

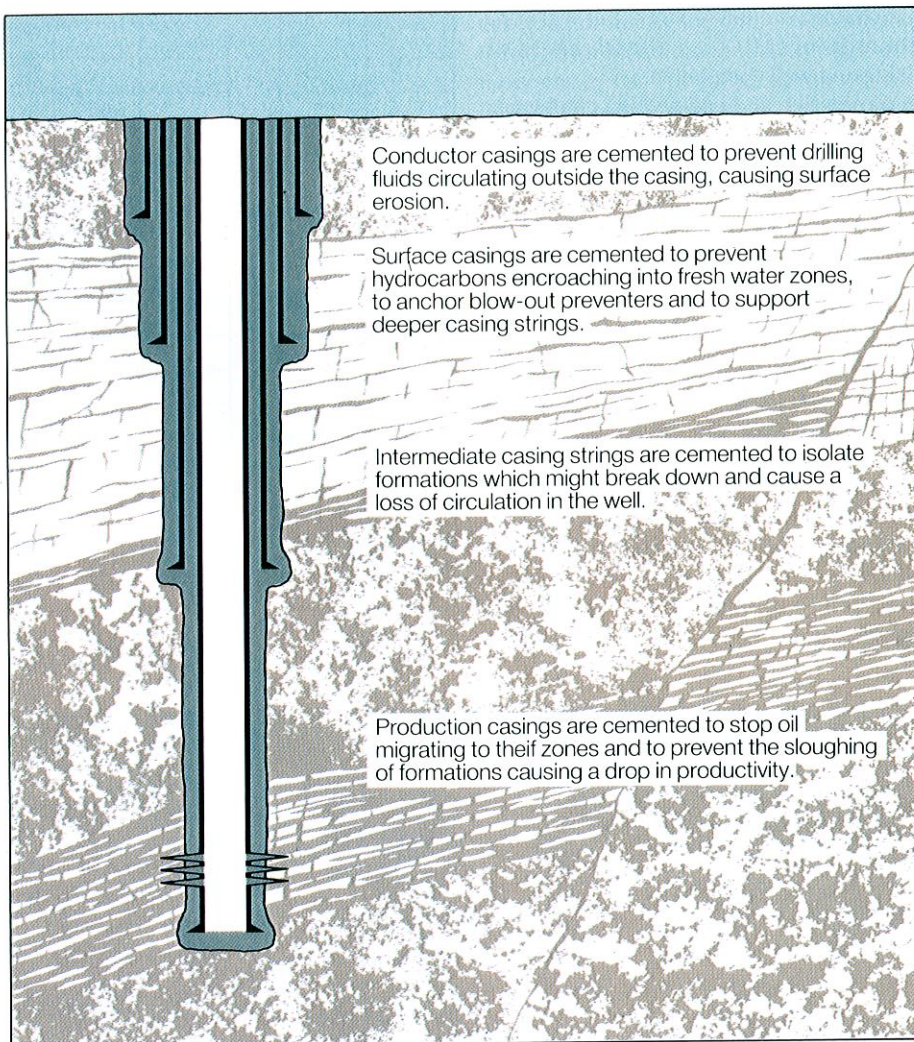
Cement Chemistry and

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Faced with the concrete skyline of an urban landscape, few people would guess that cement faces its toughest challenge underground—in oil and gas wells where environmental conditions are far more severe than any encountered on the earth's surface. This article outlines the chemistry of portland cement, the variety used to cement casings in wells and provide zonal isolation, and explains how additives facilitate cement placement and ensure stability after setting.¹

Rudimentary cementing of oil wells began at the turn of the century when few wells went deeper than 2,000 feet [610 meters]. Cementing operations were usually performed by the rig crew. Today, specialist service companies routinely cement wells of 20,000 feet [6,098 meters] and deeper. Cementing operations are either *primary*, done in the course of drilling a well, or *secondary* or *remedial*, intended to remedy deficiencies in primary cementing or alter the well completion for production (*right*).

Recently, sophisticated computer modeling has been introduced to simulate and optimize the cementing operation. Data recorded while pumping the cement are analyzed to judge whether the cement has been correctly placed. Cement evaluation logs and other cased-hole logs can indicate the strength of the set cement and whether it is bonded to the casing (*far right*). The outcome of a cementing job, however, depends ultimately on choosing the appropriate cement and additives to cope with particular well conditions.



□ Various stages in the primary cementing of a newly drilled well. Secondary, or remedial cementing, may be required after the well is completed to correct deficiencies in the primary cementing or to plug back a dry hole.

1. Portland cement was developed by Joseph Aspdin who named it after stone that it resembled from the Isle of Portland, off the English Coast.
2. *Portland Cements*. Skokie, Illinois: Portland Cement Association, 1969.
3. "The Hydration of Portland Cement" and "The Setting and Hardening of Portland Cement" in Lea FM: *The Chemistry of Cement and Concrete*, 3rd ed. New York: Chemical Publishing Co. Inc., 1971.

Additives

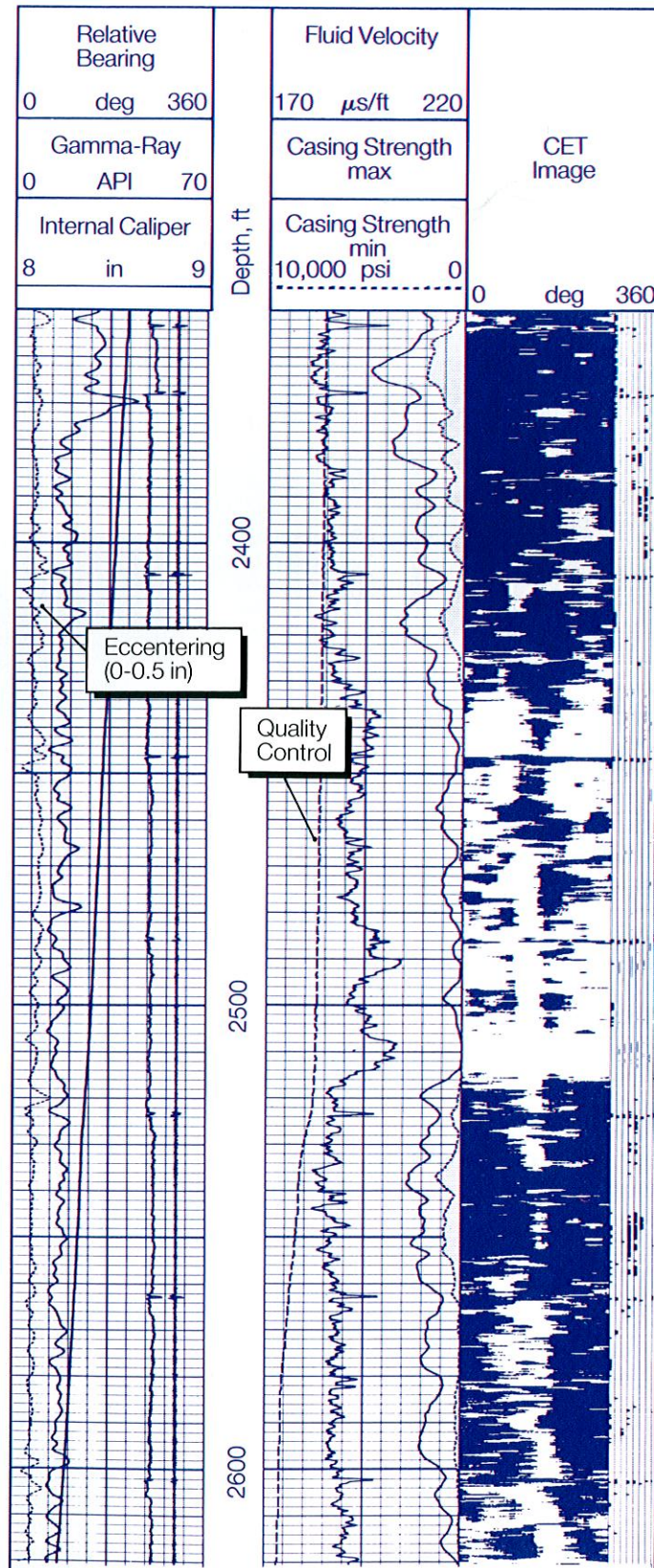
The raw ingredients of portland cement are lime, silica, alumina and iron oxide.² Lime is obtained from calcareous rock deposits and industrial alkali waste products. Alumina, silica and iron oxide are derived from clays and shales and from blast furnace slag or fly-ash waste from coal-fired power stations. These materials are pulverized into fine powder, combined to obtain a given bulk oxide composition and fed into a rotating kiln.

Heated as high as 1,500°C [2,730°F], the raw materials undergo a complex series of chemical reactions to produce the four main compounds that make up cement: tricalcium silicate, Ca_3SiO_5 [abbreviated as C_3S]; dicalcium silicate, Ca_2SiO_4 [C_2S]; tricalcium aluminate, $\text{Ca}_3\text{Al}_2\text{O}_6$ [C_3A]; and tetracalcium aluminoferrite, $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ [C_4AF] (see "Chemical Shorthand," below). These four compounds, as well as minor amounts of free lime and other oxides, leave the kiln as clinker. After the clinker has cooled, a small amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added, and the mixture is pulverized and ground to obtain finished portland cement.

Chemical Shorthand			
A	Al_2O_3	N	Na_2O
C	CaO	S	SiO_2
F	Fe_2O_3	S-	SO_3
	H		H_2O

How Cement Sets

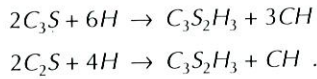
Portland cement is the most common of the "hydraulic" cements, which set and develop compressive strength through hydration, not by drying out. Hydration involves chemical reactions between water and the cement compounds.³ It therefore sets and hardens whether left in air or submerged in water. Once set, it has low permeability and resists attack from water. All these attributes make portland cement ideal for completing wells and maintaining isolation between zones.



□ A Cement Evaluation (CET*) log from a well in a Middle East carbonate reservoir. The CET tool has eight ultrasonic transducers distributed radially on a mandrel. Emitted acoustic energy resonates the casing if there is no cement bond and shows up as white on the image in track 3 of the log. A good bond shows up as black.

The top third of the log is mostly black indicating good bond. The middle third showing mostly white is poor bond that almost certainly will not prevent fluid communication. The bottom third shows a white vertical streak that probably corresponds to an open channel.

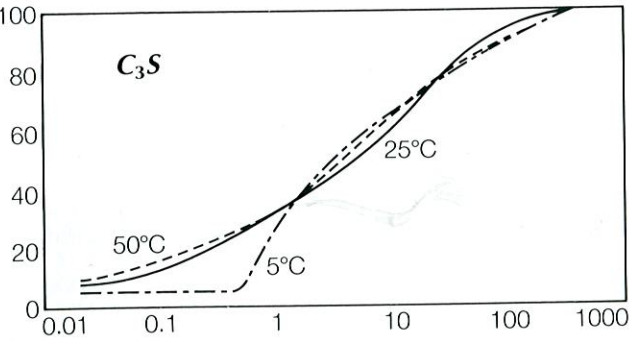
Mixed with water, silicates C_3S and C_2S , which constitute up to 80 percent of portland cement, produce similar hydration products:



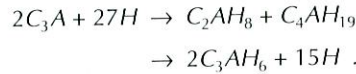
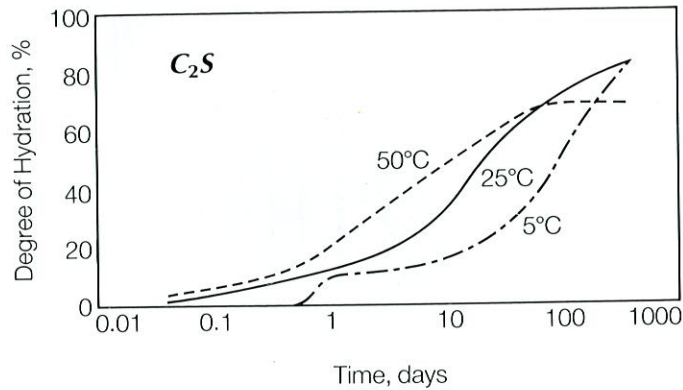
The calcium-silicate-hydrate, $C_3S_2H_3$, also called the *C-S-H* gel, is largely amorphous, comprises roughly 70 percent of the set cement and gives cement its strength. The calcium hydroxide, $Ca(OH)_2$ [*CH*], known as portlandite, saturates the cement slurry's aqueous phase raising its pH to between 12.5 and 13.

At first, these hydration reactions proceed vigorously and a dense layer of *C-S-H* gel builds up around each silicate particle. But the gel is relatively impermeable and it soon prevents more water reaching the surface of the anhydrous silicates, hindering further hydration. An interval of low reactivity follows, called the induction period. Hydration eventually picks up when the permeability of the *C-S-H* gel layer begins increasing, allowing more water to reach the silicate grain surfaces (*below*). (Why the gel becomes more permeable is not well understood.) The onset of setting and early strength development is controlled by C_3S because it hydrates quicker than C_2S and because it's more abundant. The C_2S component affects the hardened cement's final strength (*above right*).

The aluminate components, particularly C_3A , react most strongly at the beginning of hydration and therefore affect the rheology of the cement slurry and early strength development. Both C_3A and C_4AF produce the calcium-aluminate-hydrate, C_3AH_6 , through intermediate metastable reactions (only the C_3A reactions are shown):



□ Hydration rates of the two silicate components, C_3S and C_2S . The C_3S hydrates quicker than C_2S and dominates early strength development. Hydration rate of both components tends to increase with temperature.



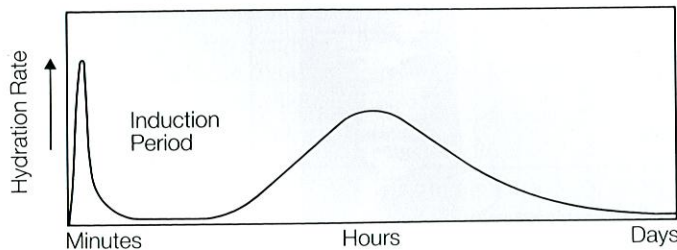
Unlike the *C-S-H* gel, calcium-aluminate-hydrates are crystalline, not amorphous, and don't form a protective layer around the aluminate grain surfaces. Consequently, hydration would normally occur rapidly and has to be controlled to prevent premature stiffening of the cement, called "flash set." This is where the gypsum, added to the clinker to produce portland cement, comes in.

Dissolved in water, gypsum releases calcium and sulfate ions. These react with aluminate and hydroxyl ions released by

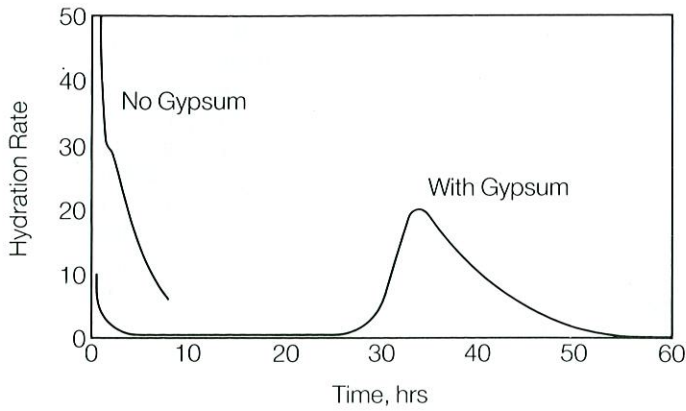
the aluminates forming a trisulfoaluminate hydrate [$C_3A \cdot 3CS \cdot 32H$] called ettringite. The ettringite precipitates as needle-shaped crystals on the C_3A grain surfaces, hindering further hydration and creating an artificial induction period (*above right*).

The hydration of portland cement as a whole can be considered a sequence of overlapping reactions leading to a continuous thickening and hardening cement slurry (*right*). During initial hydration, when the anhydrous material is added to water and hydration products begin to form, the cement grains remain independent and the cement slurry can be pumped. This state of affairs continues for most of the induction period. But when hydration picks up after the induction period, the cement grains begin to link together and the slurry is not pumpable. Compressive strength develops as the hydration products become intergrown. The reactions speed up as temperature increases.

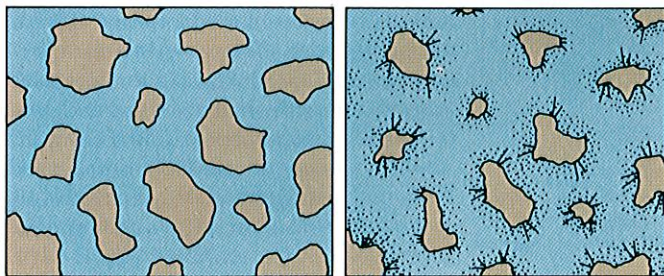
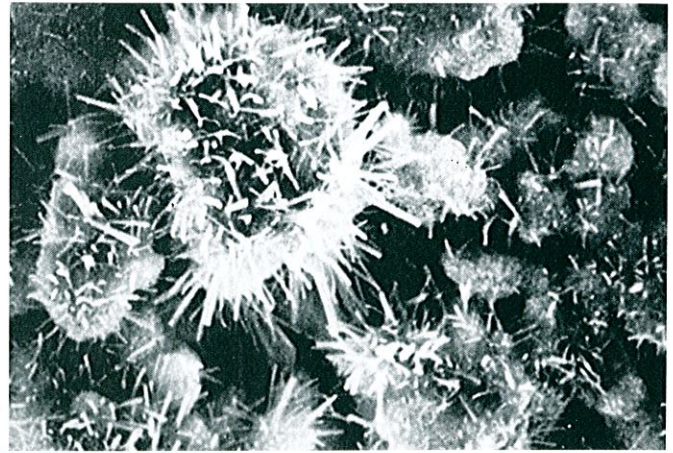
Reaction speed also depends on the relative concentrations of the cement components and their particle size or fineness. For example, the more C_3S there is relative to C_2S , the quicker a cement sets, because C_3S reacts quicker than C_2S . Generally, the finer the cement, the more water is required to prepare a pumpable slurry and the faster compressive strength develops. Speed is a key factor in designing a cement operation. Another factor is the concentration of C_3A .



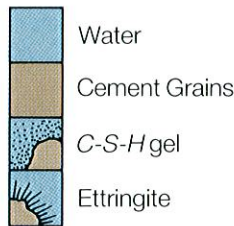
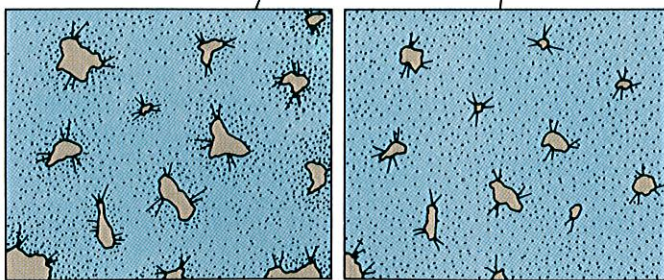
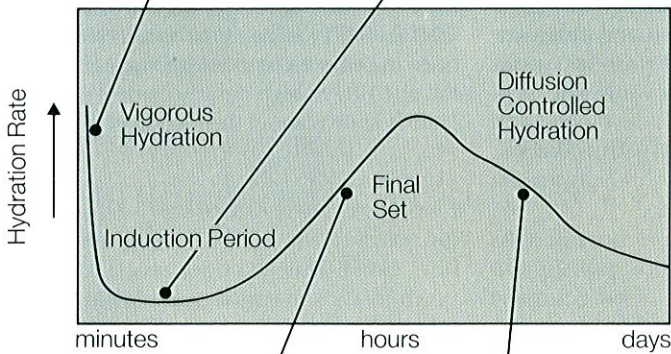
□ Hydration of the silicate components of Portland cement. Hydration is at first rapid. It then enters a slow "induction" period, caused by the hydration product, *C-S-H* gel, covering the unhydrated remnants of the silicate grains and preventing water from reaching them. Finally the gel lets water in and hydration picks up.



□ Hydration of the aluminate components, C_3A and C_4AF , with and without gypsum. The gypsum promotes formation of ettringite around the aluminate grains, which slows hydration and creates an artificial induction period. A scanning electron micrograph of the spiky ettringite growth was made at approximately 5000-X magnification.



□ Schematic of cement hydration. Final cement strength is provided mainly by the amorphous C-S-H gel created by the cement's hydrating silicate components.



Portland cements containing low amounts of C_3A are less susceptible to sulfate attack—magnesium and sodium sulfates in downhole brines react with cement's hydration products and cause loss of compressive strength.

Relative concentrations of components and fineness are criteria by which the American Petroleum Institute classifies oil-field cements (see "Typical Properties of API Portland Cements," below left).⁴ Classes A, B and C (the letters indicate a chronology) were developed in the 1950s and rated for wells less than 6,000 feet [1,830 meters] deep. Class B has less C_3A and was designed for sulfate resistance. Class C, with more C_3S and C_3A and ground much finer, was designed to give high early compressive strength. Classes D and E, so-called retarded cements, were designed for cementing wells up to 14,000 feet [4,250 meters] deep. Their low concentrations of the fast-hydrating C_3S and C_3A and their coarse grind prolongs hydration and consequently the available pumping time.

In the 1960s, the development of additives extended the depth limitation of all cements. The most recently introduced cements, classes G and H, have stringent manufacturing specifications and behave more predictably. Classes G and H have a similar composition to Class B, but Class H is normally coarser than Class G.

Typical Properties of API Portland Cements

API Class	C_3S %	C_2S %	C_3A %	C_4AF %	Fineness cm^2/g	Special Application
A	53	24	8	8	1,500 to 1,900	none
B	47	32	5	12	1,500 to 1,900	sulfate resistant
C	58	16	8	8	2,000 to 2,800	early setting
D&E	26	54	2	12	1,200 to 1,600	retarded
G&H	50	30	5	12	1,400 to 1,700	more stringent specs.

4. Section 2 in *Specification for Materials and Testing for Well Cements: API Specification 10*, Washington, DC: American Petroleum Institute, 1988.

Cement Additives

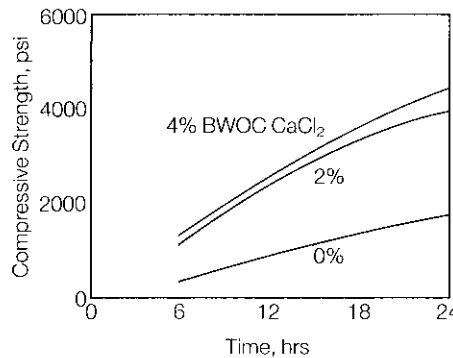
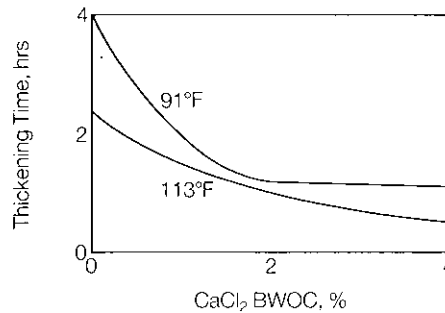
Today's well cements have to withstand an enormous range of well depths and conditions. In permafrost zones, the cement must withstand below-freezing conditions, while in thermal recovery wells or geothermal fields they must endure temperatures above 350°C [660°F]. They must contend with weak formations, formations that might cause lost circulation, and corrosive and overpressured formation fluids. How can cement be formulated to accommodate such varied conditions? The answer lies in additives, which come in eight main varieties (see "Summing Up The Additives," *opposite*).⁵

Accelerators

In shallow, low-temperature wells, accelerators speed up the early stages of hydration and cut the cement's setting time. Accelerators are also used to counteract the setting delay caused by other additives, such as dispersants and fluid-loss agents.

The most common accelerator is calcium chloride [CaCl₂]. Why it accelerates hydration is not completely understood. Evidence suggests calcium chloride may increase the permeability of the C-S-H gel building around each silicate grain and therefore give water ready access to the grain's anhydrous surface. This would shorten the induction period.

Calcium chloride is normally added at concentrations of 2 to 4 percent by weight of cement (BWOC). Higher concentration decreases thickening time—equivalent to the length of time the slurry is pumpable (*above right*).

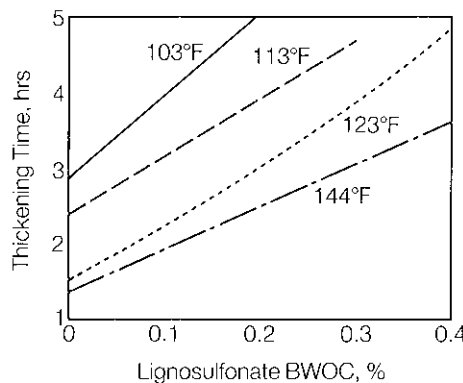


□ Thickening time, the period during which cement can be pumped, is accelerated by adding calcium chloride [CaCl₂] (top). Compressive strength also develops faster with calcium chloride (bottom).

Retarders

Retarders inhibit hydration and delay setting, allowing sufficient time for slurry placement in deep and hot wells. The technology of retarders is well developed and several types are used. Why they work is something of an enigma, although several theories have been developed.⁶

The most common retarders are derived from wood pulp. They comprise sodium and calcium salts of lignosulfonic acids and contain some saccharides. These retarders



□ Thickening time is prolonged when retarders such as lignosulfonate are added to cement.

are thought to adsorb onto the initial layer of C-S-H gel, rendering it hydrophobic and prolonging the induction period. Added in concentrations of 0.1 to 1.5 percent BWOC, they retard hydration at temperatures up to 122°C [250°F] (*below left*). When treated with other chemicals such as borax, lignosulfonates can be used to 315°C [600°F].

Hydroxycarboxylic acids, such as gluconate and glucoheptonate salts, also retard hydration but are not used when the bottomhole temperature is below 93°C [200°F]. Otherwise, thickening times become excessively long. These compounds attach themselves to calcium ions and as a result are thought to inhibit nucleation and growth of hydration products.

Cellulose derivatives such as carboxymethyl hydroxyethyl cellulose (CMHEC) have been used for many years as cement retarders. They are generally effective to 120°C [250°F]. Like the lignosulfonates, they slow hydration by rendering the C-S-H gel hydrophobic. CMHEC imparts some secondary effects such as improved fluid-loss control, which may be desirable, and higher slurry viscosity, which may be undesirable.

A relatively new class of retarders, organophosphates, are effective at bottomhole circulating temperatures as high as 204°C [400°F].⁷ They tend to tolerate variations in cement composition and can lower the viscosity of high-density cement slurries. Little is known about their mode of action.

Extenders

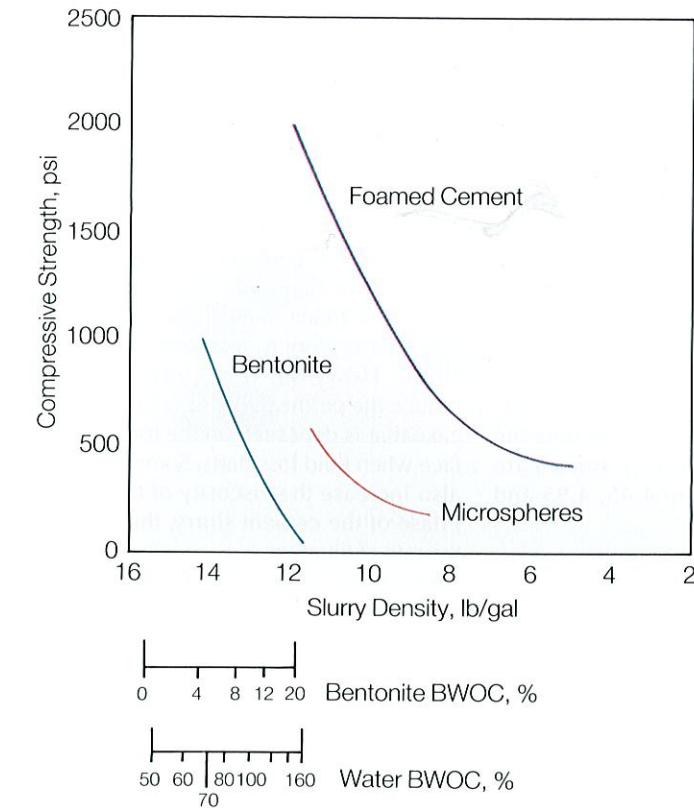
Cement extenders reduce slurry density and lower hydrostatic pressure during cementing operations. This helps prevent the breakdown of weak formations and loss of circulation. They also reduce the amount of cement needed for the cementing operation. Because they're less expensive than cement, they bring considerable savings. Three types of extenders are water extenders, low-density aggregates and gas. Often more than one type is used in the same slurry.

5. "Additives for Oil-Well Cements" in *Cementing Technology*. London: Dowell-Schlumberger, 1984.
 6. Massazza F: "Admixtures in Concrete," in Ghosh SN (ed): *Advances in Cement Technology*. Oxford: Pergamon Press Ltd., 1983.
 7. Nelson EB: "Well Treating Process and Composition," Canadian Patent No. 1,216,742 (January 20, 1987).
 8. Smith RC, Powers CA and Dobkins TA: "A New Ultra-Lightweight Cement with Super Strength," *Journal of Petroleum Technology* 32 (1980): 1438-1444.
- † Mark of Dowell Schlumberger

Water extenders allow the addition of water to the slurry while ensuring that solids remain in suspension. The most common is bentonite, a clay mineral that has the unusual property of expanding several times its original volume when placed in water. This increases the slurry's viscosity and its ability to suspend solids. Bentonite is added in concentrations as high as 20 percent BWOC. Slurry density quickly decreases with bentonite concentration. However, there is a price to be paid in terms of compressive strength (*right*). Another water extender is sodium silicate. This reacts with the calcium hydroxide in the cement slurry to produce a viscous *C-S-H* gel allowing large volumes of water to be added to the slurry.

Low-density aggregates are materials of density less than that of portland cement, which is 3.15 g/cm³. The most commonly used are pozzolans, finely-divided siliceous and aluminous materials. They are obtained from volcanic ash, diatomaceous earth and fly ash from coal-burning power stations. Pozzolans not only reduce cement-slurry density, but also increase its compressive strength by reacting with the calcium hydroxide in the slurry.

At present, the most efficient low-density aggregates are microspheres, small gas-filled beads with specific gravities as low as 0.2.⁸ Since they are lighter than water, slurry den-



□ Extenders such as bentonite, foamed cement and microspheres decrease the cement slurry density—to cut down on cementing costs and protect against the breakdown of weak formations—but also decrease final compressive strength. The bentonite and foam data were obtained on cement cured at 38°C [100°F], and the microsphere data on cement cured at 27°C [80°F]. Curing time in all cases was 24 hours.

sity is substantially reduced without adding large quantities of water. As a result, compressive strength is preserved. The improvement is dramatic when compared with bentonite (*above*).

Gases such as nitrogen, or sometimes air, are used to prepare foamed cement with exceptionally low density. As with microspheres, using gas as an extender requires no additional water (*above*).

Summing Up The Additives

Cement additives, which number more than 100, can be grouped into eight major categories:

Accelerators reduce cement setting time and speed up the development of compressive strength. They are commonly used in shallow, low-temperature wells.

Retarders extend cement setting time and allow sufficient time for slurry placement in deep wells.

Extenders reduce cement density and may also reduce the amount of cement needed for a job. Low-density cement is needed for cementing weak formations, which would otherwise break down and cause lost circulation.

Weighting agents increase cement density. These are used for cementing high-pressure formations, which might become unstable if slurry density were too low.

Dispersants reduce the viscosity of cement slurry and ensure good mud removal during placement.

Fluid-loss control agents (FLAC[†]) control water loss from the cement into the formation.

Lost-circulation control agents reduce the loss of cement slurry into weak or vuggy formations. Loss of cement may necessitate a costly, remedial cementing operation.

Special additives, such as antifoam agents and fibers, are manufactured for specific cementing tasks, such as the prevention of foaming that might lead to a loss in hydraulic pressure.

Weighting Agents

In high-pressure gas wells or in physically unstable wellbores, high-density fluids are required to maintain control. In such cases, drilling mud densities often go up to 2.16 g/cm³ [18 lb/gal] and cement slurries of equal or higher density become necessary.

The most obvious way of increasing cement density is to reduce the amount of water in the slurry. However, this can make the slurry difficult to pump. Alternatively, materials of high specific gravity can be added. These must have a particle size similar to that of the cement. The most commonly used weighting agents are ilmenite [FeTiO₃], hematite [Fe₂O₃] and barite [BaSO₄] with densities of 4.45, 4.95 and 4.33 g/cm³ respectively.

Dispersants

Successful cementing relies on good mud removal, best achieved by pumping the concrete slurry in turbulent flow. Dispersants control slurry rheology and help induce turbulence at low pumping rates. Dispersants also allow the water content of the cement to be lowered without making it difficult to pump.

Basically, dispersants neutralize positive charges on cement particles which would otherwise make them mutually attractive. They effectively break up aggregates into individual particles. At the right concentration, dispersants improve cement homogeneity and lower its permeability. However, an overdose of dispersants can produce a phase separation in the cement slurry that results in cement particles settling out of solution and the development of free water.⁹

The most common dispersants are sulfonates containing highly branched polymers. Polynaphthalene sulfonate is the most widely used.

Fluid-Loss Control Agents (FLACS)

When cement is placed across a permeable formation under pressure, a filtration process is created. Water from the slurry escapes into the formation and the cement particles are left behind. If this fluid loss is not controlled, the rheology, thickening time and density of the slurry will change and the cementing job could fail. To prevent water loss and maintain slurry characteristics, FLAC agents are added to the cement slurry. How FLAC agents work is, again, not fully understood. However, it is known that they reduce the permeability of the cement filter cake that is deposited on the formation surface when fluid loss starts. Some FLAC agents also increase the viscosity of the aqueous phase of the cement slurry, thus reducing the rate of filtration.

Two types of FLAC agents are used: finely-divided materials and water-soluble polymers. Finely-divided materials, such as bentonite, enter the filter cake, lodge between the particles and lower permeability. More commonly used are emulsion polymers made of latex particles that act the same way as bentonite. So-called latex cements have excellent fluid-loss characteristics and can be used to 176°C [350°F].¹⁰

Water-soluble polymers operate by increasing the viscosity of the aqueous phase and/or lowering the filter cake permeability. Water-soluble cellulose derivatives, such as hydroxyethyl cellulose (HEC), are also used. However, these can make the slurry more viscous and difficult to mix. Their efficiency also decreases with increasing temperature. Nonionic synthetic polymers, such as polyvinyl alcohol (PVA), are also effective. At high well temperatures, cationic polymers, such as polyethylene imine (PEI), are frequently adopted. These can control fluid loss at temperatures up to 225°C [437°F], but they also encourage slurry sedimentation.

Lost-Circulation Control Agents

If circulation is lost during a primary cementing job, expensive remedial cementing will usually be needed. Circulation loss can occur in fractured, vuggy or cavernous formations; generally, drilling parameters tell the operator when to expect lost circulation problems.¹¹

Circulation losses are normally prevented by adding materials that bridge fractures and block weak zones. Granular materials,

such as gilsonite and granular coal are excellent bridging agents but ground walnut or pecan shells, coarse bentonite or even corn cobs are sometimes used. Cellophane flake is another important bridging agent. The flakes form a mat that seals the face of the fracture and prevents cement from entering the formation.

If vugs or caverns in the formation are so large that bridging agents do not work, thixotropic cements can be used. When thixotropic cement enters the formation and slows down, it experiences less shear force and begins to gel, becoming self-supporting and eventually plugging the cavern or vug.

Special Additives

Additives performing special tasks include antifoam agents, fibrous additives and agents to prevent gas migration.

Antifoam agents prevent foaming that often arises when additives are mixed into the cement slurry. Excessive foaming can cause a loss in hydraulic pressure possibly wrecking the cementing operation. Polyethylene glycol is the cheapest and most commonly used antifoaming agent. To work properly, it is mixed with the water before slurry preparation. The more expensive silicone emulsions will defeat a foam regardless of when they are added.

Fibrous materials are mixed with cement to increase its resistance to stresses that develop around drill collars or during perforating. Nylon fibers and particulate rubber are the two most popular strengthening agents.

Gas wells present special problems. During drilling and while the cement is being pumped, the hydrostatic pressure of the borehole fluid prevents gas entering the wellbore. But as soon as the slurry begins setting, it loses its ability to transmit hydrostatic pressure and gas can migrate into it. In recent years, additives have been developed to prevent gas migration. Among the most successful are special lattices, such as GAS-BLOK[†], that coagulate at the gas-cement interface forming a membrane impermeable to gas.¹²

High-Temperature Wells

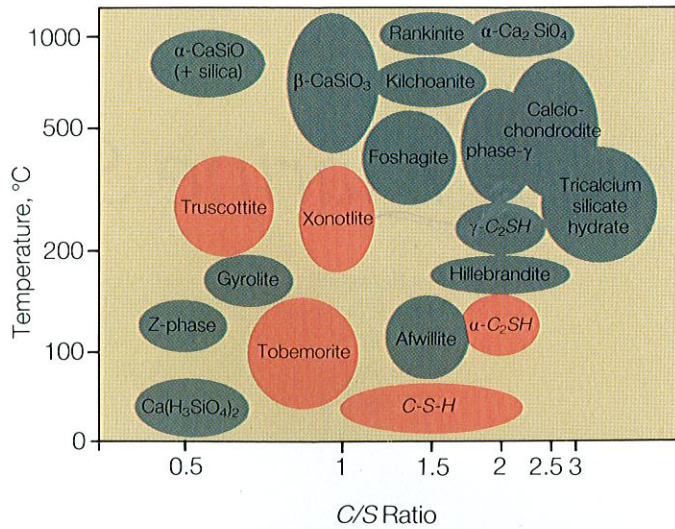
High temperatures present the greatest cementing challenge. Above 110°C [230°F], the behavior of Portland cement changes, not only during hydration but also after setting. High temperatures are encountered in deep oil and gas wells, geothermal wells (see "The Earth's Heat," page 54) and thermal recovery wells.

High temperature accelerates hydration, so retarders and other additives are used to slow reaction times and allow successful placement. But high temperature also affects cement strength after setting. Depending on temperature and the cement's *C/S* ratio, the set cement converts to a variety of calcium silicate phases. Some of these reduce compressive strength and increase permeability (right, above).¹³

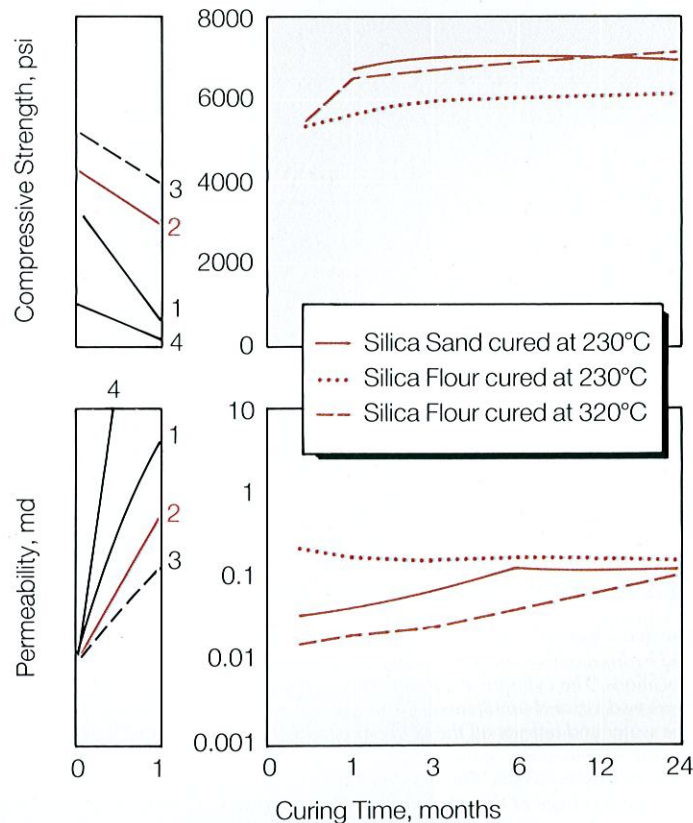
One such phase is alpha dicalcium silicate hydrate [α - C_2SH] that forms from *C-S-H* gel and calcium hydroxide, which jointly have a *C/S* ratio of 1.5 to 2.0. Formation of α - C_2SH can be prevented by adding about 35 percent BWOC of silica to the cement, altering the *C/S* ratio to about 0.8. The *C-S-H* gel then produces different calcium silicate phases—tobermorite [$C_5S_6H_5$] and xonotlite [C_6S_6H]—that are stable (right). Other calcium silicate phases have been extensively studied, and some like truscottite and a sodium-substituted calcium silicate, pectolite, have been found stable.¹⁴

Portland cement becomes totally unstable above 400°C [750°F], which is much lower than the temperature usually found in a fire-flood well. For the ultra-high temperatures of thermal recovery, special cements are used that comprise mainly monocalcium aluminate [CA].

Even with today's technology, no cement operation is entirely routine. Cement chemistry is highly complex and cements can behave unpredictably—cements and additives are routinely tested in the laboratory before taking them into the field. But our understanding is advancing and it can only increase the safety and efficiency of cementing operations as well as extend the range of well conditions in which we can reliably cement. —GC



□ Calcium-silicate phase diagram showing changes occurring to the *C-S-H* gel as temperature increases and the *C/S* ratio varies. A gel with *C/S* ratio of 1.5 to 2.0 changes to unstable α - C_2SH above 110°C [230°F]. A gel with a lower ratio of 0.8, obtained by adding silica to the cement, changes to stable calcium silicates, tobermorite and xonotlite. Another stable phase is truscottite.



□ Degradation of cement performance at high curing temperatures (left) and restored performance with added silica (right). Without extra silica, standard classes G and H cements cured at 230°C [450°F] degrade in compressive strength and permeability. Adding silica sand (grain size 80 to 100 μ m) restores performance. At the higher curing temperature of 320°C [610°F], adding silica in the form of flour (grain size 40 to 50 μ m) becomes necessary to restore performance.

- 1 Class G, 15.6 lb/gal
- 2 Class G, 16.2 lb/gal
- 3 Class H, 17.0 lb/gal
- 4 Class G, 13.0 lb/gal

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