CEMENT

1. Introduction

The term cement is used to designate many different kinds of substances that are used as binders or adhesives (qv). The cement produced in the greatest volume and most widely used in concrete for construction is portland cement. Masonry and oil well cements are produced for special purposes. Calcium aluminate cements are extensively used for refractory concretes (see ALUMINUM COMPOUNDS, ALUMINUM OXIDE; REFRACTORIES). Such cements are distinctly different from epoxies and other polymerizable organic materials. Portland cement is a hydraulic cement, ie, it sets, hardens, and does not disintegrate in water. Hence, it is suitable for construction of underground, marine, and hydraulic structures whereas gypsum plasters and lime mortars are not. Organic materials, such as latexes and water-soluble polymerizable monomers, are sometimes used as additives to impart special properties to concretes or mortars. The term cements as used herein is confined to inorganic hydraulic cements, principally portland and related cements. The essential feature of these cements is their ability to form on hydration with water relatively insoluble bonded aggregations of considerable strength and dimensional stability (see also BUILDING MATERIALS, SURVEY).

Hydraulic cements are manufactured by processing and proportioning suitable raw materials, burning (or clinkering at a suitable temperature), and grinding the resulting hard nodules called clinker to the fineness required for an adequate rate of hardening by reaction with water. Portland cement consists mainly of tricalcium silicate [12168-85-3], Ca_3SiO_5, and dicalcium silicate [10034-77-2], Ca_2SiO_4. Usually two types of raw materials are required: one rich in calcium, such as limestone, chalk, marl, or oyster or clam shells; the other rich in silica, such as clay or shale. The two other significant phases in portland cements are tricalcium aluminate [12042-78-3], $Ca_3Al_2O_6$, and ferrite phase (see FERRITES). A small amount of calcium sulfate [7778-18-9], $CaSO_4$, in the form of gypsum or anhydrite is also added during grinding to control the setting time and enhance strength development (see CALCIUM COMPOUNDS, CALCIUM SULFATE).

The demand for cement was stimulated by the growth of canal systems in United States during the nineteenth century. Process improvements were made in the calcination of certain limestones for the manufacture of natural cements, which were gradually displaced by portland cement. This latter was named in a 1824 patent because of its color and resemblance to a natural limestone quarried on the Isle of Portland in England. Research conducted since that time has provided a clear picture of the composition, properties, and fields of stability of the principal systems found in portland cement. These results led to the widely used Bogue calculation of composition based on oxide analysis (1). Details beyond the scope of this article may be found in the literature (2).

2. Clinker Chemistry

The conventional cement chemists' notation uses abbreviations for the most common constituents: calcium oxide [1305-78-8], CaO, = C; silicon dioxide [7631-86-9],

SiO_2 = S; aluminum oxide [1344-28-1], Al_2O_3 = A; ferric oxide [1309-37-1], Fe_2O_3, = F; magnesium oxide [1309-48-4], MgO, = M; sulfur trioxide [7446-11-9], SO_3, = $\bar{S}$; sodium oxide [1313-59-3], Na_2O, = N; potassium oxide [12136-45-7], K_2O, = K; carbon dioxide, CO_2, C; and water, H_2O, = H. Thus tricalcium silicate, Ca_3SiO_5, is denoted by C_3S.

Portland cement clinker is formed by the reactions of calcium oxide and acidic components to give C_3S, C_2S, C_3A, and a ferrite phase approximating C_4AF.

2.1. Phase Equilibria. During burning in the kiln, ~20–30% of liquid forms in the mix at clinkering temperatures. Reactions occur at surfaces of solids and in the liquid. The crystalline silicate phases formed are separated by the interstitial liquid. The interstitial phases formed from the liquid in normal clinkers during cooling are also shown by X-ray diffraction (XRD) to be completely

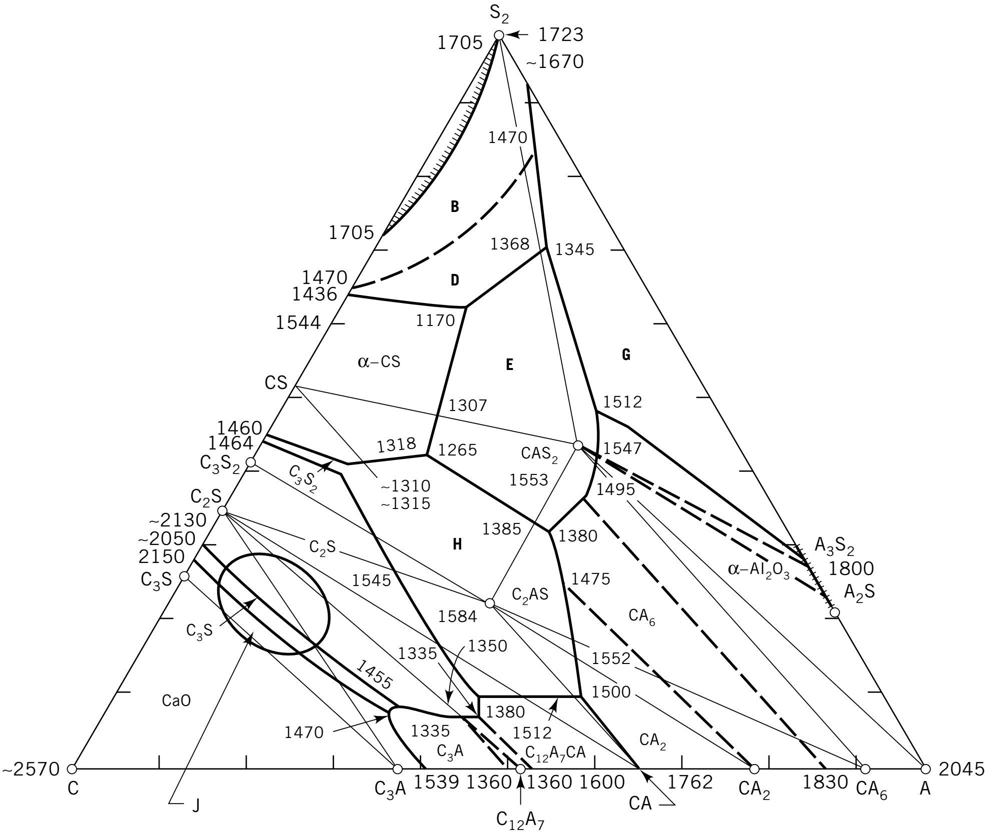


Fig. 1. Phase equilibria in the C–A–S ($CaO-Al_2O_3-SiO_2$) system (3,4); temperatures are in °C. Shaded areas denote two liquids; compositional index marks on the triangle are indicated at 10% intervals; **B** denotes cristobalite [14464-46-1], and **D** denotes tridymite [15468-32-3], both of SiO_2 composition; E is anorthite [1302-54-1], $Al_2CaSi_2O_8$; G is mullite [55964-99-3]; **H**, gehlenite [1302-56-3], $Ca_2Al_2SiO_7$; and **J** is the area of portland cement compositions.

crystalline, although they may be so finely subdivided as to appear glassy (optically amorphous) under the microscope.

The high temperature phase equilibria governing the reactions in cement kilns have been studied, eg, in the $CaO-Al_2O_3-SiO_2$ system illustrated in Figure 1. In such a ternary diagram, the primary-phase fields are plotted, ie, the composition regions in which any one solid is the first to separate when a completely liquid mix is cooled to produce negligible supercooling. The primary-phase fields are separated by eutectic points on the sides of the triangle such as that at 1436°C between tridymite and α-CS.

In the relatively small portland cement zone, almost all modern cements fall in the high-lime portion (~65% CaO). Cements of lower lime content tend to be slow in hardening and may show trouble from dusting of the clinker by transformation of β- to γ-C_2S, especially if clinker cooling is very slow. The zone is limited on the high lime side by the need to keep the uncombined CaO to low enough values to prevent excessive expansion from hydration of the free lime. Commercial manufacture at compositions near the $CaO-SiO_2$ axis can present difficulties. If the lime content is high, the burning temperatures may be so high as to be impractical. If the lime content is low, the burning temperatures may even be low, but impurities must be present in the C_2S to prevent dusting. On the high alumina side the zone is limited by excessive liquid-phase formation that prevents proper clinker formation in rotary kilns.

The relations between the compositions of portland cements and some other common hydraulic cements are shown in the $CaO-SiO_2-Al_2O_3$ phase diagram of Figure 2 (5). In this diagram, Fe_2O_3 has been combined with Al_2O_3 to yield

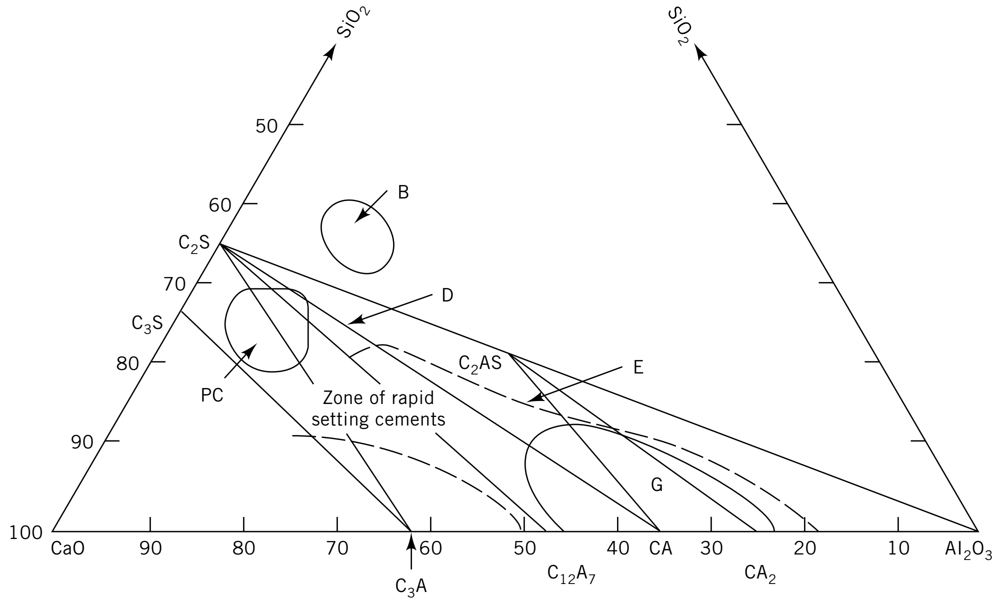


Fig. 2. Cement zones in the $CaO-Al_2O_3-SiO_2$ system (5) where B represents basic blast-furnace slag; D, cement compositions which dust on cooling; E, compositions showing no tendency to set; G, aluminous cement; and PC, portland cement.

the Al_3O_3 content used. This commonly applied approximation permits a two-dimensional representation of the real systems.

2.2. Clinker Formation. Portland cements are ordinarily manufactured from raw mixes including components such as calcium carbonate, clay or shale, and sand. As the temperature of the materials increases during their passage through the kiln, the following reactions occur: evaporation of free water; release of combined water from the clay; decomposition of magnesium carbonate; decomposition of calcium carbonate (calcination); and combination of the lime and clay oxides. The course of these last reactions (6), which occur at the high temperature end of the kiln, just before and in the burning zone, is illustrated graphically in Figure 3 (7).

From the phase diagram of the $CaO-SiO_2-Al_2O_3$ system, the sequence of crystallization during cooling of the clinker can be derived if the cooling is slow enough to maintain equilibrium. For example, a mix at 1500°C of relatively low lime content, along the C_3S-C_2S eutectic line in Figure 1, is composed of solid C_3S and C_2S and a liquid along the C_3S-C_2S eutectic at the intersection with the 1500°C isotherm to the left of the 1470–1455 line. Upon cooling, this liquid deposits more C_3S and C_2S, moving the liquid composition down to the invariant point at 1455°C, at which C_3A also separates until crystallization is complete. Although real cement clinkers contain more components, which alter the system and temperatures somewhat, the behavior is similar.

Cooling is ordinarily too rapid to maintain the phase equilibria. In the case in Figure 1, the lime-deficient liquid at 1455°C requires that some of the solid C_3S redissolve and that more C_2S crystallize during crystallization of the C_3A. During rapid cooling, there may be insufficient time for this reaction and the C_3S content is thus higher than when equilibrium conditions prevail. In this event, crystallization is not completed at 1455°C, but continues along the C_3A-C_2S boundary until the invariant point at 1335°C is reached. Crystallization of

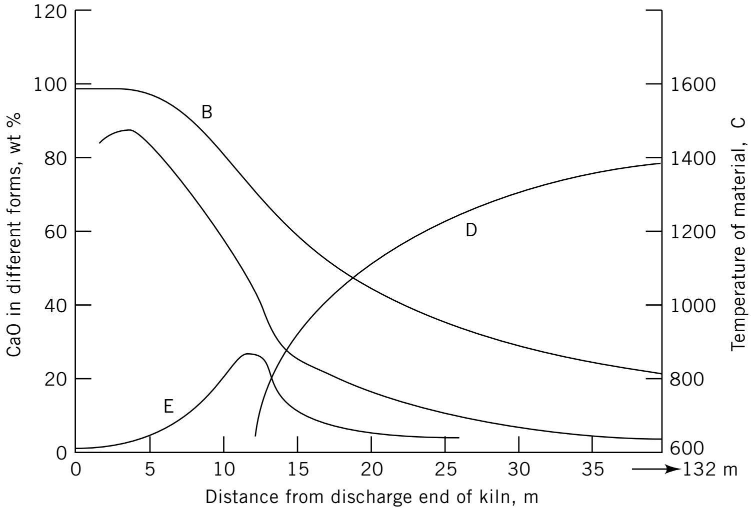


Fig. 3. Temperatures and progress of reactions in a 132-meter wet-process kiln; area B represents proportion of total CaO in new compounds; D, CaO as $CaCO_3$; and E, free CaO.

C_2S, C_3A, and $C_{12}A_7$ then occurs to reach complete solidification. Such deviations from equilibrium conditions cause variations in the phase compositions that are estimated from the Bogue calculation, and cause variations in the amounts of dissolved substances such as MgO, alkalies, and the alumina content of the ferrite phase.

The theoretical energy requirement for the burning of portland cement clinker can be calculated from the heat requirements and energy recovery from the various stages of the process. Knowledge of the specific heats of the various phases, and the heats of decomposition, transformation, and reaction then permits calculation of the net theoretical energy requirement of 1760 kJ (420 kcal) for 1 kg of clinker from 1.55 kg of dry $CaCO_3$ and kaolin (see CLAYS) (8).

The kinetics of the reactions are strongly influenced by the temperature, mineralogical nature of the raw materials, fineness to which the raw material is ground, percentage of liquid phase formed, and viscosity of the liquid phase. The percentage of liquid formed depends on the alumina and iron oxides. When the sum of these oxides is low, the amount of liquid formed is insufficient to permit rapid combination of the remaining CaO. The viscosity of the liquid at clinkering temperature is reduced by increasing the amounts of oxides such as MnO, Fe_2O_3, MgO, CaO, and Na_2O (9).

The reaction of C_2S with CaO to form C_3S depends on dissolution of the lime in the clinker liquid. When sufficient liquid is present, the rate of solution is controlled by the size of the CaO particles, which depends in turn on the sizes of the particles of ground limestone. Coarse particles of calcite fail to react completely under commercial burning conditions. The reaction is governed by the rate of solution (10):

$$\log t = \log \frac{D}{A} + 0.43\,\frac{E}{RT}$$

t is the time in minutes, D is the particle diameter in millimeters, A is a constant, T the absolute temperature, and E is the activation energy having a value of 607 kJ/mol (146 kcal/mol). For example, 0.05-mm particles require 59 min for solution at 1340°C but only 2.3 min at 1450°C. A similar relation applies for the rate of solution of quartz grains.

2.3. Phases Formed in Portland cements.

Most clinker compounds take up small amounts of other components to form solid solutions (11). Best known of these phases is the C_3S solid solution called alite. Phases that may occur in portland cement clinker are given in Table 1. In addition, a variety of minor phases may occur in portland cement clinker when certain minor elements are present in quantities above that which can be dissolved in other phases. Under reducing conditions in the kiln, reduced phases, such as ferrous oxide [1345-25-1], FeO, and calcium sulfide [20548-54-3], CaS, may be formed.

The primary phases all contain impurities. In fact, these impurities stabilize the structures formed at high temperatures so that decomposition or transformations do not occur during cooling, as occurs with the pure compounds. For example, pure C_3S exists in at least six polymorphic forms each having a sharply defined temperature range of stability, whereas alite exists in three stabilized forms at room temperature depending on the impurities. Some properties of the more common phases in Portland clinkers are given in Table 2.

Table 1. **Phases in Portland Cement Clinker**[a]

Name of impure form	CAS Registry Number	Chemical name	Cement chemists' notation
free lime	[1305-78-8]	calcium oxide	C
periclase (magnesia)	[1309-48-4] and [1317-74-4]	magnesium oxide	M
alite	[12168-85-3]	tricalcium silicate	C_3S
belite	[10034-77-2]	dicalcium silicate	C_2S
C_3A	[12042-78-3]	tricalcium aluminate	C_3A
ferrite	[12612-16-7]	calcium aluminoferrite[b]	$C_2A_xF_{1-x}$
	[12068-35-8]	tetracalcium aluminoferrite	C_4AF
	[12013-62-6]	dicalcium ferrite[c]	C_2F
mayenite	[12005-57-1]	12-calcium-7-aluminate	$C_{12}A_7$
gehlenite	[1302-56-3]	dicalcium alumino monosilicate	C_2AS
aphthitalite	[12274-74-4] and [17926-93-1]	sodium, potassium sulfate[d]	$N_xK_y\bar{S}$
arcanite	[7778-80-5] and [14293-72-2]	potassium sulfate	$K\bar{S}$
metathenardite	[7757-82-6]	sodium sulfate form I	$N\bar{S}$
calcium langbeinite	[14977-32-8]	potassium calcium sulfate	$2X\bar{S} \cdot K\bar{S}$
anhydrite	[7778-18-9] and [14798-04-0]	calcium sulfate	$C\bar{S}$
calcium sulfoaluminate	[12005-25-3]	tetracalcium trialuminate-sulfate	$C_4A_3\bar{S}$
alkali belite	[15669-83-7]	α′- or β-dicalcium (potassium) silicate[e]	$K_xC_{23}S_{12}$
alkali aluminate	[12004-54-3]	8-calcium disodium trialuminate	NC_8A_3
	[65430-58-2]	5-calcium disilicate monosulfate	$2C2S \cdot C\bar{S}$
spurrite	[1319-44-42]	5-calcium disilicate monocarbonate	$2C2S \cdot C\bar{S}$
	[12043-73-1]	calcium aluminate chloride	$C_{11}A_7 \cdot CaCl_2$[f]
	[12305-57-6]	calcium aluminate fluoride	$C_{11}A_7 \cdot CaF_2$[f]

[a] Refs. (12–14).

[b] Solid solution series where $x = A/(A + F)$; $0 < x < 0.7$.

[c] End member of series.

[d] Solid solution series when $\frac{1}{3} \leq x/y$.

[e] Solid solution series when $x \leq 1$.

[f] Mixed notation.

2.4. Structure. Examination of thin sections of clinkers using transmitted light, and of polished sections by reflected light, reveals details of the structure. The polarizing microscope has been used to determine the size and birefringence of alite crystals, and the size and color of the belite to predict later age strength (17). The clinker phases are conveniently observed by examining polished sections selectively etched using special reagents as shown in Figure 4. The alite appears as clear euhedral crystalline grains, the belite as rounded striated grains, the C_3A as dark interstitial material, and the C_4AF as light interstitial material.

Table 2. **Properties of the More Common Phases in Portland Cement Clinker**[a]

Name	Crystal system	Density, g/L	Mohs' hardness
alite	triclinic		
	monoclinic	3.14–3.25	~ 4
	trigonal		
belite	hexagonal	3.04	
	orthorhombic	3.40	
	monoclinic	3.28	>4
	orthorhombic	2.97	
C_3A	cubic	3.04	<6
ferrite	orthorhombic	3.74–3.77	~ 5
free lime	cubic	3.08–3.32	3–4
magnesia	cubic	3.58	5.5–6

[a] Refs. (11–16).

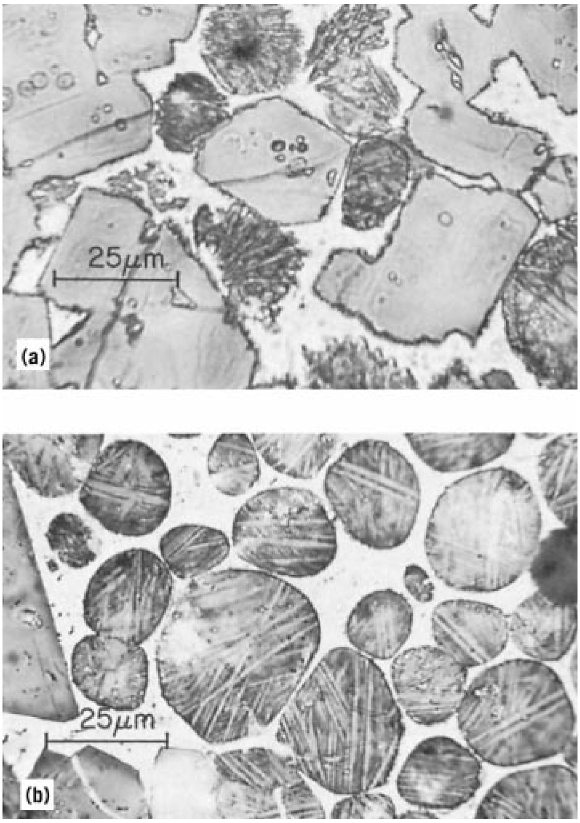


Fig. 4. Photomicrograph of polished and etched sections of portland cement clinkers. The C_3A appears as dark interstitial material, the C_4AF as light interstitial material. (**a**) Euhedral and subhedral alite crystals and rounded or ragged belite; (**b**) rounded and striated belite crystals.

Portland cement clinker structures (11,18,19) vary considerably with composition, particle size of raw materials, and burning conditions, resulting in variations of clinker porosity, crystallite sizes and forms, and aggregations of crystallites. Alite sizes range up to ~80 μm or even larger, most being 15–40 μm.

2.5. Raw Material Proportions. The three main considerations in proportioning raw materials for cement clinker are the potential compound composition; the percentage of liquid phase at clinkering temperatures; and the burnability of the raw mix, ie, the relative ease, in terms of temperature, time, and fuel requirements, of combining the oxides into good quality clinker. The ratios of the oxides are related to clinker composition and burnability. For example, as the CaO content of the mix is increased, more C_3S can be formed, but certain limits cannot be exceeded under normal burning conditions. The lime saturation factor (LSF) is a measure of the amount of CaO that can be combined (20):

$$\mathrm{LSF} = \frac{\%\ \mathrm{CaO}}{2.8\ (\%\ \mathrm{SiO_2}) + 1.1(\%\ \mathrm{Al_2O_3}) + 0.7(\%\ \mathrm{Fe_2O_3})}$$

An LSF of 100 would indicate that the clinker can contain only C_3S and the ferrite solid solution. Lime saturation factors of 88–94 are frequently appropriate for reasonable burnability; low LSF indicates insufficient C_3S for acceptable early strengths, and higher values may render the mix very difficult to burn. Several other weight ratios such as the silica modulus and the iron modulus are also important (21).

The potential liquid-phase content at clinkering temperatures range from 18 to 25% and can be estimated from the oxide analysis of the raw mix. For example (22), for 1450°C:

$$\%\ \text{liquid phase} = 1.13(\%\ \mathrm{C_3A}) + 1.35(\%\ \mathrm{C_4AF}) + \%\ \mathrm{M} + \%\ \text{alkalies}$$

The potential compound composition of a cement or cement clinker can be calculated from the oxide analyses of any given raw materials mixture, or from the oxide analyses of the cement clinker or finished cement. The simplest and most widely used method is the Bogue calculation (23). The ASTM C150 (24) calculation is somewhat modified.

The techniques of determining the proper proportions of raw materials to achieve a mix of good burnability and clinker composition may be determined by computer using an iterative program, starting with raw components of known composition. The concept of targets may be utilized, including fixed values of moduli, compound content, and amount of any raw material element in the final clinker. The number of targets that may be set is one less than the number of raw materials. The fuel ash must be considered as one of the raw materials. Representative chemical analyses of raw materials used in making portland and high alumina cements are given in Table 3, analyses of cements of various types appear in Table 4, along with their potential compound compositions.

Table 3. **Chemical Composition of Raw Materials**[a]**, wt** %

Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Loss on ignition
cement rock	13.4	3.5	1.7	42.9	1.0	37.2
limestone	1.2	0.2	0.4	53.4	1.3	43.4
dolomite	4.5	0.5	1.6	35.0	14.9	44.0
marl	6.0	0.6	2.3	49.1	0.4	40.4
oyster shells	1.5	0.4	1.2	52.3	0.7	41.8
shale	53.8	18.9	7.7	3.2	2.2	8.2
clay	67.8	14.3	4.5	0.9	1.2	8.0
mill scale			~100.0			
sandstone	76.6	5.3	3.1	4.7	1.7	6.6
bauxite	10.6	57.5	2.6			28.4

[a] Courtesy of the American Concrete Institute (25).

3. Hydration

3.1. Calcium Silicates.

In hydrations at ordinary temperatures (27) pure C_3S and β-C_2S, corresponding to the alite and belite phases in portland cements, respectively, react with water to form calcium hydroxide and a single calcium silicate hydrate (C−S−H). Table 5 shows primary compound hydration reactions but not the many minor reactions.

These are the main reactions in portland cements. The two calcium silicates constitute ~75% of the cement. The average lime/silica ratio (C/S) in calcium silicate hydrate (C−S−H) may vary from ~1.5 ~2.0 or even higher, the average value is ~1.7. The water content varies with the ambient humidity, the 3 mol of water being estimated from measurements in the dry state and structural considerations. As the lime/silica ratio of the C−S−H increases, the amount of water increases on an equimolar basis, ie, the lime goes into the structure, resulting in less free calcium hydroxide.

Calcium silicate hydrate is not only variable in composition, but is very poorly crystallized, and archaically referred to as calcium silicate hydrate gel or tobermorite gel because of the colloidal sizes ($<0.1\ \mu$m). The calcium silicate hydrates are layer minerals having many similarities to the limited swelling clay minerals found in nature. The layers are bonded together by excess lime and interlayer water to form individual gel particles only 2−3 layers thick. Surface forces, and excess lime on the particle surfaces, tend to bond these particles together into aggregations or stacks of the individual particles to form the porous gel structure.

Significant changes in the structure of the gel continue over very long periods. During the first month of hydration, appreciable quantities of the dimeric silicate anion $Si_2O_7^6$ are formed. These are reduced by later condensation to higher polysilicates, the amount of which together with the mean length of the metasilicate chains continues to increase for at least 15 years of moist curing. In one study, a mean length of 15.8 silica tetrahedra was found after such prolonged curing (28). These changes appear to have a positive effect on both strength development and reduction of drying shrinkage.

Table 4. **Chemical Composition, Compounds, and Fineness of Cements (51)**[a,b]

Type of Portland cement	Chemical composition, %					Potential compound composition, %						Blaine fineness m^2/kg
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O eq	C_3S	C_2S	C_3A	C_4AF	
I (min–max)	18.7–22.0	4.7–6.3	1.6–4.4	60.6–66.3	0.7–4.2	1.8–4.6	0.11–1.20	40–63	9–31	6–14	5–13	300–421
I (mean)	20.5	5.4	2.6	63.9	2.1	3.0	0.61	54	18	10	8	369
II[c] (min-max)	20.0–23.2	3.4–5.5	2.4–4.8	60.2–65.9	0.6–4.8	2.1–4.0	0.05–1.12	37–68	6–32	2–8	7–15	318–480
II[c] (mean)	21.2	4.6	3.5	63.8	2.1	2.7	0.51	55	19	6	11	377
III (min-max)	18.6–22.2	2.8–6.3	1.3–4.9	60.6–65.9	0.6–4.6	2.5–4.6	0.14–1.20	46–71	4–27	0–13	4–14	390–644
III (mean)	20.6	4.9	2.8	63.4	2.2	3.5	0.56	55	17	9	8	548
IV (min-max)	21.5–22.8	3.5–5.3	3.7–5.9	62.0–63.4	1.0–3.8	1.7–2.5	0.29–0.42	37–49	27–36	3–4	11–18	319–362
IV (mean)	22.2	4.6	5.0	62.5	1.9	2.2	0.36	42	32	4	15	340
V (min-max)	20.3–23.4	2.4–5.5	3.2–6.1	61.8–66.3	0.6–4.6	1.8–3.6	0.24–0.76	43–70	11–31	0–5	10–19	275–430
V (mean)	21.9	3.9	4.2	63.8	2.2	2.3	0.48	54	22	4	13	373
White (min-max)	22.0–24.4	2.2–5.0	0.2–0.6	63.9–68.7	0.3–1.4	2.3–3.1	0.09–0.38	51–72	9–25	5–13	1–2	384–564
White (mean)	22.7	4.1	0.3	66.7	0.9	2.7	0.18	63	18	10	1	482

[a] Courtesy of the American Concrete Institute (51).

[b] Values represent a summary of combined statistics. Air-entraining cements are not included. For consistency in reporting elements are reported in a standard oxide form. This does not mean that the oxide form is present in the cement. For example, sulfur is reported an SO_3, sulfur trioxide, but portland cement does not have sulfur trioxide present. "Potential Compound Composition" refers to ASTM C 150 (AASHTO M 85) calculations using the chemical composition of the cement. The actual compound composition may be less due to incomplete or altered chemical reactions.

[c] Includes fine ground cements.

Table 5. **Portland Cement Compound Hydration Reactions (Oxide Notation)**

$2(3CaO \cdot SiO_2)$ Tricalcium silicate	+	$11H_2O$ Water	=	$3CaO \cdot 2SiO_2 \cdot 8H_2O$ Calcium silicate hydrate (C-S-H)	+	$3(CaO \cdot H_2O)$ Calcium hydroxide
$2(2CaO \cdot SiO_2)$ Dicalcium silicate	+	$9H_2O$ Water	=	$3CaO \cdot 2SiO_2 \cdot 8H_2O$ Calcium silicate hydrate (C-S-H)	+	$CaO \cdot H_2O$ Calcium hydroxide
$3CaO \cdot Al_2O_3$ Tricalcium aluminate	+	$3(CaO \cdot SO_3 \cdot 2H_2O)$ Gypsum	+	$26H_2O$ Water	=	$6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$ Ettringite
$2(3CaO \cdot Al_2O_3)$ Tricalcium aluminate	+	$6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O)$ Ettringite	+	$4H_2O$ Water	=	$3(4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O)$ Calcium monosulfoaluminate
$3CaO \cdot Al_2O_3$ Tricalcium aluminate	+	$CaO \cdot H_2O$ Calcium hydroxide	+	$12H_2O$ Water	=	$4CaO \cdot Al_2O_3 \cdot 13H_2O$ Tetracalcium aluminate hydrate
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ Tricalcium aluminoferrite	+	$10H_2O$ Water	+	$2(CaO \cdot H_2O)$ Calcium hydroxide	=	$6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O$ Calcium aluminoferrite hydrate

Drying and other chemical processes can have significant effects on this structure, there being loss of hydrate water as well as physically adsorbed water, and collapse of the structure to form more stable aggregations of particles (29,30).

3.2. Tricalcium Aluminate and Ferrite. The hydration of the C_3A alone and in the presence of gypsum usually produces well-crystallized reaction products that can be identified by X-ray diffraction and other methods. C_3AH_6 is the cubic calcium aluminate hydrate; C_4AH_{19} and $C_4A\bar{S}H_{12}$ are hexagonal phases, the latter being commonly referred to as the monosulfate. The highly hydrated trisulfate, ettringite, $C_6A\bar{S}_3H_{32}$, occurs as needles, rods, or dense columnar aggregations. Its formation on the surfaces of anhydrous grains is responsible for the necessary retardation of hydration of the aluminates in Portland cements and the expansion process in expansive cements (31).

The early calcium aluminate hydration reactions in portland cements have been studied in simple mixtures of C_3A, gypsum, calcium hydroxide, and water (32). Figure 5 shows the progressive reaction of the gypsum, water, and C_3A as ettringite is formed, the reaction of the ettringite, calcium hydroxide, and water to form the monosulfate, and the solid of the monosulfate with C_4AH_{19}. These reactions are important in the portland cements to control the hydration of the C_3A, which otherwise might hydrate so rapidly as to cause flash set, or premature stiffening, in fresh concrete.

Other reactions taking place throughout the hardening period are substitution and addition reactions (29). Ferrite and sulfoferrite analogues of calcium monosulfoaluminate and ettringite form solid solutions in which iron oxide

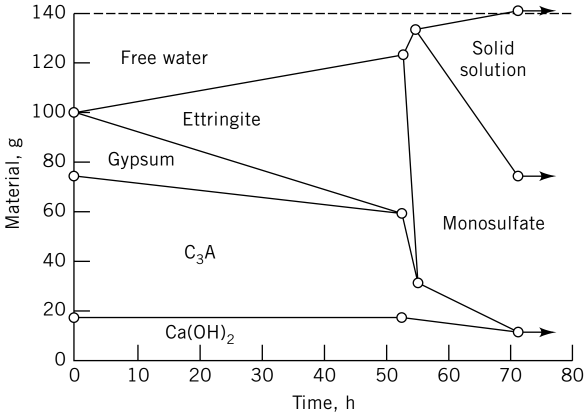


Fig. 5. The early hydration reactions of tricalcium aluminate in the presence of gypsum and calcium hydroxide. Initial molar proportions: 1-C_3A; 1-$Ca(OH)_2$; 3/4-$CaSO_4 \cdot 2H_2O$; 0.4 water–solids ratio (32).

substitutes continuously for the alumina. Reactions with the calcium silicate hydrate result in the formation of additional substituted C–S–H hydrate at the expense of the crystalline aluminate, sulfate, and ferrite hydrate phases.

The hydration of the ferrite phase (C_4AF) is of greatest interest in mixtures containing lime and other cement compounds because of the strong tendency to form solid solutions. When the sulfate in solution is very low, solid solutions are formed between the cubic C_3AH_6 and analogous iron hydrate C_3FH_6. In the presence of water and silica, solid solutions such as $C_3ASH_4 \cdot C_3FSH_4$ may be formed (33). Table 6 lists some of the important phases formed in the hydration of mixtures of pure compounds.

3.3. Other Phases. In cements free lime, CaO, and periclase, MgO, hydrate to the hydroxides. The *in situ* reactions of larger particles of these phases can be rather slow and may not occur until the cement has hardened. These reactions then can cause deleterious expansions and even disruption of the concrete and the quantities of free CaO and MgO have to be limited. The soundness of the cement can be tested by the autoclave expansion test of portland cement ASTM C151 (24).

The expansive component $C_4A_3\bar{S}$ in Type K expansive cements hydrates in the presence of excess sulfate and lime to form ettringite is

$$C_4A_3\bar{S} + 8\,C\bar{S}H_2 + 6\,CH + 74\,H \longrightarrow 3\,C_6A\bar{S}_3H_{32}$$

The reactions in the regulated-set cements containing $C_{11}A_7 \cdot CF_2$ (note mixed notation) as a principal phase resemble those in ordinary portland cements. Initial reaction rates are controlled by ettringite formation. Setting occurs with formation of the monosulfate, along with some transitory lower-limed calcium aluminate hydrates that convert to the monosulfate within a few hours.

Pozzolans contain reactive silica that reacts with cement and water by combining with the calcium hydroxide released by the hydration of the calcium silicates to produce additional calcium silicate hydrate. If sufficient silica is added,

Table 6. **Cement Phases Hydrated at Normal Temperatures**[a]

Name	CAS Registry Number	Approximate composition[b]	Stability range		Crystal system	Density, kg/m^3
			rh, 25°C	Temp, °C		
calcium sulfate dihydrate (gypsum)	[10101-41-4] [13397-24-5]	$C\bar{S}H_2$	100–35	<100	monoclinic	2.32
calcium hydroxide (portlandite)	[1305-62-0]	CH	100–0	<512	trigonal–hexagonal	2.24
magnesium hydroxide (brucite)	[1309-42-8]	MH	100–0	<350	trigonal–hexagonal	2.37
calcium silicate hydrate gel (C–S–H gel)	[12323-54-5]	$C_xS_yH_z$[c]	indefinite		indefinite	2.7[d]
tetracalcium aluminate,						
19-hydrate	[12042-86-3]	C_4AH_{19}	100–85	<15	trigonal–hexagonal	1.80
13-hydrate	[12042-85-2]	C_4AH_{13}	81–12		trigonal–hexagonal	2.02
7-hydrate	[12511-52-3]	C_4AH_7	2–0	to 120		
tetracalcium aluminate monosulfate,						
16-hydrate	[67523-83-5]	$C_4A\bar{S}H_{16}$	aq	<8	trigonal–hexagonal	
14-hydrate	[12421-30-6]	$C_4A\bar{S}H_{14}$	100–95	>9	trigonal–hexagonal	
12-hydrate	[12252-10-7]	$C_4A\bar{S}H_{12}$	95–12	>1	trigonal–hexagonal	1.95
10, 8, *x*-hydrate	[12252-09-4] [12445-38-4]	$C_4A\bar{S}H_x$	<12			
ettringite (6-calcium aluminate trisulfate, 32-hydrate)	[12252-15-2]	$C_6A\bar{S}_3H_{32}$	100–4	<60	trigonal–hexagonal	1.73–1.79
	[11070-82-9]	$C_6A\bar{S}_3H_8$	4–2	<110		
garnet-hydrogarnet solid solution series		$C_3(F_{1-x}A_x)(S_{1-y}H_{2y})_3$[e]	stable		cubic	
	[12042-80-7]	end member: C_3AH_6	100–0	>15	cubic	2.52

[a] Ref. 12,13, and 34.

[b] In cement chemists' notation.

[c] Where $1.3 < x/y < 2$ and probably $1 < z/y < 1.5$.

[d] Wet.

[e] $x = \frac{A}{A + F}$ and $y = \frac{2\,H}{2\,H + S}$.

~30% of the weight of cement, the calcium hydroxide can eventually be completely combined. Granulated blast-furnace slag is not ordinarily reactive in water, but in the presence of lime reactions occur with the silica framework. This breakdown of the slag releases other components so that a variety of crystalline hydrate phases can also form.

3.4. Hydration Process. Portland cement is generally used at temperatures ordinarily encountered in construction, ie, from 5 to 40°C. Temperature extremes have to be avoided. The exothermic heat of the hydration reactions can play an important part in maintaining adequate temperatures in cold environments, and must be considered in massive concrete structures to prevent excessive temperature rise and cracking during subsequent cooling. Heat indued delayed expansion (delayed ettringite expansion) can also be controlled by keeping the concrete temperature <70°C.

The initial conditions for the hydration reactions are determined by the concentration of the cement particles (0.2–100 μm) in the mixing water (w/c = 0.3–0.7 on a wt% basis) and the fineness of the cement (300–600 m^2/kg). Upon mixing with water, the suspension of particles as shown in Figure 6 (35) is such that these particles are surrounded by films of water having an average thickness of ~1 μm. The anhydrous phases initially react by the formation of surface hydration products on each grain, and by dissolution into the liquid phase. The solution quickly becomes saturated with calcium and sulfate ions, and the

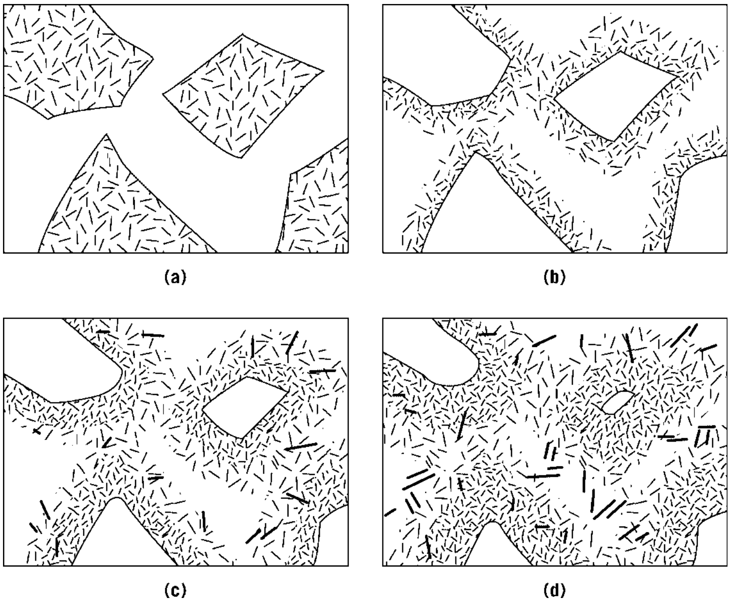

(a) (b) (c) (d)

Fig. 6. Four stages in the setting and hardening of portland cement: simplified representation of the sequence of changes. (**a**) Dispersion of unreacted clinker grains in water. (**b**) After a few minutes; hydration products eat into and grow out from the surface of each grain. (**c**) After a few hours; the coatings of different clinker grains have begun to join up, the hydration products thus becoming continuous (setting). (**d**) After a few days; further development of hydration products has occurred (hardening. Courtesy of Academic Press Inc. (London) Ltd. (35).

concentration of alkali cations increases rapidly. These reactions consume part of the anhydrous grains, but the reaction products tend to fill that space as well as some of the originally water-filled space. The porous hydration products occupy about twice the volume of the reacted anhydrous material (36). The hydration products at this stage are mostly colloidal ($<0.1\ \mu$) but some larger crystals of calcium aluminate hydrates, sulfoaluminate hydrate, and hydrogarnets form. As the reactions proceed the coatings increase in thickness and eventually form bridges between the original grains. This is the stage of setting. Despite the low solubility and mobility of the silicate anions, growths of the silicate hydrates also form on the crystalline phases formed from the solution and become incorporated into the calcium hydroxide and other phases. Upon further hydration the water-filled spaces become increasingly filled with reaction products to produce hardening and strength development.

The composition of the liquid phase during the early hydration of portland cements is controlled mainly by the solution of calcium, sulfate, sodium, and potassium ions. Very little alumina, silica, or iron are present in solution. Calcium hydroxide, as calcium oxide, and gypsum, as calcium sulfate, alone have solubilities of ~1.1 and 2.1 g/L at 25°C, respectively. In the presence of alkalies released in the first 7 min, the composition tends to be governed by the equilibrium:

$$\mathrm{CaSO_4 + 2\,MOH \rightleftarrows M_2SO_4 + Ca(OH)_2}$$

where M represents the alkalies. At advanced stages of hydration of low water/cement ratio pastes, the alkali solution concentration may exceed 0.4 N with a $\mathrm{pH} > 13$. Saturated lime/water has a pH of 12.4 at 25°C.

The exact course of the early hydration reactions depends mainly on the C_3A, ferrite, and soluble alkali contents of the clinker, and the amount of gypsum in the cement. Following the rate of reaction by calorimetric measurements, at least two and sometimes three distinct peaks in the rate of heat liberation can be observed (33,37). A large initial peak lasts only a few minutes and may reach 6 J/(g · min)[1.4 cal/(g · min)] resulting mainly from the solution of soluble constituents and the surface reactions, especially the formation of the sulfoaluminate coating on the highly reactive C_3A phase. After the initial heat peak, the reactions are strongly retarded, producing a 1–2-h delay referred to as the induction period during which the cement/water paste remains plastic and the concrete is workable. The cause of the induction period is a subject of much debate. The most widely supported explanation of the induction period involves an initial reaction which forms a protective layer on the C_3S particles (38). Within 30 s, the C_3S is almost isolated from the solution. Eventually, C–S–H nucleates and grows. The protective layer is disrupted and increased access to the C_3S leads to an increasing rate of hydration, which produces the second heat peak. Around the time of the second heat peak the concrete sets and establishes its familiar monolithic structure. A third heat peak may be observed depending on the gypsum and C_3A contents. If present, the third peak corresponds to the exhaustion of the solid gypsum, a rapid decrease of sulfate in solution, conversion of the ettringite to monosulfate, and renewed rapid reaction of the remaining C_3A and ferrite phases. At optimum gypsum content the third peak ordinarily occurs between 18 and 24 h.

In these early reactions, the reactivities of the individual phases are important in determining the overall reaction rate. However, as the cement particles become more densely coated with reaction products, diffusion of water and ions in solution becomes increasingly impeded. The reactions then become diffusion controlled at some time depending on various factors such as temperature and water/cement ratio. After ~1 or 2 days, ie, at ~40% of complete reaction, the remaining unhydrated cement phases react more nearly uniformly.

Microscopic examination of sections of hardened cement paste show that the unhydrated cores of the larger cement particles can be distinguished from the hydrated portion or inner product, which is a pseudomorph of the original grain, and the outer product formed in the originally water-filled spaces. Measurements of these cores indicate the depth of penetration of the hydration reactions (39). The overall hydration rate increases with the temperature, the fineness of the cement, and to a lesser extent with the water/cement ratio; measurements of the activation energy indicate that the reaction becomes increasingly diffusion controlled (33). Although more finely ground cements hydrate more rapidly in the first month or more of hydration, these differences gradually disappear at later ages. After 1 year, most portland cements at usual water/cement ratios are >90% hydrated if continuously moist cured. At complete hydration the chemically combined water (the water retained after strong drying) is ~20–25% of the weight of the cement, depending on its composition. However, a minimum water/cement ratio of ~0.4 is required to provide enough space to permit complete hydration of the cement (36). If moist curing is stopped and the hardened cement is dried sufficiently, eg, to 80% relative humidity (rh), the hydration process stops.

4. Cement Paste Structure and Concrete Properties

The properties of both fresh and hardened mortars and concretes depend mainly on the cement/water paste properties. Practical engineering tests are usually made using concrete specimens because their properties also depend on the proportions, size gradation, and properties of the aggregates. Quality control testing and research on cement properties is usually done on cement pastes or cement mortars made with standard sands. The properties of hardened cement pastes, mortars, and concretes are similar functions of the water/cement ratio and degree of hydration of the cement. The properties of fresh concretes that determine the workability, or ease of mixing and placement into forms, also depend strongly on, but are not so simply related to, the cement paste rheological properties (40,41).

The fresh paste even in the dormant period is normally thixotropic, or shear thinning, indicating that the structure is being continuously broken down and re-formed during mixing. It is an approximately Bingham plastic body having a finite yield value and plastic viscosity from 5000 to 500 $\mathrm{mPa \cdot s} (= \mathrm{cP})$ as the water/cement ratio increases from 0.4 to 0.7 (42). The viscosity and yield values can be greatly reduced by the addition of certain organic water-reducing admixtures especially formulated for this purpose. Workability of concrete is measured by the slump of the concrete determined after removal of a standard slump cone (305 mm high) (43). Workable concretes have slumps of 75 mm or more.

After mixing and casting, sedimentation of the cement particles in the water results in bleeding of water to the top surface and reduction of water/cement ratio in the paste. At high water/cement ratios, some of the very fine particles may be carried with the bleed water to the top resulting in laitance and perhaps the formation of flaws called bleeding channels. In concretes, sedimentation may cause flaws under the larger aggregate particles. If the fresh concrete is not protected from too rapid surface drying, capillary forces cause drying shrinkage that may cause plastic shrinkage cracks. Good construction practices are designed to minimize all of these flaws.

The engineering properties of the concrete, such as strength, elastic moduli, permeability to water and aggressive solutions, and frost resistance, depend strongly on the water/cement ratio and degree of hydration of the cement. A variety of empirical water/cement ratio laws express the strength as functions of water/cement ratio or porosity. The fraction of the original water-filled space, which is occupied by hydration products at any stage of hydration, is termed the gel-space ratio X. The compressive strength of hardened cement or mortar then approximately fits the power law:

$$\sigma = \sigma_o X^n$$

where n is $\sim$3.0 and σ is the intrinsic strength of the densest ($X = 1$) gel produced by a given cement under normal hydrating conditions. Values of σ_o range upward from 100 MPa (15,000 psi), depending on the cement composition (44). Several direct relationships between porosity, p, and strength have been applied to cement pastes (45–48):

$$\sigma = \sigma_o\ (1 - p)^{\mathrm{B}}$$

$$\sigma = \mathrm{D}\ \ln\ (p/p_o)$$

$$\sigma = \sigma_o(1 - \mathrm{E}p)$$

where B, D, and E are constants. Whereas some of these equations break down at very low or very high porosities, they all provide reasonable estimates within an intermediate porosity range. One comparative study concluded that the last equation was the most satisfactory (49). Under extreme conditions, eg, hot pressing at very low water/cement ratios, strengths as high as 655 MPa (95,000 psi) have been reported (50). Tensile strengths and elastic moduli are similarly dependent on porosity or gel/space ratio, but the tensile strength is only about one-tenth of the compressive strength. The Young's modulus of the densest gels produced under normal hydrating conditions is about 34 GPa (5×10^6 psi) (30).

Under sustained loads, hardened cements and concrete creep or deform continuously with time, in addition to the initial elastic deformation. Under normal working loads this deformation may in time exceed the elastic deformation and must be considered in engineering design. This is especially true in prestressed concrete structural members in which steel tendons under high tensile stress maintain compressive stress in the concrete to prevent tensile cracking during bending. Both creep and drying shrinkage of the concrete may lead to loss of prestress. Some creep in ordinary concrete structures and in the cement paste between the aggregate particles can also be an advantage because it tends to reduce stress concentrations, cracking, and microcracking around aggregate particles.

Drying of hardened cements results in shrinkage of the paste structure and of concrete members. Linear shrinkage of hardened cements is ~0.5% when dried to equilibrium at normal (~50%) relative humidities. The cement gel structure is somewhat stabilized during drying so that upon subsequent wetting and drying smaller changes occur. Concretes shrink much less (~0.05%), depending on the volume fractions of cement paste and aggregates, water/cement ratio, and other factors. Drying of concrete structural members proceeds very slowly and results in internal shrinkage stresses because of the moisture gradients during drying. Thick sections continue to dry and shrink for many years. Atmospheric carbon dioxide penetrates the partly dried concrete and reacts with the calcium silicate hydrate gel, as well as with calcium aluminate hydrates, releasing additional water and causing additional shrinkage. The density of the hydration products is increased, however, and the strength is actually increased. This reaction is sometimes used to advantage in the manufacture of precast concrete products to improve their ultimate strength and dimensional stability by precarbonation.

The slowness of drying and the penetration of the hardened cement by carbon dioxide or chemically aggressive solutions, eg, seawater or sulfate ground waters, is a result of the small sizes of the pores. Initially, the pores in the fresh paste are the water-filled spaces (capillaries) between cement particles. As these spaces become subdivided by the formation of the hydration products, the originally continuous pore system becomes one of more discrete pores or capillary cavities separated from each other by gel formations in which the remaining pores are very much smaller. These gel pores are so small (~3-nm nominal diameter) that most of the water contained in them is strongly affected by the solid surface force four fields. These force fields are responsible for a large increase in the viscosity of the water and a decrease in mobility of ionic species in solution. Hence, the permeability of the paste to both water and dissolved substances is greatly reduced as hydration proceeds. This in part accounts for the great durability of concrete, especially when water/cement ratios are kept low and adequate moist curing ensures a high degree of hydration. High water/cement ratios result in large numbers of the capillary spaces (0.1 μm and larger) interconnected through capillaries that are 10 nm or larger. These capillaries not only lower the strength, but also permit the easy penetration of aggressive solutions. Furthermore, these capillary spaces may become filled with water which freezes $< 0°C$, resulting in destructive expansions and deterioration of the concrete.

5. Chemical Admixtures

Admixtures include materials other than cement, water, or aggregate added immediately before or during mixing. Admixtures serve a broad range of purposes including the control of setting, control of workability, and control of air content.

5.1. Retarders and Accelerators. Materials that control hardening of cement may be either organic or inorganic. Retarders are often incorporated in oil well cementing and hot-weather concrete applications, whereas accelerators may be useful for cold-weather concrete applications in which higher rates of reactivity are desirable. In most cases, these admixtures are used in low concentrations, suggesting that they act by adsorption.

5.2. Water-Reducers and Plasticizers. Common admixtures that improve fluidity of concrete mixes are often used in high strength concrete. These admixtures make possible the incorporation of silica fume while maintaining necessary workability. Three principal types of superplasticizers are in common use: salts of sulfonated melamine formaldehyde polymers; salts of sulfonated naphthalene formaldehyde polymers; and modified lignosulfonate materials (see AMINO RESINS; LIGNIN; PHENOLIC RESINS). One benefit of these admixtures is improved dispersion of cement grains in the mixing water.

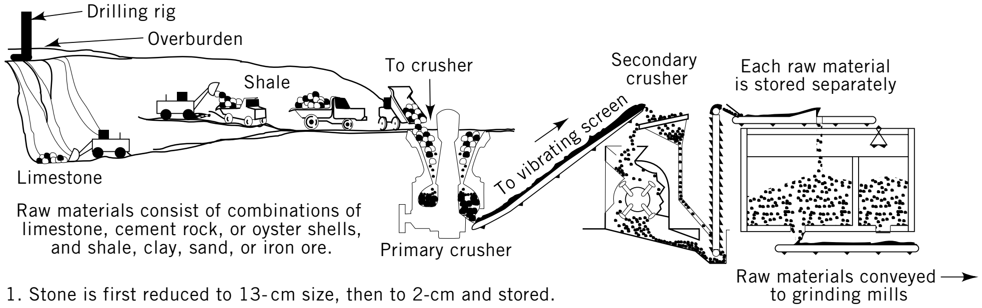
5.3. Air-Entraining Admixtures. Materials that are used to improve the ability of concrete to resist damage from freezing are generally known as air-entraining admixtures. These surfactant admixtures (see SURFACTANTS) produce a foam that persists in the mixed concrete, and serves to entrain many small spherical air voids that measure from 10 to 250 μm in diameter. The air voids alleviate internal stresses in the concrete that may occur when the pore solution freezes. In practice, up to 10% air by volume may be entrained in concrete placed in severe environments.

6. Manufacture

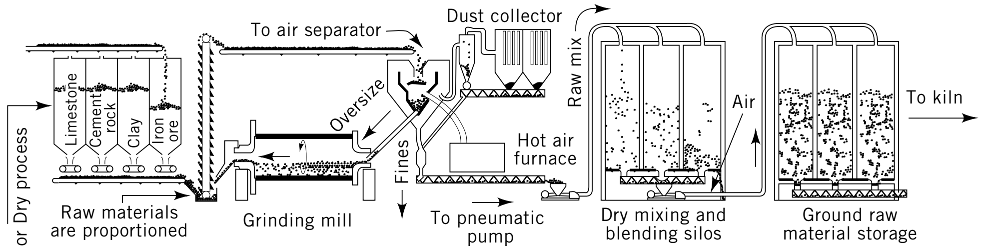
6.1. Portland Cements. The process of portland cement manufacture consists of (*1*) quarrying and crushing the rock, (*2*) grinding the carefully proportioned materials to high fineness, (*3*) subjecting the raw mix to pyroprocessing in a rotary kiln, and (*4*) grinding the resulting clinker to a fine powder. A layout of a typical plant is shown in Figure 7 (51). Figure 8 gives the layout of a newer dry process plant (52). No new wet process plants are being built, and existing wet process plants are gradually being replaced by dry process plants (only 32.8% are wet process). The plants outlined are typical of installations producing approximately 1000 metric tons per day. Modern installations (53–55) are equipped with innovations such as suspension or grate preheaters, roller mills, or precalciner installations.

Because calcium oxide comprises ~65% of portland cement, these plants are frequently situated near the source of their calcareous material. The requisite silica and alumina may be derived from a clay, shale, or overburden from a limestone quarry. Such materials usually contain some of the required iron oxide, but many plants need to supplement the iron with mill scale, pyrite cinders, or iron ore. Silica may be supplemented by adding sand to the raw mix, whereas alumina can be furnished by bauxites and Al_2O_3-rich kaolinitic clays.

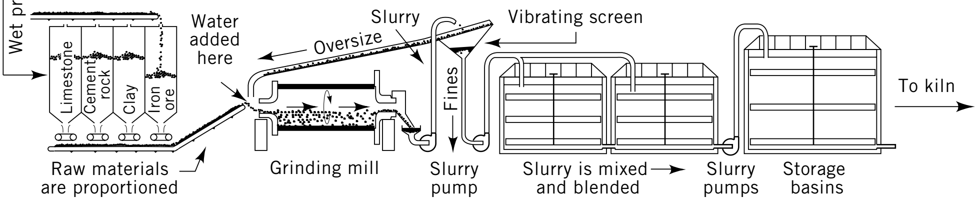
Industrial byproducts are becoming more widely used as raw materials for cement, eg, slags contain carbonate-free lime, as well as substantial levels of



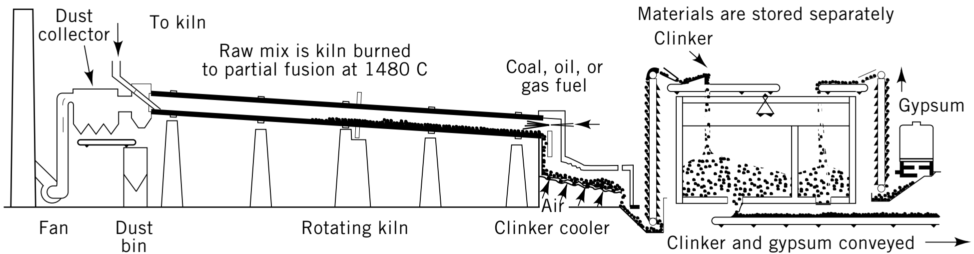
1. Stone is first reduced to 13-cm size, then to 2-cm and stored.



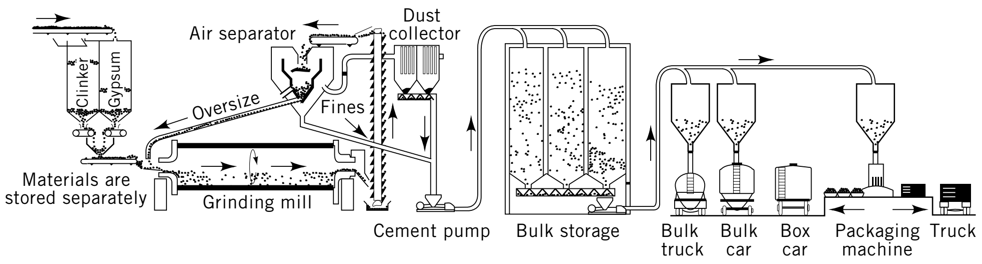
2. Raw materials are ground to powder and blended.



2. Raw materials are ground, mixed with water to form slurry, and blended.

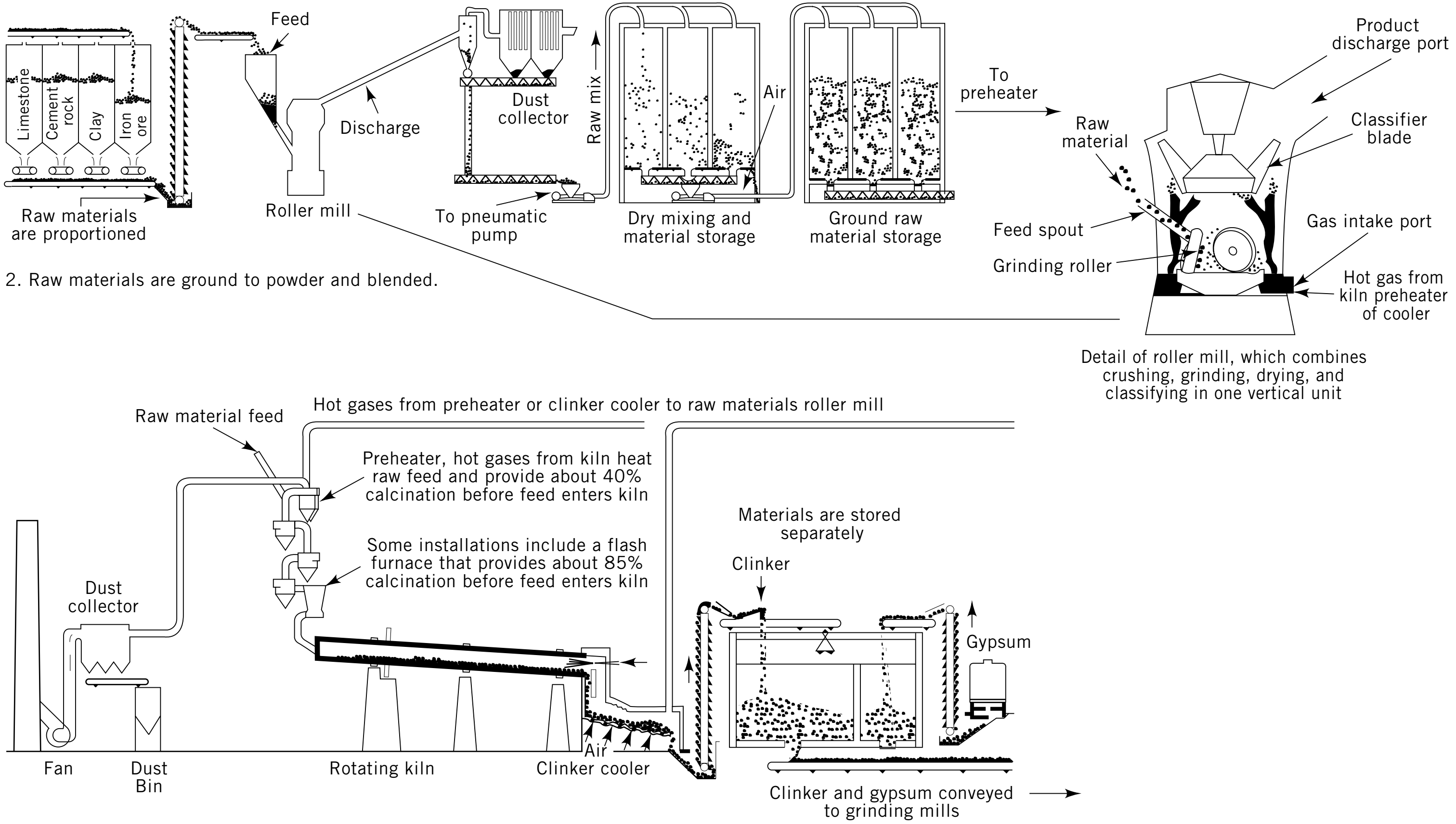


3. Burning changes raw mix chemically into cement clinker.



4. Clinker with gypsum is ground into Portland cement and shipped.

Fig. 7. Steps in the manufacture of portland cement (51). Courtesy of Portland Cement Association.



1. Stone first reduced to 13-cm size, then to 2-cm and stored (see Fig. 7).

2. Raw materials are ground to powder and blended.

3. Burning changes raw mix chemically into cement clinker. Note four-stage preheater, flash furnaces, and shorter kiln.

4. Clinker with gypsum is ground into Portland cement and shipped (see Fig. 7).

Fig. 8. Technology in dry-process cement manufacture (52). Courtesy of Portland Cement Association.
]

silica and alumina. Fly ash from utility boilers can often be a suitable feed component, because it is already finely dispersed and provides silica and alumina. Even vegetable wastes, such as rice hull ash, provide a source of silica. Probably 50% of all industrial byproducts are potential raw materials for portland cement manufacture.

Clinker production requires large quantities of fuel. In the United States, coal (qv) and natural gas are the most widely used kiln fuels but fuels derived from waste materials, eg, tires, solvents, etc, are increasing in importance (53) (see FUELS FROM WASTE; GAS, NATURAL). In addition to the kiln fuel, electrical energy is required to power the equipment. This energy, however, amounts to only about one-ninth that of the kiln fuel. The cement industry carefully considers all measures that can reduce fuel demand.

Raw Materials Preparation. The bulk of the raw material originates in the plant quarry when control of the clinker composition starts with systematic core drillings and selective quarrying. A primary jaw or roll crusher is frequently located within the quarry reducing the quarried limestone or shale to ~100-mm top size. A secondary crusher, usually roll or hammer mills, gives a product of ~10–25-mm top size. Clays may require treatment in a wash mill to separate sand and other high silica material. Combination crusher-dryers utilize exit gases from the kiln or clinker cooler to dry wet material during crushing.

Argillaceous, siliceous, and ferriferous raw mix components are added to the crusher product. At the grinding mills, the constituents are fed into the mill separately, using weigh feeders or volumetric measurements. Ball mills are used for wet and dry processes to grind the material to a fineness such that only 15–30 wt% is retained on a 74 μm (200 mesh) sieve. In the wet process the raw materials are ground with ~30–40% water, producing a well-homogenized mixture called slurry. Low concentrations of slurry thinners may be added, such as sodium carbonates, silicates, and phosphates, as well as lignosulfonates and modified petrochemicals. Filter presses or other devices are sometimes used to remove water from slurries before feeding into the kiln.

Raw material for dry process plants is ground in closed-circuit ball mills with air separators, which may be set for any desired fineness. Autogenous mills, which operate without grinding media are not widely used. For suspension preheater-type kilns, a roller mill utilizes the exit gas from the preheater to dry the material in suspension in the mill.

A blending system provides the kiln with a homogeneous raw feed. In the wet process, the mill slurry is blended in a series of continuously agitated tanks in which the composition, usually theCaO content, is adjusted as required. These tanks may also serve as kiln feed tanks, or the slurry after agitation is pumped to large kiln feed basins. Dry-process blending is usually accomplished in a silo with compressed air.

Pyroprocessing. Nearly all cement clinker is produced in large rotary kiln systems. The rotary kiln is a highly refractory-lined cylindrical steel shell (3–8 m dia, 50–230 m long) equipped with an electrical drive to rotate at 1–3 rpm. It is a countercurrent heating device slightly inclined to the horizontal so that material fed into the upper end travels slowly by gravity to be discharged onto the clinker cooler at the discharge end. The burners at the firing end produce a current of hot gases that heats the clinker and the calcined and raw materials in succession as it passes upward toward the feed end. Highly refractory bricks of magnesia or alumina (see REFRACTORIES) line the firing end, whereas in the less heat-intensive midsection of the kiln bricks of lower refractoriness and thermal conductivity can be used, changing to abrasion-resistant bricks or monolithic castable lining at the feed end. To prevent excessive thermal stresses and chemical reaction of the kiln refractory lining, it is necessary to form a protective coating of clinker minerals on the hot face of the burning zone brick. This coating also reduces kiln shell heat losses by lowering the effective thermal conductivity of the lining.

It is desirable to cool the clinker rapidly as it leaves the burning zone. This is best achieved by using a short, intense flame as close to the discharge as possible. Heat recovery, preheating of combustion air, and fast clinker cooling are achieved by clinker coolers of the traveling-grate, planetary, rotary, or shaft type. Most commonly used are grate coolers where the clinker is conveyed along the grate and subjected to cooling by ambient air, which passes through the clinker bed in crosscurrent heat exchange. The air is moved by a series of undergrate fans, and becomes preheated to 370–800°C at the hot end of the cooler. It then serves as secondary combustion air in the kiln; the primary air is that portion of the combustion air needed to carry the fuel into the kiln and disperse the fuel.

During the burning process, the high temperatures cause vaporization of alkalies, sulfur, and halides. These materials are carried by the combustion gases into the cooler portions of the kiln system where they condense, or they may be carried out to the kiln dust collector, usually a fabric filter or electrostatic precipitator, together with partially calcined feed and unprocessed raw feed. This kiln dust is reusable. However, the levels of total SO_3 and alkali content of cement are limited by considerations of product performance and some national specifications, so that it is not always feasible to recycle all the dust in the process. Other potential and actual uses of dust include fertilizer supplements (see FERTILIZERS), acid mine waste neutralization (see WASTES, INDUSTRIAL), boiler SO_2 control, and soil stabilization (qv).

Wet-Process Kilns. In a long wet-process kiln, the slurry introduced into the feed end first undergoes simultaneous heating and drying. The refractory lining is alternately heated by the gases when exposed and cooled by the slurry when immersed; thus the lining serves to transfer heat, as do the gases themselves. Large quantities of water must be evaporated, thus most wet kilns are equipped with chains to maximize heat transfer from the gases to the slurry. Large, dense chain systems permit energy savings of up to 1.7 MJ/kg (731 Btu lb) clinker in exceptionally favorable situations (53). After most of the moisture has been evaporated, nodules, which still contain combined water, move down the kiln and are gradually heated to ∼550°C. At this temperature, aluminosilicates decompose, evolving combined water, and leaving a mixture to highly reactive microcrystalline silica and alumina together with alkaki hydroxides.

At ∼650°C low temperature melts of alkali chlorides, sulfates and silicates start to form. These promote the decomposition of calcium carbonate. Initially, the decomposing calcium carbonate reacts directly with reactive silica and alumina to form the low-temperature forms of belite and a mixture of low lime aluminates. In these conditions, silica can be thought of as an “acid” chemically decomposing the calcite. Little free calcium oxide forms. This reaction accelerates as the temperature reises, and when the equilibrium temperature of decomposition of calcium carbonate (898.6°C) is reached the combination of silica and alumina is almost complete. This uses up ~70% of the available calcium carbonate and the initial endothermic silicate formation is as follows:

$$\mathrm{CaCO_3 + 0.5\ SiO_2 \rightarrow 0.5\ Ca_2SiO_4 + CO_2 \uparrow} \qquad (\Delta H = +115\ \mathrm{kJ \cdot mol^{-1}})$$

Above 900°C, thermal decomposition of the remaining calcite proceeds rapidly with the formation of free calcium oxide in another endothermic reaction:

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2 \uparrow} \qquad (\Delta H = +178\ \mathrm{kJ \cdot mol^{-1}})$$

Because these two reaction involve a large enthalpy transfer, a large proportion of the kiln system (the calcinations zone) is used for their completion. Once the latter reaction is complete, at ~1050°C the temperature of the charge rises rapidly. At 1300°C, the aluminates begin to melt. The resulting liquid then acts as a solvent for the finishing reaction in which belite is converted to alite:

$$\mathrm{Ca_2SiO_4 + CaO \rightarrow Ca_3SiO_5} \qquad (\Delta H = +13\ \mathrm{kJ \cdot mol^{-1}})$$

This occurs in the burning zone. The reaction proceeds at an economically viable rate when the charge is raised to a peak temperature between 1400 and 1450°C in commercial kilns–the temperature needed depending on the burnability of the mix. Burnability depends on the fineness, homogeneity, and LSF of the mix.

As the charge leaves the burning zone it begins to cool, and tricalcium aluminate and magnesia crystallize from the melt and the liquid phase finally solidifies to produce the ferrite phase. The material drops into the clinker cooler for further cooling by air.

Dry-Process Kilns, Preheaters, and Precalciners. The dry process for cement manufacture utilizes a dry kiln feed rather than a slurry. Early dry-process kilns were short, and the substantial quantities of waste heat in the exit gases from such kilns were frequently used in boilers for electric power generation (qv); the power generated was frequently sufficient for all electrical needs of the plant. In one modification, the kiln has been lengthened and chains have been added; however, these serve almost exclusively a heat-exchange function (see HEAT EXCHANGE TECHNOLOGY). Refractory heat-recuperative devices, such as crosses, lifters, and trefoils, have also been installed so that the long dry kiln is energy efficient. Other than the need for evaporation of water, its operation is similar to that of a long wet kiln.

A second type of modern dry-process kiln is the suspension preheater system (56). The dry, pulverized feed passes through a series of cyclones where it is separated and preheated several times. The partially calcined feed exits the preheater tower into the kiln at ~800–900°C. The kiln length required for completion of the process is considerably shorter than that of conventional kilns, and heat exchange is very good. Suspension preheater kilns are very energy efficient: as low as 3.1 MJ/kg (1334 Btu/lb) clinker in large installations. The intimate mixing of the hot gases and feed in the preheaters promotes condensation of alkalies and sulfur on the feed, sometimes resulting in objectionably high alkali and sulfur contents in the clinker. To alleviate this problem, some of the salt-laden kiln exit gases can be deverted to waste (bypassed) and fewer cyclone stages used in the preheater. The wasteage of the heat in these gases results in lower thermal efficiency.

The success of preheater kiln systems led to the development of precalciner kiln systems. These units utilize a second burner to carry out calcination in a separate vessel attached to the preheater. The flash furnace (57), eg, utilizes preheated combustion air drawn from the clinker cooler and kiln exit gases and is equipped with burner that burns ~60% of the total kiln fuel. The raw material is calcined almost 95%, and the gases continue their upward movement through successive preheater stages in the same manner as in an ordinary preheater.

The precalciner system permits the use of smaller kilns because only actual clinkering is carried out in the rotary kiln. Energy efficiency is comparable to that of a preheater kiln, except that the energy penalty for bypass of kiln exit gases is reduced because only ~40% of the fuel is being burned in the kiln. Precalciner kilns produce up to 10,000 metric tons of clinker per day; the largest long wet-process kiln, in the United States produces only 3270 t/day by comparison. The burning process and clinker cooling operations for the modern dry-process kiln systems are the same as for long wet kilns.

Finish Grinding. The cooled clinker is conveyed to clinker storage or mixed with 4–6% gypsum and introduced directly into the finish mills. The clinker and gypsum are ground to a fine, homogeneous powder having a surface area of ~300–600 m^2/kg. About 85–96% of the product is in particles having <45 μm dia. These objectives may be accomplished by two different mill systems. In open-circuit milling, the material passes directly through the mill without any separation. A wide particle size distribution range is usually obtained with substantial amounts of very fine and rather coarse particles. In closed-circuit grinding the mill product is carried to a cyclonic air separator in which the coarse particles are rejected from the product and returned to the mill for further grinding. Energy requirements for finish grinding vary in the range $33 - 77\ \mathrm{kW \cdot h/t}$ cement, depending primarily on the required fineness, but also on the nature of the clinker.

Computer Control. Process computer control was introduced to the cement industry in the 1960s and a plant of a capacity of 1 million metric tons per year was built and placed in operation in 1973 having complete computer process and segmental control (58). Other plants have been built and some older plants computerized (59). Variables can be measured at intervals of 0.25 s and overall optimum response to operating problems is programmed, not always possible with manual operation. The rotary kiln is the largest and most difficult equipment to operate. Due to the hot, corrosive and abrasive condition. Temperature-sensing and gas-analyzing devices present special problems.

Quality Control. Beginning at the quarry operation, product quality is maintained by adjustments of composition, burning conditions, and finish grinding. Control checks are made for fineness of materials, chemical composition, and uniformity. Clinker burning is monitored by weighing a portion of sized clinker, known as the liter weight test, a free lime test, or checked by microscopic evaluation of the crystalline structure of the clinker compounds. Samples may be analyzed by X-ray fluorescence, atomic absorption, and flame photometry (see Spectroscopy optical). Wet chemical analysis is described in ASTM C114 (24) and EN 680, but X-ray fluorescence analysis is usually used for quality control in most cement plants. Standard cement samples are available from the National Institute of Standards and Technology. Fineness of the cement is most commonly measured by the air permeability method. Finally, standardized performance tests are conducted on the finished cement (24).

Environmental Pollution Control. The cement industry has had an intensive program of capital expenditure to install dust collection equipment on kilns and coolers since the 1970s (60). Modern equipment collects dust at 99.8% efficiency. Many smaller dust collectors are installed in new plants (61).

Government agencies have (62) established limits for cement plant effluents including water run-off from manufacturing facilities, quarrying, raw material storage piles, and wastewater. Compliance with these standards has required construction of diversion ditches for surface water, ponds for settling and clarification, dikes and containment structures for possible oil spills, and chemical water treatment in some cases. Since the cement industry obtains most of its raw material by quarrying, the standards for the mineral industry also apply.

One of the primary waste products of cement manufacturing is cement kiln dust (CKD). The CKD is collected from exhaust gases and either returned to the kiln with other raw materials or disposed of as landfill. CKD is also used in other applications, such as synthetic aggregate and tends to accumulate very low concentrations of heavy metals that originate in the fuels or in the raw materials. These metals volatilize in the high temperatures of the kiln and become associated with exhaust gases. Two significant studies of CKD (63,64) concluded that the environmental considerations are minor and that neither CKD nor cement have characteristics of hazardous waste as defined under the U.S. *Resource Conservation and Recovery Act*. The cement industry continues to search for new uses for CKD in construction applications.

6.2. Special Purpose and Blended Cements. Special purpose and blended portland cements are manufactured essentially by the same processes as ordinary portland cements, but have specific compositional and process differences. White cements are made from raw materials of very low iron content. This type is often difficult to burn because almost the entire liquid phase must be furnished by calcium aluminates. As a consequence of the generally lower total liquid-phase content, high burning-zone temperatures may be necessary. Fast cooling (quenching) and occasionally supplementary reducing flame impinging on the charge at the kiln exit (bleaching) are needed to maintain both quality and color.

Regulated set cements are made using fluorite, CaF_2, additions which also act as fluxing agents, or mineralizers, to reduce burning temperatures. The clinker produced then contains$C_{11}A_7 \cdot CaF_2$, (mixed notation) as a principal phase. Another regulated set cement can be made in which the principal constituents are $C_4A_3\bar{S}$ and belite. Both cements rapidly harden and can reach modest compressive strengths within several hours. Final material properties are in most respects similar to comparable concretes made with portland cement.

Concern with regard to energy conservation has prompted the use of byproduct materials in portland cement concrete. Blended hydraulic cements are produced by intimately and uniformly blending two or more types of fine materials. The primary blending materials are portland cement, ground granulated blast-furnace slag, fly ash, calcined clay, silica fume, and hydrated lime. Cement kiln dust and other materials are undergoing research for use in blended cements. Blended hydraulic cements can conform to the requirements of ASTM C 595, or ASTM C 1157. ASTM C 595 recognizes five classes of blended cements: portland blast-furnace slag cement, Type IS; portland–pozzolan cement, Type IP and Type P; slag cement, Type S; pozzolan-modified portland cement, Type I (PM); and slag-modified portland cement, Type I (SM). ASTM C 1157 cement types, which apply to both portland and blended cements, include general purpose cement, Type GU; high early strength cement, Type HE; moderate heat cement, Type MH; low heat cement, Type LH; moderate sulfate resistant cement, Type MS; and high sulfate resistant cement, Type HS.

Blended cements represent $\sim 2\%$ of the cement shipped in the United States. In Europe, the use of blended cement is very common. Most of the blended cement used in the United States is Type IP and it is used in the same applications as that of regular Type I or II portland cement.

ASTM C845 Type E-I (K) expansive cement manufactured in the United States usually depends on aluminate and sulfate phases that result in more ettringite formation during hydration than in normal portland cements. Type K contains an anhydrous calcium sulfoaluminate. This cement can be made either by integrally burning to produce the desired phase composition, or by intergrinding a special component with ordinary portland cement clinkers and calcium sulfate.

Oil well cements are manufactured similarly to ordinary portland cements except that the goal is usually sluggish reactivity. For this reason, levels of C_3A, C_3S, and alkali sulfates are kept low. Hydration–retarding additives are also employed.

Pozzolans include natural materials such as diatomaceous earths (see DIATOMITE), opaline cherts, and shales, tuffs, and volcanic ashes or pumicites, and calcined materials such as some clays and shales. Byproducts such as fly ashes and silica fume are also employed. In the United States the proportion of pozzolan interground with clinker has varied from 15 to $>30\%$, whereas in Italy, cements with a 30–40% pozzolan content are produced.

Portland cement clinker is also interground with 10–65% granulated blast-furnace slag to produce a Portland blast-furnace slag cement. The composition of the slag varies considerably but usually falls within the following wt% composition ranges: CaO, 40–50%, SiO_2, 30–40%, Al_2O_3, 8–18%; MgO, 0–8%; S (sulfide), 0–2%; and FeO, and MnO, 0–3%.

Masonry cements are used for making mortar for bricklaying. They are not suitable for use in concrete. Most masonry cements are finely interground mixtures where portland cement is a principal constituent. These cements also include finely ground limestones, hydrated lime, natural cement, pozzolans, clays, or air-entraining agents. Secondary materials are used to impart the required water retention and plasticity to mortars.

6.3. Non-Portland Cements. *Calcium Aluminate Cements.* These cements are manufactured by heating until molten or by sintering a mixture of limestone and a bauxite containing low amounts of SiO_2, FeO, and TiO_2 (see

ALUMINUM COMPOUNDS, ALUMINUM OXIDE, CALCINED, TABULAR, AND ALUMINATE CEMENTS). The process is usually carried out in an open-hearth furnace having a long vertical stack into which the mixture of raw materials is charged. The hot gases produced by a blast of pulverized coal and air pass through the charge and carry off the water and carbon dioxide. Fusion occurs when the charge drops from the vertical stack onto the hearth at ~1425–1500°C. The molten liquid runs out continuously into steel pans on an endless belt in which the melt solidifies. Special rotary kilns, provided with a tap hole from which the molten liquid is drawn intermittently, and electric arc furnaces have also been used.

When calcium aluminate cements are made by the fusion process, the solidified melt must be crushed and then ground. The material is very hard to grind and power consumption is high.

6.4. Hydraulic Limes. These materials are produced by heating below sintering temperature a limestone containing considerable clay, during which

Table 7. **United States Portland Cement Consumption**[a]

U.S Cement Industry Consumption — Exports — Imports — Shipments[b]

Year	Consumption[c] Portland cement	Masonry cement	Total	Cement exports	Cement imports	Total shipments by domestic[d] products
1979	75,523	3,343	78,866	244	4,101	75,032
1980	66,940	2,721	69,661	346	2,732	67,710
1981	63,456	2,440	65,896	614	2,287	64,338
1982	57.191	2,166	59,357	384	2,367	57,544
1983	62,918	2,615	65,533	292	2,522	63,584
1984	71,792	2,945	74,737	266	6,004	70,435
1985	74,434	2,960	77.394	258	8,845	70,235
1986	78,643	3,230	81,873	227	11,661	71,386
1987	80,291	3,375	83,666	271	13,184	71,243
1988	80,715	3,292	84,007	197	14,001	70,427
1989	79,155	3,071	82,226	300	12,547	70,321
1990	77,785	3,005	80,790	293	10,461	71,535
1991	69,098	2,495	71,593	272	7,215	64,842
1992	73,354	2,704	76,058	351	6,097	70,502
1993	76,566	3,014	79,580	398	6,151	73,934
1994	82,159	3,267	85,426	452	8,912	77,021
1995	82,825	3,160	85,985	485	11,625	74,936
1996	87,416	3,399	90,815	461	11,999	79,411
1997	92,708	3,458	96,166	519	13,814	82,978
1998	99,153	4,101	103,254	322	18,278	85,417
1999	104,074	4,352	108,426	315	22,534	86,328
2000	105,195	4,333	109,528	394	22,740	87,599
2001	108,090	4,475	112,565	443	22,397	91,097

[a] Ref. 69.

[b] Thousands of metric tons.

[c] Excludes Alaska and Puerto Rico.

[d] Excludes Puerto Rico.

Note: Domestic Shipments include cement shipments from domestic manufacturers and cement shipments ground from imported clinker, but exclude finished cement imports.

Source: U.S. Geological Survey/PCA Economic Research.

some combination takes place between the lime and the oxides of the clay to form hydraulic compounds.

7. Economic Aspects

From the beginning of the United States portland cement industry in 1872, annual cement consumption grew through 1970. From 1975 to 1990, cement consumption changed little. During the 1990s, cement consumption continued to grow. Table 7 gives United States' production figures and Table 8 gives the world production. China, having an annual output of >580 million metric tons in 2000, has emerged as the world's leading cement producer (68).

Since the 1940s, the cement industry reduced labor and energy costs by increased investment in capital equipment and larger plants to remain competitive with other building materials industries (see BUILDING MATERIALS, SURVEY; BUILDING MATERIALS, PLASTIC). The average plant size more than doubled between 1950 and 1990.

7.1. Energy Use. From 1972 to 2000, the cement industry has reduced unit energy usage by 32.9%. The wet process, used in 60% of the plants in the 1960s, was less labor-intensive than the dry process. However, as energy costs escalated in the early 1970s, the more energy efficient dry-process manufacturing was preferred. According to 1989 figures, wet-process plants consume 38% more energy per ton of cement than dry-process plants.

Coal is the primary kiln fuel as seen in Table 9. Energy from coal rose from 36 to 60% of the total energy required for cement production between 1972 and 2000.

7.2. Marketing Patterns. The cement industry reduced its dependence on bag (container) shipments (54.7% in 1950) and turned to the more labor-efficient bulk transport (96% in 2000). In addition, the amount of cement shipped by rail transportation declined from 75% of industry shipments in 1950 to <2% in 2000. Table 10 summarizes the shipment distribution by cement type.

In the past 30 years, the ready-mixed concrete industry became the primary customer for cement manufacturers. In 2000, >73.7% of the cement shipped was sold to the ready-mixed concrete industry, compared with 63% in 1975. The other primary uses are in building materials, concrete products, and highway construction.

8. Environmental Aspects

Cement plants in the United States are carefully monitored for compliance with Environmental Protection Agency (EPA) standards for emissions of particulates, SO_x, NO_x, and hydrocarbons. All plants incorporate particulate collection devices such as baghouses and electrostatic precipitators (see AIR POLLUTION CONTROL METHODS). The particulates removed from stack emissions are called cement kiln dust (CKD). It has been shown that CKD is characterized by low concentrations of metals which leach from the CKD at levels far below regulatory limits (63,64).

Table 8. **Top World Producers of Portland Cement**[a]

	Top World Producers of Hydraulic Cement[b]									
	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000[c]
China	252,610	308,220	367,880	421,180	475,910	491,190	511,730	536,000	573,000	583,190
India	51,000	50,000	53,812	57,000	62,000	75,000	80,000	85,000	90,000	95,000
United States[d]	68,465	70,883	75,117	79,353	78,320	80,818	84,255	85,522	87,777	89,510
Japan	89,564	88,253	88,046	91,624	90,474	94,492	91,938	81,328	80,120	81,300
Korea, Republic of	34,999	44,444	47,313	50,730	55,130	58,434	60,317	46,091	48,157	51,255
Brazil	27,490	23,903	24,843	25,230	28,256	34,597	38,096	39,942	40,270	39,208
Germany	34,396	37,529	36,649	36,130	33,302	31,533	35,945	36,610	38,099	38,000
Italy	40,806	41,347	33,771	32,713	33,715	33,327	33,721	35,512	34,000	36,000
Turkey	26,091	28,607	31,241	29,493	33,153	35,214	36,035	38,200	34,358	35,825
Russia						27,800	26,700	26,000	28,400	32,400
Thailand	18,054	21,832	26,870	29,900	34,900	38,749	37,086	30,000	34,000	32,000
Mexico	25,100	26,880	27,120	29,700	24,043	25,366	27,548	27,744	29,413	31,677
Spain	25,119	24,615	22,878	25,150	26,423	25,157	27,632	27,943	30,800	30,000
Total World[e]	1,181.8	1,231.1	1,290.9	1,370.0	1,445.0	1,493.0	1,547.0	1,547.0	1,603.0	1,643.0

[a] Ref. 69.

[b] Thousands of metric tons.

[c] estimate.

[d] Includes Puerto Rico.

[e] Million metric tons.

Source: U.S. Geological Survey.

Table 9. **United States Portland Cement Industry Energy Consumption**[a]

	Summary of Energy Consumption[b] % Change								
	1972	1995	1996	1997	1998	1999	2000	00/72	00/95
Gasoline	7.4	2.4	2.0	1.8	1.9	2.2	4.6	–37.8%	91.7%
Middle distillates	88.3	38.1	43.6	39.7	41.3	44.7	39.4	–55.4%	3.4%
Residual oil	808.9	17.1	6.0	8.1	6.9	3.6	3.9	–99.5%	–77.2%
LPG	1.4	0.6	0.6	0.4	0.4	0.3	0.3	–78.8%	–50.0%
Total Petroleum Products	*906.0*	*58.2*	*52.2*	*50.0*	*50.5*	*50.8*	*48.2*	–94.7%	–17.2%
Natural gas	3,347.1	564.0	374.6	305.2	372.4	327.7	261.6	–92.2%	–53.6%
Coal	2,639.0	2,887.2	3,052.6	3,110.2	2,998.6	2,984.0	2,984.1	13.1%	3.4%
Petroleum Coke	39.6	814.9	798.1	732.8	744.1	748.8	760.7	1821.0%	–6.7%
Total Coal and Coke	*2,678.6*	*3,702.1*	*3,850.7*	*3,843.0*	*3,742.7*	*3,732.8*	*3,744.8*	*39.8%*	*1.2%*
Waste fuel	–	416.2	389.5	444.4	413.5	407.8	402.5	–	–3.3%
Total Fossil Fuels	*6,931.7*	*4,740.5*	*4,667.0*	*4,642.6*	*4,579.1*	*4,519.1*	*4,457.1*	–35.7%	–6.0%
Electricity	488.6	520.9	533.7	528.7	528.1	520.8	524.6	7.4%	0.7%
Total Fuel and Power	*7,420.3*	*5,261.4*	*5,200.7*	*5,171.3*	*5,107.2*	*5,039.9*	*4,981.7*	–32.9%	–5.3%

[a] Ref. 69.

[b] Thousands of BTUs per equivalent metric ton. Weighted average of 92% clinker production plus 8% finished cement production.

Source: PCA U.S. and Canadian Labor-Energy Input Services.

Table 10. **United States Portland Cement Shipments by Type**[a]

Portland Cement Shipped from U.S. Plants by Type of Product[b]

	1998		1999		2000	
	Quantity	% of Total	Quantity	% of Total	Quantity	% of Total
General Use and Moderate Heat *(Types I and II)*	85,066	90.1	90,891	90.2	90,644	88.0
High Early Strength *(Type III)*	3,151	3.3	3,297	3.3	3,815	3.7
Sulfate-Resisting *(Type V)*	2,757	2.9	3,046	3.0	4,453	4.3
Block	594	0.6	632	0.6	636	0.6
Oil Well	797	0.8	578	0.6	1,039	1.0
White	790	0.8	848	0.8	894	0.9
Blended						
Portland Slag and Pozzolan	449	0.5	529	0.5	579	0.6
Portland Fly Ash and Other	672	0.7	664	0.7	718	0.7
Miscellaneous	132	0.1	260	0.3	171	0.2
Total Shipments	*94,408*		*100,745*		*102,949*	

[a] Refs. (66,69).

[b] Thousands of metric tons.

Source: U.S. Geological Survey.

9. Specifications and Types

Portland cements are manufactured to comply with specifications established in each country (70). In the United States, several different specifications are used, including those of the American Society for Testing and Materials and American Association of State Highway and Transportation Officials (AASHTO). The ASTM annually publishes test methods and standards (24), which are established on a consensus basis by its members which include consumers and producers.

In the United States, portland cement is classified in five general types designated by ASTM Specification C150 (24): Type I, when the special properties are not required; Type II, for general use, and especially when moderate sulfate resistance or moderate heat of hydration is desired; Type III, for high early strength; Type IV, for low heat of hydration; and Type V, for high sulfate resistance. Types I, II, and III may also be specified as air entraining. Chemical compositional, physical, and performance test requirements are specified for each type; optional requirements for particular uses may also be specified. Portland cement can also be specified under ASTM C 1157 as general purpose cement, Type GU; high early strength cement, Type HE; moderate heat cement, Type MH; low heat cement, Type LH; moderate sulfate resistant cement, Type MS; and high sulfate resistant cement, Type HS. Tables 11 and 12 list applications

Table 11. **Applications of Portland Cement Using U.S. Standards**

Cement specification	Applications[a]						
	General purpose	Moderate heat of hydration	High early strength	Low heat of hydration	Moderate sulfate resistance	High sulfate resistance	Resistance to alkali-silica reactivity (ASR)[b]
ASTM C 150 (AASHTO M B5) portland cements	I	II (moderate heat option)	III	IV	II	V	Low alkali option
ASTM C 595 (AASHTO M 240) blended hydraulic cements	IS, IP I (PM) I (SM), S, P	IS(MH) IP(MH) I(PM)(MH) I(SM)(MH)		P(LH)	IS(MS) IP(MS) P(MS) I(PM)(MS) I(SM)(MS)		Low reactivity option
ASTM C 1157 hydraulic cements[c]	GU	MH	HE	LH	MS	HS	Option R

[a] Check the local availability of specific cements as all cements are not available everywhere.

[b] The option for low reactivity with ASR susceptible aggregates can be applied to any cement type in the columns to the left.

[c] For ASTM C 1157 cements, the nomenclature of hydraulic cement, portland cement, air-entraining portland cement, modified portland cement, or blended hydraulic cement is used with the type desiganation.

Table 12. **Applications of Special Cements**

Special cements	Type	Application
White portland cements, ASTM C 150	I, II, III, V	White or colored concrete, masonry, mortar, grout, plaster, and stucco
White masonry cements, ASTM C 91	M, S, N	White mortar between masonry units
Masonry cements, ASTM C 91	M, S, N	Mortar between masonry units,[a] plaster, and stucco
Mortar cements, ASTM C 1329	M, S, N	Mortar between masonry units[a]
Plastic cements, ASTM C 1328	M, S	Plaster and stucco[b]
Expansive cements, ASTM C 845	E-1(K), E-1(M), E-1(S)	Shrinkage compensating concrete
Oil-well cements, API-10	A, B, C, D, E, F, G, H	Grouting wells
Water-repellent cements		Tile grout, paint, and stucco finish coats
Regulated-set cements		Early strength and repair[c]
Cements with functional additions ASTM C 595 (AASHTO M 240), ASTM C 1157		General concrete construction needing special characteristics such as; water-reducing retarding air entraining set control, and accelerating properties
Finely ground (ultrafine) cement		Geotechnical grouting[c]
Calcium aluminate cement		Repair, chemical resistance, high temperature exposures
Magnesium phosphate cement		Repair and chemical resistance
Geopolymer cement		General construction, repair, waste stabilization[c]
Ettringite cement		Waste stabilization[c]
Sulfur cements		Repair and chemical resistance
Rapid hardening hydraulic cement		General paying where very rapid (~4 h) strength development is required

[a] Portland cement Types I, II, and III and blended cement Types IS, IP, and I(PM) are also used in making mortar.

[b] Portland cement Types I, II, and III and blended cement Types IP, I(SM) and I(PM) are also used in making plaster.

[c] Portland and blended hydraulic cements are also used for three applications.

of portland and special cements. In Europe, cements are made to meet the requirements of EN 197. EN 197 cement Types CEM I, II, III, IV and V do not correspond to the cement types in ASTMC 150. CEM I is a portland cement and CEM II through V are blended (composite) cements. EN 197 also has strength classes and ranges (32.5, 42.5, and 52.5 MPa).

10. Uses

Hydraulic cements are intermediate products used for making concretes, mortars, grouts, and other composite materials (qv). High early strength cements may be required for precast concrete products or in high rise building frames to permit rapid removal of forms and early load carrying capacity. Cements of low heat of hydration may be required for use in massive structures, such as gravity dams, to prevent excessive temperature rise and thermal contraction and cracking during subsequent cooling. Concretes exposed to seawater or sulfate-containing ground waters require cements that are sulfate-resistant after hardening.

Air-entraining cements produce concretes that protect the concrete from frost damage. They are commonly used for concrete pavements subjected to wet and freezing conditions.

Low alkali cements may be used with certain concrete aggregates containing reactive silica to prevent deleterious expansions.

Expansive, or shrinkage-compensating cements cause slight expansion of the concrete during hardening. The expansion has to be elastically restrained so that compressive stress develops in the concrete (71). Subsequent drying and shrinkage reduces the compressive stresses but does not result in tensile stresses large enough to cause cracks. Special highly expansive cements have been used for demolition purposes.

Finely ground cements, often called ultrafine cements, having particles $<10\ \mu m$ and an average size of $4\ \mu m$ are used to grout soils with fine pore spaces, such as fine sand with a permeability of 10^{-4} cm/s. These cements can be made with a wide combination of portland cement, slag, or silica fume (72).

Regulated-set cement, called jet cement in Japan, is formulated to yield a controlled short setting time, <1 h, and very early strength (73). It is a modified cement that can be manufactured in a conventional portland cement kiln. It incorporates set control and early strength development components.

Natural cements (74) that may be regarded as intermediate between portland cements and hydraulic limes in hydraulic activity, are no longer available in the United States.

Blended Cements. Portland cement clinker is also interground with suitable other materials such as granulated blast-furnace slags and natural or artificial pozzolans. These substances also show hydraulic activity when used with cements, and the blended cements (75) bear special designations such as portland blast-furnace slag cement or portland–pozzolan cement. Pozzolans are used in making concrete both as an interground or blended component of the cement or as a direct addition to the concrete mix. It is only when the two materials are supplied as an intimate blend that the mixture can be referred to as portland–pozzolan cement. Portland–pozzolan cements (76) were developed originally to provide concretes of improved durability in marine, hydraulic, and underground environments; they may also prevent deleterious alkali–aggregate reactions. Blast-furnace slag cements (77) may also reduce deleterious alkali–aggregate reactions and can be resistant to seawater if the slag and cement compositions are suitably restricted. Both cements hydrate and harden more slowly than portland cement. This can be an advantage in mass concrete structures where the lower rates of heat liberation may prevent excessive temperature rise, but when used at low temperatures the rate of hardening may be excessively slow. Portland blast-furnace slag cements may be used to advantage in steam-cured products which can have strengths as high as obtained with portland cement. Interest in the use of blended cements is stimulated by energy conservation and solid waste utilization considerations.

Oil well cements (78) are usually made from portland cement clinker and may also be blended cements. The American Petroleum Institute Specification for Materials and Testing for Well Cements (*API Specification 10*) (78) includes requirements for eight classes of oil well cements. They are specially produced for cementing the steel casing of gas and oil wells to the walls of the bore–hole and to seal porous formations (79). Under these high temperature and pressure conditions ordinary portland cements would not flow properly and would set prematurely. Oil well cements are more coarsely ground than normal, and contain special retarding admixtures.

Masonry cements (80) are cements for use in mortars for masonry construction. They are formulated to yield easily workable mortars and contain special additives that reduce the loss of water from the mortar to the porous masonry units.

Calcium aluminate cement (81) develops very high strengths at early ages. It attains nearly its maximum strength in one day, which is much higher than the strength developed by portland cement in that time. At higher temperatures, however, the strength drops off rapidly. Heat is also evolved rapidly on hydration and results in high temperatures; long exposures under moist warm conditions can lead to failure. Resistance to corrosion in sea or sulfate waters, as well as to weak solutions of mineral acids, is outstanding. This cement is attacked rapidly, however, by alkali carbonates. An important use of high alumina cement is in refractory concrete for withstanding temperatures up to 1500°C. White calcium aluminate cements, with a fused aggregate of pure alumina, withstand temperatures up to 1800°C.

Trief cements (83), manufactured in Belgium, are produced as a wet slurry of finely ground slag. When activators such as portland cement, lime, or sodium hydroxide are added in a concrete mixer, the slurry sets and hardens to produce concretes with good strength and durability.

Hydraulic limes (84) may be used for mortar, stucco, or the scratch coat for plaster.They harden slowly under water, whereas high calcium limes, after slaking with water, harden in air to form the carbonate but not under water at ordinary temperatures. However, at elevated temperatures achieved with steam curing, lime–silica sand mixtures do react to produce durable products such as sand–lime bricks.

Specialty Cements. For special architectural applications, white portland cement with a very low iron oxide content can be produced. Colored cements are usually prepared by intergrinding 5–10% of pigment with white cement.

Numerous other specialty cements composed of various magnesium, barium, and strontium compounds as silicates, aluminates, and phosphates, as well as others, are also produced (85).

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