studies. Figure 2 shows the compressive strength and permeability behavior of three systems: 1. 20% silica flour BWOC (by weight of cement), 2. 35% silica BWOC, 3. 50% silica BWOC. System 2, close to the optimum in Menzel's study has the highest strength and lowest permeability, and is the basis for the vast majority of high temperature treatments performed in the completion industry.

It is important to note that the particle size of the silica flour mentioned thus far has been about 325 mesh (44 μm average). Silica sand, 80-200 mesh (140 μm average), will effectively prevent strength retrogression in the 120-190°C, 250-375°F) range, but begins to lose effectiveness as temperature increases.[9] Such behavior is illustrated in Figure 3, which compares the strengths and permeabilities of cements stabilized with silica sand and silica flour at 230°C (450°F) and 320°C (600°F). Strength retrogression is prevented by the silica sand, but strength is lower than that of the silica flour counterparts. Permeability of the silica sand system, however, is much higher than that of the silica flour systems. The declining effectiveness of silica sand with increasing curing temperature is especially evident in a geothermal environment due to the extremely high temperatures (700°F+) and presence of corrosive brines.[10]

Extenders containing large amounts of silica have been applied in high temperature treatments with surprisingly varied results, and must be used with care to avoid severe strength loss and increased permeability. Fly ashes, perlite, diatomaceous earth and bentonite contain high silica in different forms: glass, diatoms and aluminosilicates; thus, significant differences occur in the chemical behavior of these extenders.

As shown in Figure 4, fly ash as a source of stabilizing silica in the 230-320°C (450-600°F) range is ineffective in the long run. Systems 1 and 2 are typical 1:1 fly ash-Portland cement formulations cured at 230 and 320°C, respectively. At 230°C adequate strength and permeability is observed up to 180 days; at this point, serious degradation starts to occur. Such behavior is drastically accelerated at 320°C where degradation begins within 30 days.

Fly ash was the only extender that exhibited a delayed degradation. An investigation was conducted to determine why. The samples were analyzed by x-ray diffraction with the following results. Xonotlite was found at early periods. With time, it converted to a phase known as the mineral reyerite - $K_2Ca_{14}Si_{24}O_{60}(OH_5)\cdot 5H_2O$. It is highly similar to truscottite but is evidently very weak.[9]

Figure 4 also gives high temperature results on typical systems extended with bentonite. System 3, containing 12% bentonite showed relatively low, but adequate, compressive strength and barely acceptable permeability. System 4 was a much lighter weight bentonite slurry containing 100% water. Strength retrogressed to zero within 30 days. Slurries containing bentonite are typically very sensitive to elevated temperature. Such systems should thus be used with caution at high temperature.

Two diatomaceous earths were tested and found to be completely ineffective at high temperature. A Portland cement system with one of these developed about 50 psi strength within 1 day with subsequent degradation.

The effect of perlite with Class G cement cured at elevated temperatures is illustrated in Figure 5. Compressive strength data for System 1, Class G + 1 ft^3 perlite per sack of cement + 40% silica flour BWOC, indicated the cement was performing satisfactorily after six months exposure. At one year the strength retrogressed to zero. System 2, Class G + 1 ft^3 perlite per sack of cement + 80% silica flour BWOC performed satisfactorily up to one year, but not nearly as well as cements stabilized with silica flour alone. System 3, Class G + 2 ft^3 perlite per sack of cement + 40% silica flour performed excellently from a permeablity standpoint but was marginally acceptable as to strength. X-ray data for these systems revealed that the principal binder was generally xonotlite which eventually converted to truscottite. Despite the formation of these desired phases, the high perlite content interfered with strength development. It can be speculated that the crystallinity of the binder was high,resulting in less bonding within the cement.[11]

The results on extenders other than silica flour or silica sand at high temperature indicate that their performance may be highly unsatisfactory in oil well completions.

It is important to remember that the results reported in this paper were gathered at 230 to 320°C (450-600°F). In the more commonly encountered 120 to 190°C (250-350°F) range in oil well completions, the extenders described may generally be used with no adverse effects. However, it is important to realize that fly ash and other pozzolans represented above are not to be relied upon to prevent strength retrogression by themselves. Either silica sand or silica flour must always be added at or near the 35% optimum proportion BWOC. The extenders are simply to be regarded as cementitious materials. Extensive data has previously been published concerning extended cements below 230°C (450°F). The reader is referred to such references for details.[1,2,3,12,13]

There are a number of commercially prepared cements that have been designed specifically for high temperature applications. Perhaps the best known of these is Class J cement (tentative API classification). Class J mainly consists of βC_2S with silica in a C/S ratio of about 0.85. Because βC_2S hydrates so much more slowly than C_3S, Class J requires little or no retardation. As Figure 6 shows, Class J usually performs adequately when mixed neat with 40 percent water. This cement can generally be used with confidence; however, equally good results are possible with silica stabilized Portland cement.

Commercial lightweight modified Portland-based cements have shown promise in high temperature cementing. Most of them contain a highly silicious aggregate material. Typical performance of a commonly used lightweight cement is depicted in Figure 6 as System 2.

DISCUSSION

The adverse effects that extenders other than silica as α-quartz impart to Portland cement at 230°C (450°F) and higher are still not completely understood. The most plausible explanation relates to the crystalline form of the silica. Silicate minerals occur in several classifications depending upon the manner in which the $(SiO_4)^{-4}$ tetrahedra are arranged. Quartz belongs to the most complex silicate group, the tektosilicates, where the tetrahedra are closely packed in a three-dimensional framework. Bentonite belongs to the phyllosilicate group or clays, where the tetrahedra occur in layered sheets. The tetrahedra are not as closely packed and other elements such as Fe and Mg are intimately associated with them. Diatomaceous earth, fly ash and perlite are largely amorphous.

At high temperatures the development of calcium silicate hydrates is evidently heavily dependent upon solid-solid chemical interactions. Because of the high silicate density of quartz and its freedom from interfering species, it can enter into such reactions with great efficiency. The other extenders presumably interfere with the desired reactions at high temperatures resulting in poor cement performance.

Another explanation that has been put forth is simply that the extenders somehow promote crystal growth within the cement resulting in degradation. These hypotheses are admittedly limited and are currently being investigated.

From a practical standpoint, the information presented in this paper may be summarized into several observations concerning high temperature well completion.

1. Strength retrogression accompanied by an increase in permeability must be dealt with when cementing wells with a bottom hole temperature greater than 120°C (250°F).

2. Silica as α-quartz, as silica sand or as silica flour, appears required in the range of 30-35% by weight of cement for all high temperature completions.

3. Extenders such as fly ash, perlite, etc., may be used up to about 230°C (450°F), but generally silica should also be added simultaneously. The extenders should be regarded only as cementitious material.

4. Above 230°C (450°F) use of extenders other than silica is not advisable. They cause degradation of the cement. At these temperatures silica sand is not as effective as silica flour.

5. Organic additives such as retarders, fluid-loss additives, etc., do not have a significant impact upon cement strength <u>in the long run</u>.

6. In many cases shown in this paper, a high temperature system maintained adequate strength, but the permeability rose to an unacceptable level. Thus, high temperature cements must not be evaluated on the basis of strength alone as degradation frequently does not manifest itself in the form of strength loss. Permeability should be a major consideration when designing a high temperature cement system.

This paper is an attempt to condense a very complex subject to a reference work of reasonable length. Hopefully it will aid in designing cements for high temperature wells and give the reader a chemical awareness of the problems involved.

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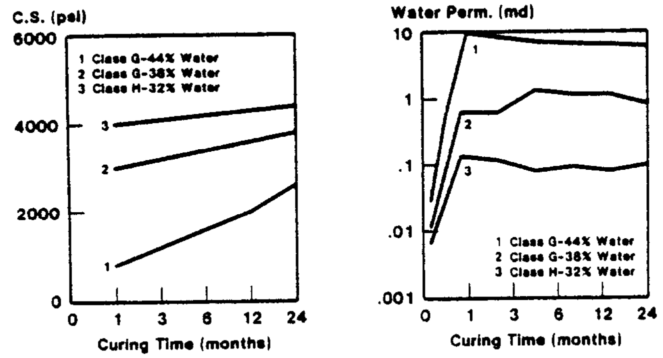

FIGURE 1—COMPRESSIVE STRENGTH AND PERMEABILITY BEHAVIOR OF NEAT PORTLAND CEMENT SYSTEMS AT 230°C

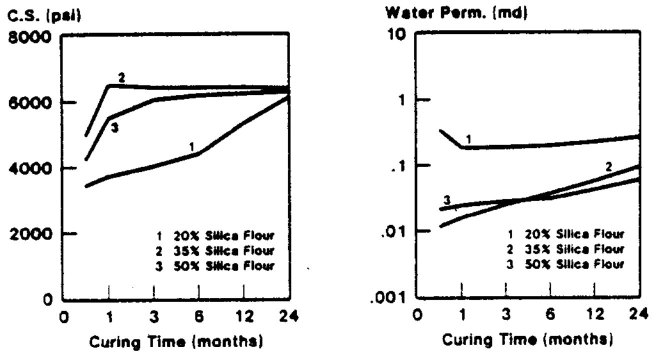

FIGURE 2—COMPRESSIVE STRENGTH AND PERMEABILITY BEHAVIOR OF PORTLAND CEMENT/SILICA FLOUR SYSTEMS AT 230°C

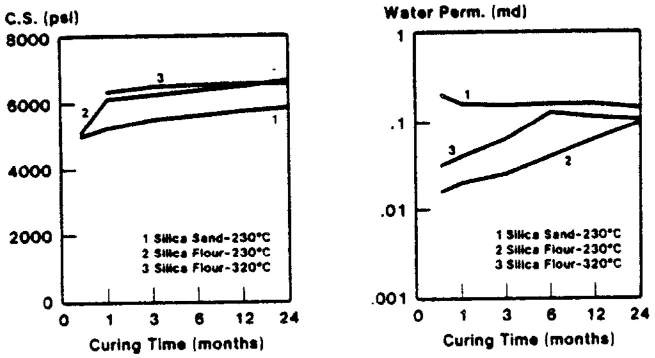

FIGURE 3—COMPRESSIVE STRENGTH AND PERMEABILITY BEHAVIOR OF PORTLAND CEMENT STABILIZED WITH 35% SILICA

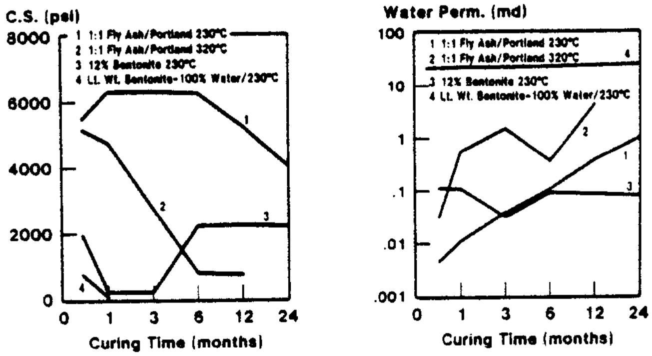

FIGURE 4—COMPRESSIVE STRENGTH AND PERMEABILITY BEHAVIOR OF EXTENDED CEMENT SYSTEMS AT HIGH TEMPERATURES

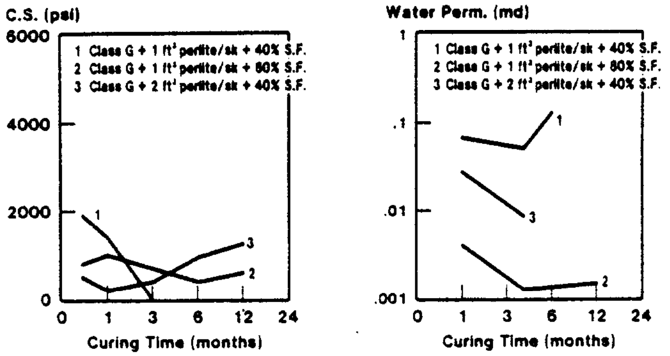

FIGURE 5—COMPRESSIVE STRENGTH AND PERMEABILITY BEHAVIOR OF CEMENT SYSTEMS EXTENDED WITH PERLITE AT HIGH TEMPERATURES (average of 230°C and 320°C)

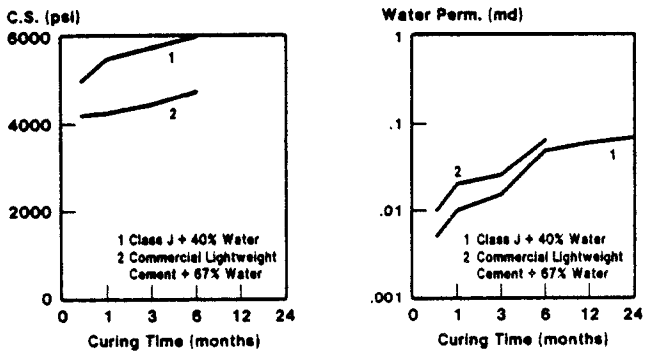

FIGURE 6—COMPRESSIVE STRENGTH AND PERMEABILITY BEHAVIOR OF COMMERCIAL HIGH TEMPERATURE CEMENTS AT 230°C