

Chapter 7

Portland Cements, Calcium, and Compounds Magnesium

The industrial uses of limestone and cements have provided important undertakings for chemists and engineers since the early years when lime mortars and natural cements were introduced. In modern times one need only mention reinforced-concrete walls and girders, tunnels, dams, and roads to realize the dependence of present-day civilization upon these products. The convenience, cheapness, adaptability, strength, and durability of cement products have been a foundation of these applications

PORTLAND CEMENTS

In spite of the modern concrete roads and buildings everywhere around us, it is difficult to realize the tremendous growth of the cement industry during the past century. Humans had early discovered certain natural rocks which, through simple calcination, gave a product that hardened on the addition of water. Yet the real advance did not take place until physiochemical studies and chemical engineering laid the basis for the modern efficient plants working under closely controlled conditions with a variety of raw materials

HISTORICAL. Cement dates back to antiquity, and one can only speculate as to its discovery.¹ A cement was used by the Egyptians in constructing the Pyramids. The Greeks and Romans used volcanic tuff mixed with lime for cement, and a number of these structures are still standing. In 1824 an Englishman, Joseph Aspdin, patented an artificial cement made by the calcination of an argillaceous limestone. He called this "portland" because concrete made from it resembled a famous building stone obtained from the Isle of Portland near England. This was the start of the portland cement industry of today. The hard clinker resulting from burning a mixture of clay and limestone or similar materials is known by the term portland cement to distinguish it from natural or pozzolan and other cements. Concrete and cement are not synonymous terms. Concrete is artificial stone made from a carefully controlled mixture of cement, water, and fine and coarse aggregate (usually sand and coarse rock)

¹ECT, 3d ed., vol. 5, 1979, pp. 163-192 (excellent summary); Skalny and Daugherty, Everything You Always Wanted to Know About Portland Cement, *CHEMTECH* 2 (1) 38 (1972).

USES AND ECONOMICS. Before 1900 concrete was relatively little used in this country because the manufacture of portland cement was an expensive process. Thanks to the invention of labor-saving machinery, cement is now low in cost and is applied everywhere in the construction of homes, public buildings, roads, industrial plants, dams, bridges, and many other structures. Table 7.1 indicates the large volume of this industry. In 1980 there were 142 plants in the United States producing portland cement. It is interesting that the 10 largest plants produced 48 percent of the total and the 20 largest plants produced 72 percent.

TYPES OF PORTLAND CEMENTS. *Portland cement* has been defined as² "the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates, usually containing one or more forms of calcium sulfate as an interground addition." Hydraulic calcium silicates possess the ability to harden without drying or by reaction with atmospheric carbon dioxide, thus differentiating them from other inorganic binders such as plaster of paris. The reactions involved in the hardening of cement are hydration and hydrolysis. Five types (Table 10.2) of portland cement are recognized in the United States.

Type I. *Regular* portland cements are the usual products for general construction. There are other types of this cement, such as white, which contains less ferric oxide, oil-well cement, quick-setting cement, and others for special uses.

Type II. *Moderate-heat-of-hardening* and *sulfate-resisting* portland cements are for use where moderate heat of hydration is required or for general concrete construction exposed to moderate sulfate action. The heat evolved from these cements should not exceed 295 and 335 J/g after 7 and 28 days, respectively.

Type III. *High-early-strength* (HES) cements are made from raw materials with a lime-to-silica ratio higher than that of Type I cement and are ground finer than Type I cements. They contain a higher proportion of tricalcium silicate (C_3S) than regular portland cements. This, with the finer grinding, causes quicker hardening and a faster evolution of heat. Roads constructed from HES cement can be put into service sooner than roads constructed from regular cement.

²ASTM Specification 150-81.

Table 7.1 Portland Cement Shipments by Types, 1981
(in thousands of metric tons and thousands of dollars)

	Quantity	Value	Average Value per Metric Ton
General use and moderate (Types I and II)	56,852	192,940	56.16
High-early-strength (Type III)	2,333	135,214	57.94
Sulfate-resisting (Type V)	182	12,633	69.49
Oil well	2,974	203,990	68.58
White	302	42,721	141.56
Portland slag and pozzolan	621	38,189	61.51
Expansive	50	3,648	72.97
Miscellaneous*	524	36,376	69.47
Total or average	63,838	665,711	57.43

*Includes waterproof cement and low-heat (Type IV).

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, p. 194.

Table 7.2 Chemical Specifications for Portland Cements

Constituent	Regular, Type I	Moderate-Heat- of-Hardening Type II	High-Early- Strength, Type III	Low-Heat- of- Hydration, Type IV	Sulfate- Resisting, Type V
Silicon dioxide (SiO_2), min %	—	20.0			
Aluminum oxide (Al_2O_3), max %	—	6.0	—	—	—
Ferric oxide (Fe_2O_3), max %	—	6.0	—	6.5	—
Magnesium oxide (MgO), max %	5.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO_3), max %	—	—	—	—	—
When $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is 8% or less	2.5	3.0	3.5	2.3	2.3
When $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is more than 8%	3.0	—	4.5	—	—
Loss on ignition, max %	3.0	3.0	3.0	2.5	3.0
Insoluble residue, max %	0.75	0.75	0.75	0.75	0.75
Tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), max %	—	—	—	35	—
Dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), min %	—	—	—	40	—
Tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), %	—	8	15	7	5

*The tricalcium aluminate shall not exceed 5% and the tetracalcium aluminoferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) plus twice the amount of tricalcium aluminate shall not exceed 20%.

SOURCE: ASTM Designation C 150-80.

Type IV. *Low-heat* portland cements contain a lower percentage of C_3S and tricalcium aluminate (C_3A), thus lowering the heat evolution. Consequently, the percentage of tetracalcium aluminoferrite (C_4AF) is increased because of the addition of Fe_2O_3 to reduce the amount of C_3A (Table 7.4). Actually, the heat evolved should not exceed 250 and 295 J/g after 7 and 28 days, respectively, and is 15 to 35 percent less than the heat of hydration of regular or HES cements.

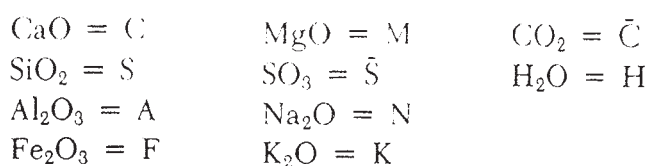
Type V. *Sulfate-resisting* portland cements are those which, by their composition or processing, resist sulfates better than the other four types. Type V is used when high sulfate resistance is required. These cements are lower in C_3A than regular cements. In consequence of this, the C_4AF content is higher.

Air Entrainment. The use of air-entraining agents (minute quantities of resinous materials, tallow, and greases) is important. These agents increase the resistance of the hardened concrete to scaling from alternate freezing and thawing and the use of de-icers (such as CaCl_2). Federal specifications permit the addition of an air-entraining material to each of the three types, which are then designated IA, IIA, and IIIA.

MANUFACTURING PROCEDURES. Two types of materials are necessary for the production of portland cement, one rich in calcium (calcareous), such as limestone, chalk, etc., and one

rich in silica (argillaceous) such as clay. Formerly a large amount of cement was made from argillaceous limestone, known as *cement rock*, found in New Jersey and the Lehigh district of Pennsylvania. In addition to natural materials, some plants use blast-furnace slag and precipitated calcium carbonate obtained as a by-product in the alkali and synthetic ammonium sulfate industry. Sand, waste bauxite, and iron ore are sometimes used in small amounts to adjust the composition of the mix. Gypsum (4 to 5%) is added to regulate the setting time of the cement.

These raw materials (Table 7.3) are finely ground, mixed, and heated (burned) in a rotary kiln to form cement clinker. Table 7.4 lists the predominant compounds that are formed during calcining. The cement industry uses the following abbreviations for these clinker compounds:



Thus Ca_3SiO_5 ($3\text{CaO} \cdot \text{SiO}_2$) = C_3S

Various reactions, such as evaporation of water, evolution of carbon dioxide, and reaction between lime and clay, take place during the burning (Table 7.5). Most of these reactions proceed in the solid phase, but, toward the end of the process, the important fusion occurs. Liquid formation begins at 1250°C and probably no appreciable formation of C_3S occurs below this temperature. C_3S is the chief strength-producing constituent of cement and during

Table 7.3 Raw Materials Used in Producing Portland Cement in the United States (in thousands of metric tons)

Raw Materials	1979	1980	1981
Calcareous			
Limestone (includes aragonite, marble, chalk)	73,725	71,164	66,380
Cement rock (includes marl)	28,167	22,717	24,204
Oyster shell	3,089	3,080	2,809
Argillaceous			
Clay	6,378	5,654	5,219
Shale	3,899	3,811	3,317
Other (includes Staurolite, bauxite, aluminum dross, pumice and volcanic material)	329	284	193
Siliceous			
Sand	1,934	1,813	1,631
Sandstone and quartz	734	607	667
Ferrous			
Iron ore, pyrites, mill-scale and other iron-bearing material	966	1,068	1,040
Other			
Gypsum and anhydrite	3,931	3,508	3,272
Blast furnace slag	439	120	86
Fly ash	463	546	688
Other	5	155	147
Total	124,059	114,529	109,654

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, p. 183.

Table 7.4 Clinker Compounds

Formula	Name	Abbreviation
$2\text{CaO} \cdot \text{SiO}_2$	Dicalcium silicate	C_2S
$3\text{CaO} \cdot \text{SiO}_2$	Tricalcium silicate	C_3S
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	Tricalcium aluminate	C_3A
$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	Tetracalcium aluminoferrite	C_4AF
MgO	Magnesium oxide in free state	M

NOTE: See Table 10.7 for amounts in cement.

its formation the free lime present is reduced to a small amount. Between 20 and 30 percent of the reactions take place in the final fluid phase.³

Cement clinker is manufactured by both wet and dry processes. In both processes *closed-circuit grinding* is preferred to *open-circuit grinding* in preparing the raw materials because in the former the fines are passed on and the coarse material returned, whereas in the latter the raw material is ground continuously until its mean fineness has reached the desired value (see Fig. 10.2 for some grinding hookups). However, Perry⁴ presents more details of actual grinding circuits with power requirements. The *wet process*, though the original one, is being displaced by the *dry process*, especially for new plants, because of the saving in heat, accurate control, and mixing of the raw mixture it affords. At the end of 1980, dry process plants accounted for 45 percent of the total cement production capacity,⁵ but used only 40.4 percent of the industry's total energy consumption. These processes are illustrated in the generalized flowchart in Fig. 10.1. In the wet process the solid material, after dry crushing, is reduced to a fine state of division in wet tube or ball mills and passes as a slurry through bowl classifiers or screens. The slurry is pumped to correcting tanks, where rotating arms make the mixture homogeneous and allow the final adjustment in composition to be made. In some plants, this

³Lea, *The Chemistry of Cement and Concrete*, 3d ed., Edward Arnold, London, 1970.

⁴Perry, *Cement, Lime, and Gypsum*, pp. 8-50 to 8-52.

⁵*Energy Report of U.S. Portland Cement Industry*, Portland Cement Association, July, 1981.

Table 7.5 Reactions during Clinker Formation

Temperature, °C	Reaction	Heat Change
100	Evaporation of free water	Endothermic
500 and above	Evolution of combined water from clay	Endothermic
900 and above	Crystallization of amorphous dehydration products of clay	Exothermic
900 and above	Evolution of carbon dioxide from calcium carbonate	Endothermic
900-1200	Main reaction between lime and clay	Exothermic
1250-1280	Commencement of liquid formation	Endothermic
1280 and above	Further formation of liquid and completion of formation of cement compounds	Probably endothermic on balance

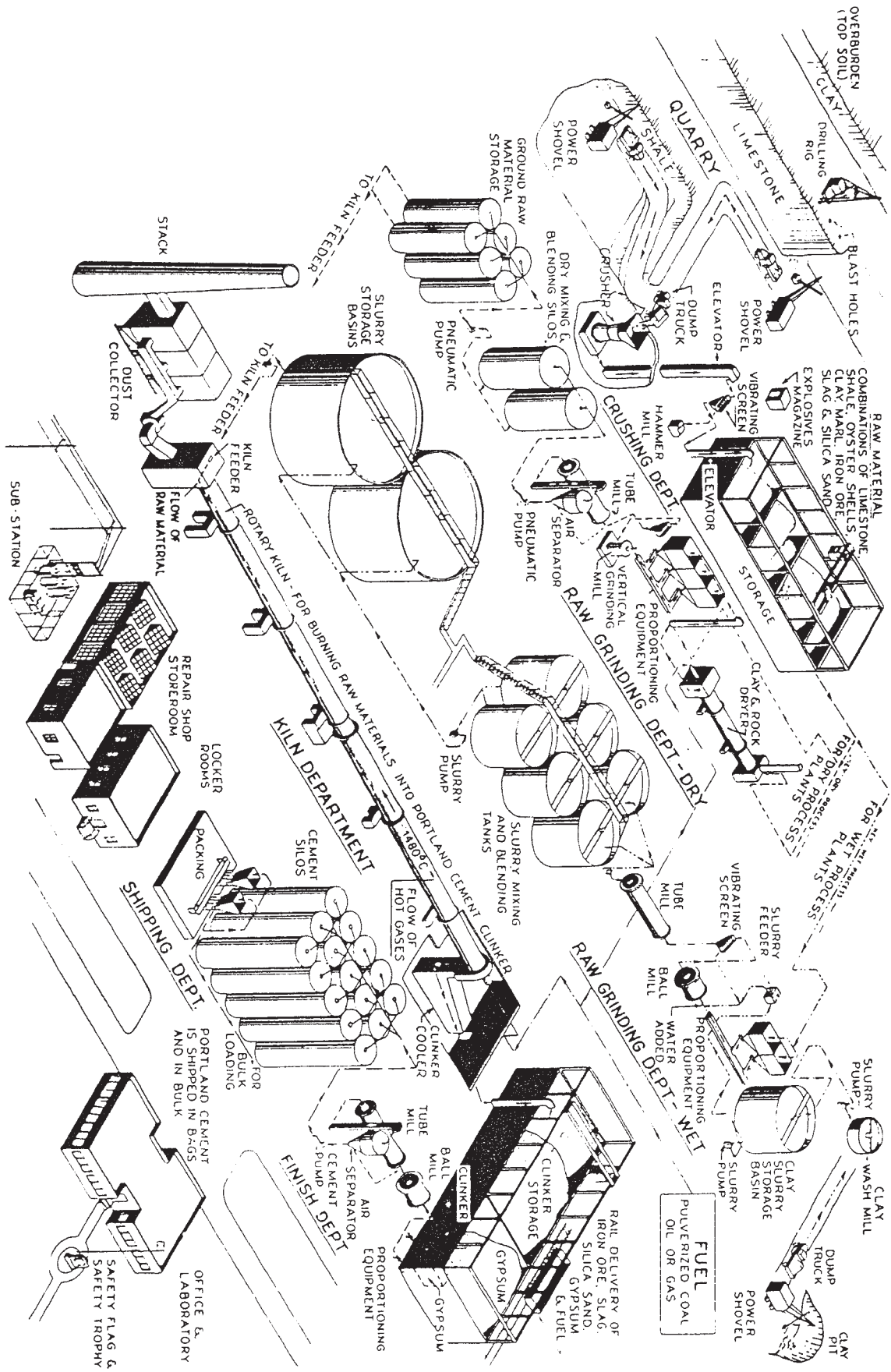


Fig. 7.1. Isometric flowchart for the manufacture of portland cement by both dry and wet processes. (Portland Cement Assoc.)

slurry is filtered in a continuous rotary filter and fed into the kiln. The *dry process* is especially applicable to natural cement rock and to mixtures of limestone and clay, shale, or slate. In this process the materials may be roughly crushed, passed through gyratory and hammer mills, dried, sized, and more finely ground in tube mills, followed by air separators. Proportioning equipment is included in the sequences. Before entering the kiln a thorough mixing and blending by air or otherwise takes place. This dry, powdered material is fed directly to rotary kilns, where the previously mentioned chemical reactions take place. Heat is provided by burning oil, gas, or pulverized coal, using preheated air from cooling the clinker. The tendency in recent years has been to lengthen the rotary kiln in order to increase its thermal efficiency. Dry-process kilns may be as short as 45 m, but in the wet process, 90- to 180-m kilns are not uncommon. The internal diameter is usually from 2.5 to 6 m. The kilns are rotated at from $\frac{1}{2}$ to 2 rpm depending on size. The kilns are slightly inclined, so that materials fed in at the upper end travel slowly to the lower firing end, taking from 1 to 3 h. In order to obtain greater heat economy, part of the water is removed from wet process slurry. Some of the methods used employ slurry filters and Dorr thickeners. Efficient air pollution control equipment such as baghouses or electrostatic precipitators are now required for kilns.⁶ Waste-heat boilers are sometimes used to conserve heat and are particularly economical for dry process cement, since the waste gases from the kiln are hotter than those from the wet process and may reach 800°C. Because the lining of the kiln has to withstand severe abrasions and chemical attack at the high temperatures in the clinkering zone, the choice of a refractory lining is difficult. For this reason high-alumina and high-magnesia bricks are widely used. Computers are now used to improve kiln control. The final product formed consists of hard, granular masses from 3 to 20 mm in size, called *clinker*. The clinker is discharged from the rotating kiln into the air-quenching coolers, which quickly bring its temperature down to approximately 100 to 200°C. These coolers simultaneously preheat the combustion air. Pulverizing, followed by fine grinding in the tube ball mills and automatic packaging, completes the process. During the fine grinding, setting retarders, such as gypsum, plaster, or calcium lignosulfonate, and air-entraining, dispersing, and waterproofing agents are added. The clinker is ground dry by various hookups, as illustrated in Fig. 7.2 and by Perry.

The entire cement process can be monitored by x-ray machines connected with programmable calculators in order to constantly sample the product and then automatically adjust the raw mill feed to produce the desired product.⁷ The cement industry is the nation's sixth largest industrial user of energy. In 1980 the production of 61.75×10^6 t of clinker consumed 11×10^6 t of coal, 500×10^3 m³ oil, and 1.78×10^6 m³ natural gas.^{7a} For this reason, much effort has been expended in devising more energy efficient technology. One proposal suggests the use of fluoride-containing fluxes to reduce the temperature necessary for clinker formation.⁸

COMPOUNDS IN CEMENTS. Portland cements contain a mixture of compounds (previously listed) present in amounts partly dependent on the degree of attainment of equilibrium conditions during burning. Tables 7.6 and 7.7 give analyses of various types of portland cement and some typical compositions of regular cements. From these analyses it is seen that portland cement composition approaches a rough approximation to the system CaO-SiO₂ and succes-

⁶Cements' Changing Scene, *Chem. Eng.* 81 (13) 103 (1974); Voldbaek and Cooke, *Rock Prod.* 83 (4) 108 (1980).

⁷Kruegel, X-Ray Control of Cement Process, *Rock Prod.* 81 (4) 132 (1979).

^{7a}t = 1000 kg.

⁸Chen, L. H., Fluoride Compounds Research in Cement Manufacture, *Rock Prod.* 82 (4) 52 (1980).

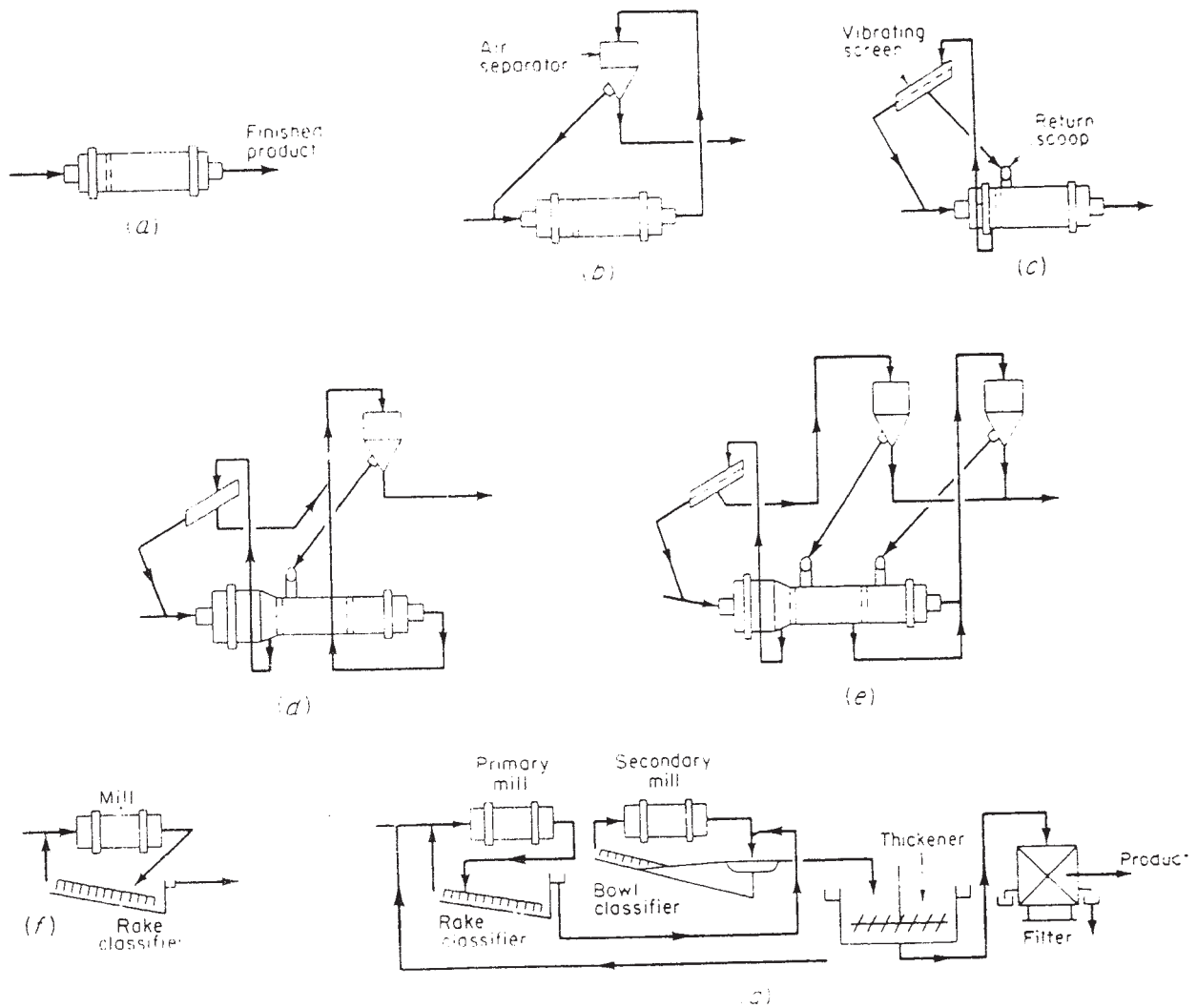


Fig. 7.2. Dry and wet-grinding hookups. (a) Simple two-compartment mill in open circuit; (b) two-compartment mill closed-circuited with air separator; (c) two-stage setup with primary compartment closed-circuited; (d) efficient two- or three-compartment circuit closed with a screen and air separator; (e) highly efficient three-stage system closed-circuited in each stage; (f) single-stage mill closed-circuited with rake classifier; (g) modern double-stage circuit employing four different types of separating equipment (Source: CPI Co.)

Table 7.6 Analyses of Portland Cements (in percentage)

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Alkali Oxides	SO ₃
Regular Cement (Average of 102)							
Minimum	61.17	18.58	3.86	1.55	0.60	0.66	2.52
Maximum	66.92	23.26	7.44	6.18	5.24	2.9	2.26
Average	63.85	21.08	5.79	2.86	2.47	1.4	1.73
High-Early-Strength (Average of 87 High C ₃ S)							
Minimum	62.7	18.0	4.1	1.7	—	—	2.2
Maximum	67.5	22.9	7.5	4.2	—	—	2.7
Average	64.6	19.9	6.0	2.6	—	—	2.3
Low-Heat-of-Hardening (Average of 57 Lower C ₃ S and C ₃ A, Higher C ₂ S and C ₄ AF)							
Minimum	59.3	21.9	3.3	1.9	—	—	1.6
Maximum	61.5	26.4	5.4	5.7	—	—	1.9
Average	60.2	23.8	4.9	4.9	—	—	1.7

Table 7.7 Potential Compound Composition of Some Typical Cements (in percentage)

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Type I	55	19	10	7
Type II	51	24	6	11
Type III	56	19	10	7
Type IV	28	49	4	12
Type V	38	43	4	9

SOURCE: ECT, 3d ed., vol. 5, 1979, p. 171.

sively closer approximations to the systems $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MgO}$. A complete understanding of portland cement would require knowledge of the phase-equilibrium relations of the high-lime portions of all the two-, three-, four-, and five-component systems involved. Of these, all 12 of the principal two- and three-component systems, and the parts of the four-component systems, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$, in which portland cement compositions are located, are known. In 1946 part of the five-component system, $\text{CaO-MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$, was studied by Swayze;⁹ such studies are being continued. Modern cement technology owes much to Rankin and Wright¹⁰ of the Geophysical Laboratory.

SETTING AND HARDENING OF CEMENT. Although many theories have been proposed to explain the setting and hardening of cement, it is generally agreed that *hydration* and *hydrolysis*¹¹ are involved. The hydration products have very low solubility in water. If this were not true, concrete in contact with water would be rapidly attacked. Much attention has been given to the heat evolved during the hydration of cement. The various compounds contribute to the heat of hardening (basis, equal weights, i.e., gram for gram) after 28 days, as follows:¹²

$$\text{C}_3\text{A} > \text{C}_3\text{S} > \text{C}_4\text{AF} > \text{C}_2\text{S}$$

Table 10.8 shows why low-heat-of-hardening cements are made low in C_3A and C_3S but high in C_2S . This is accomplished (1) by adding more Fe_2O_3 , which takes the Al_2O_3 out of circulation as C_4AF , thereby diminishing the amount of C_3A , and (2) by decreasing the CaO/SiO_2 ratio. Notice these facts in the analyses in Table 10.6. Thus low-heat-of-setting cement is used in the construction of all large dams to avoid cracking the structure from heat stresses during setting and cooling. As an additional safeguard, the structures are cooled during setting by circulating cold water through lightweight 2.5-cm pipes, placed in the concrete mass.¹³ Tables 10.9 and 10.10 present further facts regarding the functions of the different compounds in

⁹Swayze, *Am. J. Sci.* **244** (1) 63 (1946).

¹⁰The Ternary System: $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, *Am. J. Sci.* **39** 1-79 (1915).

¹¹For hydration studies see Lea, *op. cit.*, Chap. 9.

¹²Woods, Steinour, and Strake, Effect of Composition of Portland Cement on Heat Evolved during Hardening, *Ind. Eng. Chem.* **24** 1207 (1932); Bogue and Lerch, Hydration of Portland Cement Compounds, *J. Res. Natl. Bur. Stand.* **12** 645 (1934).

¹³Robertson, Boulder Dam, *Ind. Eng. Chem.* **27** 242 (1935).

Table 7.8 Heat of Hydration (in joules per gram)

Compound	Days				
	3	7	28	90	365
C ₄ AF	290	495	495	416	377
C ₃ A	888	1557	1378	1302	1168
C ₂ S	50	42	105	176	222
C ₃ S	243	222	377	435	490

SOURCE: *Proc. Am. Soc. Test. Mater* 50 1235 (1950)

Table 7.9 Strength Contribution of Various Compounds in Portland Cement

(The Relative Strengths Are the Apparent Relative Contributions of Equal Weights of the Compounds Listed)

1 day	C ₃ A > C ₃ S > C ₄ AF > C ₂ S
3 days	C ₃ A > C ₃ S > C ₄ AF > C ₂ S
7 days	C ₃ A > C ₃ S > C ₄ AF > C ₂ S
28 days	C ₃ A > C ₃ S > C ₄ AF = C ₂ S
3 months	C ₂ S > C ₃ S = C ₃ A = C ₄ AF
1 year	C ₂ S > C ₃ S > C ₃ A = C ₄ AF
2 years	C ₂ S > C ₃ S > C ₄ AF > C ₃ A

SOURCE: Steinour, Chemistry of Cement, *Portland Cement Assoc. Res. Develop. Lab. Develop. Dept. Bull.* 130; *J. Portland Cement Assoc. Res. Develop. Lab.* 3 (2) 2-11 (1961)

Table 7.10 Function of Compounds

Compound	Function
C ₃ A	Causes set but needs retardation (by gypsum)
C ₃ S	Responsible for early strength (at 7 or 8 days)
C ₂ S and C ₃ S	Responsible for final strength (at 1 year)
Fe ₂ O ₃ , Al ₂ O ₃ , Mg, and alkalis	Lower clinkering temperature

the setting and hardening of cement. To hold up the "flash set" caused by C₃A, the gypsum added as a retarder causes the formation of C₃A·3CaSO₄·31H₂O.

Admixtures (additives to cement for concrete formulations) extend the supply of cement and add other important properties. These usually give specific results from individual additions. One important group is the superplasticizer naphthalene derivatives.¹⁴ Calcium nitrite may be added to inhibit the corrosion of steel reinforcing bars in concrete.¹⁵

¹⁴*Chem. Week* 126 (11) 45 (1980).

¹⁵*Chem. Week* 130 (5) 21 (1982).