

to Mr. D. M. Andrews. Ten brands of Portland cement were submitted to the Government at prices ranging from \$2.77 to \$3.29.* Experiments showed that sample No. 5 was the strongest, with No. 4 a close second. The relative strength of the different brands in proportions 1:3, based on the strongest as 100.0, is given in the column headed Relative Strength of Mortar, and the column following this gives the product of the relative strength multiplied by the relative cheapness. In the case under consideration brand No. 5 was selected for purchase, because, although No. 4 gave higher economy, it appeared slightly unsound. Other data with reference to each brand was observed, including the volumes of the barrels, their gross net weights, the percentages of water used in mixing the pastes and mortar, the time of setting of the mortar, and the strength and relative economy of mortars with sand proportioned to price of cement, that is, for example, using 19% more sand with cement No. 10 than with No. 1, because the former's price was 19% greater.

*The price of Portland cement has since been materially lowered.

Relative Economy of Different Priced Portland Cements.

BY D. M. ANDREWS.

No. of Sample Barrel.	PRICE PER BARREL.	Relative cheapness.	FINENESS.		TIME OF SETTING		TENSILE STRENGTH.						Relative Strength of Mortar 1:3	Relative Economy 1:3 Mortar. Strength × Cheapness.	REMARKS
			No. 50 sieve.	No. 100 sieve.	INITIAL.	FINAL.	NEAT.			1:3 MORTAR.					
							7 days.	30 days.	60 days.	7 days.	30 days.	60 days.			
			Hours.	Hours.	60 days.	60 days.	60 days.								
1	\$2.77	100.0	93.3	87.6	2	8	324	437	430	66	128	168	79.7	79.7	
2	2.79	99.3	99.3	87.3	8†	8†	282	429	408	62	103	124	59.1	58.7	
3	2.82	98.2	98.2	89.7	2	3‡	272	373	431	35	65	87	41.2	40.5	
4	2.82	98.2	100.0	99.6	5	9‡	309	460	504	144	184	209	99.4	97.7	Air pat cracked very slightly.
5†	2.89	95.8	99.0	86.2	7‡	7‡	449	543	631	114	175	210	100.0	95.8	
6	2.90	95.5	94.6	77.0	4	6‡	150	227	204	25	57	90	42.8	40.9	Lumpy and gritty on mixing.
7	2.93	94.5	100.0	90.0	4	8	440	588	568	127	156	202	96.2	90.9	
8	3.02	91.7	99.5	89.4	2‡	7	418	476	561	89	134	174	82.4	75.6	Pats crack'd slightly.
9	3.05	90.8	98.5	91.2	3‡	7‡	436	518	502	93	126	144	68.2	62.0	
10	3.29	84.2	99.4	92.7	2‡	5	365	496	573	78	117	141	67.1	56.5	

†Accepted in preference to No. 4 because air pat slightly defective.
‡Cement not yet set.
§Based on the highest, No. 5, as 100.0.

CHAPTER V

CLASSIFICATION OF CEMENTS.

From an engineering standpoint, limes and cements may be classified as
 Portland cement.
 Natural cement.
 Puzzolan cement.
 Hydraulic lime.
 Common lime.

Typical analyses of each of these are presented in the following table. The composition of Natural cement, even different samples of the same brand, is so extremely variable that their analyses cannot be regarded as characteristic of locality.

Typical Analyses of Cements.

	PORTLAND CEMENT		NATURAL CEMENT					COMMON LIME			
	Lehigh Valley ¹ (mixed rock)	Western ² (marl and clay)	AMERICAN		ENGL ¹ H		Puzzolan Cement ⁷	Hydraulic Lime (Le Fiel) ⁸	Lime ⁹	Magnesian Lime ¹⁰	
			Eastern Rosendale ³	Western Louisville ³	Roman ⁴	Vassy ⁵					Crappiers ⁶
Silica Si O ₂	21.31	21.93	18.38	20.42	25.48	22.60	26.5	28.95	21.70	1.03	1.12
Alumina Al ₂ O ₃	6.89	5.98	15.20	4.76	10.30	8.90	2.5	11.40	3.19		0.68
Iron Oxide Fe ₂ O ₃	2.53	2.35	3.40	7.44	5.30	1.5	0.54	0.66			1.27
Calcium Oxide Ca O	62.89	62.92	35.84	46.64	44.54	52.69	63.0	50.29	60.70	97.02	58.51
Magnesian Oxide Mg O	2.64	1.10	14.02	12.00	2.92	1.15	1.0	2.96	0.85	0.68	39.60
Sulphuric Acid S O ₃	1.34	1.54	0.93	2.57	2.61	3.25	0.5	1.37	0.60		
Loss on Ignition	1.39	2.91	3.73	6.75	3.68	6.11	5.0	3.39	12.20		
Other constituents	0.75		11.46	3.74	1.46		0.30	0.10			

¹W. F. Hillebrand, Society of Chemical Industry, 1902, Vol. XXI.
²W. F. Hillebrand, Journal American Chemical Society, 1903, 25, 1180.
³Clifford Richardson, Brickbuilder, 1897, p. 229.
⁴Stanger & Blount, Mineral Industry, Vol. V, p. 69.
⁵Candlot, Ciments et Chaux Hydrauliques, 1898, p. 174.
⁶Le Chatelier, Annales des Mines, September and October, 1893, p. 36.
⁷Report of the Board of U. S. Army Engineers on Steel Portland Cement, 1900, p. 52.
⁸Candlot, Ciments et Chaux Hydrauliques, 1898, p. 24.
⁹Rockland-Rockport Lime Co.
¹⁰Western Lime and Cement Co.

PORTLAND CEMENT†

Portland cement is defined by Mr. Edwin C. Eckel of the U. S. Geological Survey as follows: "By the term Portland cement is to be understood the material obtained by finely pulverizing clinker produced by burning to semi-fusion an intimate artificial mixture of finely ground calcareous and argillaceous materials, this mixture consisting approximately of 3 parts of lime carbonate to 1 part of silica, alumina and iron oxide."

The definition is often further limited by specifying that the finished product must contain at least 1.7 times as much lime, by weight, as of silica, alumina, and iron oxide together.

The only surely distinguishing test of Portland cement is its chemical analysis and its specific gravity. (See pp. 64 and 65.) In the field it may often be recognized by its cold bluish gray color (see p. 113), although the color of Puzzolan and of some Natural cements is so similar that this is by no means a positive indication.

The term **Natural Portland Cement** arose from the discovery in Boulogne-sur-Mer, France, as early as 1846, of a natural rock of suitable composition for Portland cement. A similar discovery in Pennsylvania gave rise to the same term in America, but the manufacturers soon found it necessary to add to the cement rock a small percentage of purer limestone. Since the chemical composition of Portland cement, as defined above, is substantially uniform regardless of the materials from which it is made, in the United States the terms "natural" and "artificial" are meaningless.

In France, cements intermediate between Roman and Portland are called "natural Portlands."*

Sand Cement. Sand or silica cement is a mechanical mixture of Portland cement with a pure, clean sand very finely ground together in a tube mill or similar machine. For the best grades the proportions of cement to sand are 1:1, although as lean a mixture as 1:6 has been made to compete with Natural cements. The coarser particles in any Portland cement have little cementitious value, hence if a portion of the cement is replaced by inert matter and the whole ground extremely fine, its advocates maintain that the product is scarcely inferior to the unadulterated article. As made in the United States, the mixture is ground so fine that 95% of it will pass through a sieve having 200 meshes to the linear inch, and all of the 5% of residuum is said to be sand. In other words, all of the cement passes a No. 200 sieve.

† A sub-classification of Portland cement is presented on page 53.
* Candlot's Ciments et Chaux Hydrauliques. 1898, p. 164.

NATURAL CEMENT

Natural cement is "made by calcining natural rock at a heat below incipient fusion, and grinding the product to powder."* Natural cement contains a larger proportion of clay than hydraulic lime, and is consequently more strongly hydraulic. Its composition is extremely variable on account of the difference in the rock used in manufacture.

Natural cements in the United States in numerous instances bear the names of the localities where first manufactured. For example, Rosendale cement, a term heard in New York and New England more frequently than Natural cement, was originally manufactured in Rosendale, Ulster County, N. Y. Louisville cement first came from Louisville, Ky. The James River, Milwaukee, Utica, and Akron are other Natural cements named for localities.

The United States produces a few brands of "Improved Natural Hydraulic Cement," intermediate in quality between Natural and Portland, by mixing inferior Portland cement with Natural cement clinker.

In England the best known Natural cement is called Roman cement. Occasionally one hears the term Parker's Cement, so called from the name of the discoverer in England.

LE CHATELIER'S CLASSIFICATION OF NATURAL CEMENTS

In France there are several classes of Natural cement. Mr. H. Le Chatelier† classifies Natural cements as those obtained "by the heating of limestone less rich in lime than the limestone for hydraulic lime. They may be divided into three classes:

"Quick-setting cements, such as Vassy and Roman (Ciments à prise rapide, Vassy, romain);

"Slow-setting cements (Ciments à prise demi-lente);

"Grappiers cement (Ciments de grappiers).

"**Vassy Cements** are obtained by the heating of limestone containing much clay, at a very low temperature, just sufficient to decarbonate the lime. They are characterized by a very rapid set, followed afterwards by an extremely slow hardening, much slower than that of Portland cements."

"They differ from Portland cements by containing a much higher percentage of sulphuric acid, which appears to be one of their essential elements, and a much lower percentage of lime.

*Professional Papers, No. 28, U. S. Army Engineers, p. 33.

†Procédés d'Essai des Matériaux Hydrauliques, Annales des Mines, 1893.

"**Slow-Setting Cements**, by the high temperature of calcination, approach Portland cements, but the natural limestones never possess the homogeneity of artificial mixtures, so that it is impossible to avoid in these cements the presence of a large quantity of free lime." The composition of these products varies from that of the Vassy cements to that of the real Portlands.

"**Grappiers Cements*** are obtained by the grinding of particles which have escaped disintegration in the manufacture of hydraulic limes. These grappiers are a mixture of four distinct materials, two of which, completely inert, are unburned limestone and the clinkers formed by contact with the siliceous walls of furnaces, and two of which, strongly hydraulic, are unslaked lime and true slow-setting cement. It is necessary that the latter should predominate in the grappiers for their grinding to give a useful product. The grappier of cement is obtained regularly only by the heating of a limestone but slightly aluminous and containing about three equivalents of carbonate of lime for one of silica; its production necessitates a heating at high temperature.

"These grappiers cements are even more apt to contain free lime than the Natural cements of slow set which are obtained by the heating of limestone containing much more alumina. Because of their constitution, also, the grappiers cements may vary greatly in composition since they are produced by the grinding of a mixture of grains of cement and of various inert materials. The cement grains have very nearly the composition of tricalcium silicate ($\text{SiO}_2 \cdot 3 \text{CaO}$)."

PUZZOLAN OR SLAG CEMENT

Puzzolan cement is the product resulting from mixing and grinding together in definite proportions slaked lime and granulated blast furnace slag or natural puzzolanic matter (such as puzzolan, santorin earth, or trass obtained from volcanic tufa).

The ancient Roman cements belonged to the class of Puzzolans. They were made by mechanically mixing slaked lime with natural puzzolana formed from the fusion of natural rock found in the volcanic regions of Italy. In Germany, trass, a volcanic product related to Puzzolan, has been used with lime in the manufacture of cements.

Blast furnace slag is essentially an artificial puzzolana, formed by the combustion in a blast furnace, and the puzzolan or slag cements of the United States are ground mixtures of granulated blast furnace slag, of special composition, and slaked lime.

*Cements essentially of the Grappiers class in the United States are termed "Non-Staining Cements." These may closely approach Portland cement in strength.

A Board of Engineers officers, U. S. A., presented in 1901 the following conclusions,* based, undoubtedly, on the exhaustive studies upon the subject made by a previous Board† having the same chairman, Major W. L. Marshall:

This term (slag or Puzzolan cement) is applied to cement made by intimately mixing by grinding together granulated blast-furnace slag of a certain quality and slaked lime, without calcination subsequent to the mixing. This is the only cement of the Puzzolan class to be found in our markets (often branded as Portland), and as true Portland cement is now made having slag for its hydraulic base, the term "slag cement" should be dropped and the generic term Puzzolan be used in advertisements and specifications for such cements.

Puzzolan cement made from slag is characterized physically by its light lilac color; the absence of grit attending fine grinding and the extreme subdivision of its slaked lime element; its low specific gravity (2.6 to 2.8) compared with Portland (3 to 3.5); and by the intense bluish green color in the fresh fracture after long submersion in water, due to the presence of sulphides, which color fades after exposure to dry air.

The oxidation of sulphides in dry air is destructive of Puzzolan cement mortars and concretes so exposed. Puzzolan is usually very finely ground, and when not treated with soda sets more slowly than Portland. It stands storage well, but cements treated with soda to quicken setting become again very slow setting, from the carbonization of the soda (as well as the lime) element after long storage.

Puzzolan cement properly made contains no free or anhydrous lime, does not warp or swell, but is liable to fail from cracking and shrinkage (at the surface only) in dry air.

Mortars and concretes made from Puzzolan approximate in tensile strength similar mixtures of Portland cement, but their resistance to crushing is less, the ratio of crushing to tensile strength being about 6 to 7 to 1 for Puzzolan, and 9 to 11 to 1 for Portland. On account of its extreme fine grinding Puzzolan often gives nearly as great tensile strength in 3 to 1 mixtures as neat.

Puzzolan permanently assimilates but little water compared with Portland, its lime being already hydrated. It should be used in comparatively dry mixtures well rammed, but while requiring little water for chemical reactions, it requires for permanency in the air constant or continuous moisture.

Puzzolanic material has been suggested by Dr. Michaelis, of Germany, and Mr. R. Feret, of France (see Chapter XVI), as a valuable addition to Portland cement designed for use in sea water.

*Professional Papers No. 28, p. 28.

†Report of the Board of U. S. Army Engineers on Steel Portland Cement, 1900, p. 52.

HYDRAULIC LIME

The hydraulic properties of a lime, — its ability to harden under water, — are due to the presence of clay, or, more correctly, to the silica contained in the clay. Hydraulic lime is still used to quite an extent in Europe, especially in France, as a substitute for hydraulic cement. The celebrated lime-of-Teil of France is a hydraulic lime.

Mr. Edwin C. Eckel states* that "theoretically the proper composition for a hydraulic limestone should be calcium carbonate 86.8%, silica 13.2%. The hydraulic limestones in actual use, however, usually carry a much higher silica percentage, reaching at times to 25%, while alumina and iron are commonly present in quantities which may be as high as 6%. The lime content of the limestones commonly used varies from 55% to 65%."

Although the chemical composition of hydraulic lime is similar to Portland cement, its specific gravity is much lower, lying between 2.5 and 2.8.†

In the manufacture of hydraulic lime the limestone of the required composition is burned, generally in continuous kilns, and then sufficient water is added to slake the free lime produced so as to form a powder without crushing.

COMMON LIME

The commercial lime of the United States is "quicklime," which is chiefly calcium oxide (CaO).

Lime is now manufactured by a continuous process. Limestone of a rather soft texture, so as to be as free as possible from silica, iron and alumina, is charged into the top of a kiln which may be, say, 40 ft. high by 10 ft. in diameter. The fuel is introduced into combustion chambers near the foot of the shaft, and the finished product is drawn out from time to time through another opening in the bottom of the shaft. The temperature of calcination may range from 1400° Fahr. (760° Cent.) to, at times, 2,000° Fahr. (1,090° Cent.). The product (see analysis, p. 47), in ordinary lime of the best quality, is nearly pure calcium oxide (CaO). Upon the addition of water the lime slakes, forming calcium hydrate (CaH₂O₂), and, with the continued addition of water, increases in bulk to twice to three times the original loose and dry volume of the lump lime as measured in the cask. In this plastic condition it is termed by plasterers "putty" or "paste."

The setting of lime mortar is the result of three distinct processes which, however, may all go on more or less simultaneously. First, it

**American Geologist*, March, 1902, p. 152.

†Candlot's *Ciments et Chaux Hydrauliques*, 1898, p. 26.

dries out and becomes firm. Second, during this operation, the calcic hydrate, which is in solution in the water of which the mortar is made, crystallizes and binds the mass together. Hydrate of lime is soluble in 831 parts of water at 78° Fahr; in 759 parts at 32° and in 1136 parts at 140°. Third, as the per cent. of water in the mortar is reduced and reaches five per cent., carbonic acid begins to be absorbed from the atmosphere. If the mortar contains more than five per cent. this absorption does not go on. While the mortar contains as much as 0.7 per cent. the absorption continues. The resulting carbonate probably unites with the hydrate of lime to form a sub-carbonate, which causes the mortar to attain a harder set, and this may finally be converted to carbonate. The mere drying out of mortar, our tests have shown, is sufficient to enable it to resist the pressure of masonry, while the further hardening furnishes the necessary bond.*

Magnesian Limes evolve less heat when slaking, expand less, and set more rapidly than pure lime. A typical analysis is given on page 47.

Hydrated Lime is the powdered product formed by slaking quick lime with the requisite amount of water. The material as it comes into commerce is a very finely divided white powder, and if properly prepared contains no unhydrated particles of lime.

SUB-CLASSIFICATION OF PORTLAND CEMENTS

In addition to the gray-colored cements for ordinary uses, Portland cements are made from raw materials low in iron so as to produce a light-colored cement, and also from raw materials low in aluminum and high in iron to produce a cement which better resists the action of sea water. This leads to a sub-classification suggested by Mr. Eckel. The distinction is somewhat arbitrary, since the classes grade into each other, while normal Portlands vary in the relative proportions of iron and alumina.

(1) **Normal Portlands.** Containing, with the silica and lime, both alumina and iron oxide in appreciable quantity; usually from 4 to 10 per cent alumina with 1.5 to 5 per cent iron oxide. Product: the ordinary gray-colored commercial cement.

(2) **Low Iron Portlands.** Containing relatively high alumina, with only 1 per cent or less of iron oxide. Product; white or very light colored, quick setting, usually low in tensile strength.

(3) **High Iron Portlands.** Containing relatively high iron, with less than 2 per cent of alumina. Product: slow setting, high tensile strength in long time tests, resistant to sea and alkaline waters.

* The authors are indebted to Mr. Clifford Richardson for this paragraph.