CHAPTER VI

CHEMISTRY OF HYDRAULIC CEMENTS*

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INTRODUCTION

Hydraulic cements are compounds consisting chiefly of lime, silica, and alumina, which have the property, when mixed to a paste with water, of hardening to a stone-like mass. They may be classified as follows:

1. **Portland cement,** made by calcining at high heat an artificial mixture of carbonate of lime and clay or slag, in exactly correct proportions, and grinding the resulting clinker to powder.

2. **Natural cement,** made by burning at low heat limestone containing excess of clay and usually much magnesia, and grinding the product to powder.

3. **Hydraulic lime,** obtained by burning limestone containing a small amount of clay, slaking by sprinkling with water, and bolting the product.

4. **Puzzolan or slag cement,** consisting of a mixture of certain kinds of volcanic scoria, or of blast furnace slag, and slaked lime, ground together.

Each of these classes of cement shows peculiar qualities, and each may have advantages for certain purposes. Puzzolan cement is that used by the Romans, and many striking examples of its durability are seen in ancient structures. Slag cement, a mechanical mixture of slag and slaked lime, is made to a considerable extent in this country, and finds extended use for mortar and in work in which the greatest strength and hardness are not required. Hydraulic lime is made chiefly in France, and is but little known in the United States. Natural cement is manufactured on a very large scale from limestones containing a large proportion of clay. It is usually quick-setting, and the better qualities gain very good strength at long periods. Owing to its cheapness it is extensively used, chiefly as mortar for brickwork and masonry. All these earlier hydraulic materials, however, have gradually given way before the advance of Portland cement, as this product has been improved in quality and manufactured on a constantly increasing scale.

Portland cement was first made in England in 1827, and named from the resemblance in color of the hardened cement to the building stone quarried at the Island of Portland.

*The authors are indebted to Mr. Newberry for this chapter, which has been especially prepared by him for this Treatise.

MATERIALS*

As above stated, hydraulic lime and natural cements are made by burning natural limestones containing suitable amounts of clay. Portland cement, on the other hand, is made from an artificial mixture of materials, of exactly correct composition. Limestones containing clay are of frequent occurrence. If a deposit of stone containing exactly the right amount of clay, and of exactly uniform composition, could be found, Portland cement could be made from it simply by burning and grinding. For good results, however, the composition of the raw material must be *exact*, and the proportion of carbonate of lime in it must not vary even by one per cent. No natural deposit of rock of exactly this correct and unvarying composition is known or likely ever to be found; therefore Portland cement is always made from an artificial mixture, usually, if free from organic matter, containing about 75% carbonate of lime and 25% clay.

For the manufacture of Portland cement the materials chiefly used are limestone, chalk or marl, and clay. In southeastern Pennsylvania and western New Jersey occurs an unlimited deposit of *cement rock*, which consists of a slate-like limestone containing usually rather more clay than is required for a correct mixture. This is largely used for Portland cement manufacture, and is generally ground with a small amount of purer limestone to bring it to correct composition. At some of the factories in that section a correct mixture is obtained by grinding together, in suitable proportions, the upper and lower layers of the quarry. In the Central States, pure limestone, or marl (a soft and finely divided form of carbonate of lime) and clay, are the materials employed. Whatever the materials used, the first stage of the process is the preparation of an intimate and finely ground mixture of carbonate of lime and clay, of a certain definite composition, and if this is accomplished the resulting cement will be the same, whatever the original materials may have been. Success in Portland cement manufacture depends, more than upon all other features of the process, in extremely fine grinding of the raw materials. Most of the faults found in inferior Portland cement are due to neglect in this regard. Either the wet or dry process may be used in preparing the mixture. The material is then dried and calcined at white heat, generally in revolving cylindrical kilns, from which it issues in the form of small, black, rounded fragments of clinker. By grinding this clinker to fine powder the finished Portland cement is obtained.

*The materials for cement and the manufacture of cement are also treated in Chapter XXX.

Magnesia in Portland cement, beyond a small percentage, has generally been considered objectionable. But little positive evidence on this point is, however, available. A committee of the German Portland Cement Manufacturers Association, many years ago, reported that magnesia up to 8 per cent. is harmless. Dyckerhoff, a member of the committee, presented a minority report stating that he had found more than 4 per cent. injurious. The subject was referred to another committee, in 1896, but this committee laid out a program of work which proved impracticable to complete, and nothing further has been accomplished. Van Blaese, in the *Thonindustriezeitung*, 1899, page 213, published a long series of tests of cements containing variable proportions of magnesia, which show that cement containing 8 per cent. is faultless, while that containing 15 per cent. is defective. The writer has made a similar series of experiments and has found that properly prepared cement with 9 per cent. magnesia passes the boiling test perfectly, while that with 15 per cent. magnesia shows expansion cracks after several hours boiling. Comparative tests of tensile strength and expansion of bars of these cements, over long periods, are now in progress. From the evidence now available it appears that the presence of magnesia up to 8 per cent., in a properly prepared Portland cement, is no disadvantage.

Sulphate of lime, in quantities exceeding about 2 per cent., is objectionable in the raw material, owing to liability of reduction to sulphide, causing the cement to turn dark blue in hardening and to give poor tests, especially with sand. This fault is more frequent with cement burned in vertical kilns than in those of the rotary type, since the former are more liable to imperfect draft and consequent reducing action.

Clay for Portland cement manufacture should be highly siliceous and practically free from coarse sand. Siliceous clays, in which the silica is from 2.5 to 3.0 times the sum of alumina and iron oxide, give mixtures which stand the high heat of the kiln without fusing, produce a clinker which is comparatively easy to grind, and yield slow-setting cements which show steady gain in strength over long periods. More aluminous clays give hard, fusible clinker and quick-setting cement, and are in many respects troublesome to use. Highly aluminous cements are believed to be especially severely attacked by sea water.

Alkalies (potash and soda) appear to exert very little influence, in the small amounts present in ordinary clays, on the character of burning or quality of the resulting cement. Excess of alkalies is believed to make cement unsound.

PROPORTION OF INGREDIENTS

Although Portland cement has been manufactured since 1827, definite rules for proportioning the ingredients have only lately been established, and are yet by no means generally accepted. In Germany it has been customary to adjust the ingredients, as recommended by Michaelis, so that the "hydraulic modulus," the ratio by weight of lime to silica, alumina and iron oxide, shall be from 1.8 to 2.2. It has, however, become generally recognized by cement chemists that much more lime combines with silica than with alumina or iron oxide. The "hydraulic modulus" is therefore a variable, and must be much higher in the case of siliceous materials than with those high in alumina and iron.

A clear explanation of the composition of Portland cement clinker was first given by Le Chatelier in 1887. From microscopic examination of clinker and hardened cement he came to the conclusion that the chief constituent of Portland cement is tri-calcium silicate, $3CaO.SiO_2$, which is the active element in the hardening. This tri-silicate is produced by chemical precipitation from a mass of a multiple silico-aluminate which serves as a vehicle for the silica and lime and permits their combination, but remains inert during the hardening. Le Chatelier stated that the lime and magnesia in Portland cement should not exceed a maximum,

$$\frac{CaO+MgO}{SiO_2+Al_2O_3} \leq 3 \qquad (1)$$

nor be less than a minimum,

$$\frac{CaO+MgO}{SiO_2-Al_2O_3-Fe_2O_3} \geq 3 \qquad (2)$$

These formulas represent chemical equivalents and not weights.

The best brands of modern Portland cement approach pretty closely to the above maximum formula, while one corresponding to the minimum formula would be so greatly over-clayed as to be practically useless.

The hardening of cement, according to Le Chatelier, consists in the decomposition of the tri-silicate by water, with the formation of crystalline calcium hydrate and hydrated mono-silicate.

Since the publication of the above researches the constitution of clinker and hardened cement have been investigated by numerous experimenters, and a great number of new theories have been propounded. It cannot be said, however, that any of Le Chatelier's important statements have been disproved, nor that any material advance has been made upon the theory which he proposed. At the present time Portland cement clinker is regarded by nearly all cement chemists as a crystalline mass of tri-calcium silicate, imbedded in a non-crystalline magma consisting of a fusible compound of silica and lime with practically all the alumina and iron oxide.

Le Chatelier's formulas are inconvenient in form and incomprehensible except to those familiar with chemical formulas. The writer published in 1897 (*Journal of the Society of Chemical Industry*, Nov. 30, 1897) a paper on the constitution of hydraulic cements, containing an account of a series of experiments based on the work of Le Chatelier. It was found that the maximum of lime which could be brought into combination to produce a sound cement is three molecules for each molecule of silica present, and two molecules for each molecule of alumina. The composition of cement containing the maximum of lime would therefore be expressed by the formula

$$X(3CaO.SiO_2) + Y(2CaO.Al_2O_3) \qquad (3)$$

It is understood that this formula is merely empirical, representing the relative proportions present, since the aluminate remains for the most part in the magma in combination with part of the silica and with other substances.

Substituting weights for equivalents, the above formula may be expressed as follows:

$$\text{Lime} = \text{silica} \times 2.8 + \text{alumina} \times 1.1.$$

It should be remembered that this formula represents the *maximum* of lime which a Portland cement, burned in the usual manner, may contain without showing unsoundness. This maximum can be reached only by extremely fine grinding of the raw material. This formula, also, by no means represents the composition of finished cement, since the ash of the fuel lowers the lime and raises the silica and alumina, above that calculated from the raw material, by at least 2 per cent.

In the laboratory, using gas as fuel, it will be found practicable to prepare sound cements corresponding to the above formula. In actual manufacture it is safer to reduce the lime slightly, to counterbalance possible defective grinding of raw material or unavoidable variations in composition. It will be found that the raw material at factories where the best Portland cements are made rarely falls below the composition,

$$\text{Lime} = \text{silica} \times 2.7 + \text{alumina} \times 1.0. \qquad (4)$$

This may be taken as a safe practical formula for commercial use. With fine grinding of the raw material it will invariably yield sound cements,

while the use of a lower proportion of lime will be likely to produce quick-setting cement, low in tensile strength. As already explained, commercial cements are considerably lower in lime, owing to change in composition produced by the fuel-ash.

The writer's experiments have shown that magnesia forms with clay no products having hydraulic properties It should therefore be disregarded in calculating cement mixtures, the composition of which should be calculated on the basis of the silica, alumina and lime only, without regard to the magnesia present. Iron oxide, also, in the quantities usually met with in ordinary clays, plays an insignificant part so far as the proportions of the constituents are concerned, and may be disregarded in the calculation.

As a practical example of the use of the above formula, let us suppose that we wish to make cement from limestone and clay of the following composition:

	Limestone	Clay
Lime	52.6	2.2
Magnesia	0.7	1.9
Silica	3.2	65.4
Alumina	1.0	16.5
Iron Oxide	0.3	6.1
Loss on ignition, etc.	42 2	7.9
	100.0	100.0

The silica and alumina in the limestone will require

$3.2 \times 2.7 + 1.0 = 9.6\%$ lime, leaving $52.6 - 9.6 = 43.0\%$ lime available for combination with clay.

The silica and alumina in 100 parts clay will require

$65.4 \times 2.7 + 16.5 \times 1.0 = 193.1$ parts lime. Subtracting the lime contained in the clay we have

$193.1 - 2.2 = 190.9$ parts lime required for 100 parts clay.

As the 100 parts stone contain 43 parts available lime, that amount of stone will require

$$\frac{43 \times 100}{190.9} = 22.5 \text{ parts clay.}$$

The composition of the charge and of the resulting cement may be tabulated as follows:

	100 STONE	22.5 CLAY	122.5 MIX	78.52 CEMENT	100 CEMENT
Lime	52.60	0.50	53.10	53.10	67.63
Magnesia	0.70	.43	1.13	1.13	1.44
Silica	3.20	14.71	17.91	17.91	22.81
Alumina	1.00	3.71	4.71	4.71	6.00
Iron Oxide	0.30	1.37	1.67	1.67	2.12
Loss, etc.	42.20	1.78	43.98	....	....
	100.00	22.50	122.50	78.52	100.00

As stated above, the ash of the fuel will change the composition of the resulting cement materially; analysis of the product, burned with coal, will probably show about 65 per cent. lime and perhaps 24 per cent. silica. This fuel-ash is, however, not uniformly distributed through the product, but attaches itself chiefly to the surfaces of the clinker. It is not, therefore, found practicable to materially raise the proportion of lime to counterbalance the silica and alumina of the ash.

It will be noted that in the above calculated analysis of raw mixture and cement the

$$\frac{\text{Lime—alumina}}{\text{silica}} = 2.7$$

The writer proposes to call this figure the *lime factor* of the mixture. Adoption of this factor will give cements of practically maximum quality with any materials, whether siliceous or aluminous, provided the mix is finely ground and properly burned. Owing to the influence of the ash of the fuel, as above explained, the factor of finished cements will be found about 0.2 lower than that of the raw material. The best commercial cements generally show a factor of 2.5 to 2.6, though made from mixtures with a factor of 2.7 to 2.8.

The following analyses, taken from a paper by the writer in *Cement and Engineering News*, November, 1901, show the influence of the fuel-ash on the composition of the clinker. The samples of clinker were taken one

hour later than those of raw material, since the passage through the kiln required about one hour.

Lehigh Portland Cement Co., Allentown, Pa.

	Mix	Clinker, calculated from mix	Clinker found
SiO_2	14.33	22.18	22.96
Al_2O_3	4.32	6.68	6.78
Fe_2O_3	1.46	2.26	2.54
CaO	42.69	66.08	63.95
MgO and SO_3	1.81	2.80	2.94
Loss	35.14	....	....
	99.75	100.00	99.17
Factor $\frac{CaO - Al_2O_3}{SiO_2}$	....	2.68	2.49

Sandusky Portland Cement Co., Syracuse, Ind.

	Mix	Clinker, calculated from mix	Clinker found
SiO_2	13.50	22.02	22.33
Al_2O_3	3.43	5.60	5.53
Fe_2O_2	1.27	2.07	3.28
CaO	40.76	66.49	64.40
MgO and SO_3	3.27	3.82	3.61
Loss	38.30	....	....
	100.53	100.00	99.15
Factor $\frac{CaO - Al_2O_3}{SiO_2}$	....	2.76	2.63

Comparison of the above analyses of mix and clinker shows how greatly the ash of the fuel affects the composition. In commercial cement a still further reduction in the proportion of lime is caused by the addition of gypsum and the absorption of moisture and carbonic acid from the air. It will be readily seen, therefore, that analysis of finished cement gives but little indication of the true proportion of ingredients or of the quality of the product.

EFFECT OF COMPOSITION ON QUALITY

Too high proportion of lime (lime factor of mix above 2.8) will give a slow-setting cement which will fail in the boiling test. If the excess of lime is great, pats of cement kept in cold water will show radial expansion cracks at the edges after a certain time, perhaps even within a few days. The same defects result from *imperfect grinding of the raw material*, and are far more often due to this cause than to excess of lime. Cement which is unsound and shows expansion from either cause may be improved and perhaps made sound by storage or by exposure to air. It is not, however, safe to rely greatly on this remedy. Lack of soundness is in all cases due to faulty manufacture, since well-burned cement made from suitably prepared raw material will invariably pass all soundness tests when fresh from the grinding mills. Consumers are advised to accept no cement which fails to pass a reasonable boiling test, as they will thus err, if at all, on the safe side, and will influence careless manufacturers to improve their process.

Too low proportion of lime, giving an over-clayed mixture, produces a fusible clinker, liable to overburning. This is especially the case with aluminous materials. If hard-burned, such mixtures give a fused clinker liable to fall to dust on cooling, hard to grind, and yielding slow-setting cement of poor hardening properties. If light-burned, an over-clayed mixture yields soft brownish clinker, grinding to a brownish, quick-setting cement of inferior strength.

Overburning rarely occurs except with over-clayed mixtures or in consequence of the fluxing action of the fuel-ash or the brick lining of the kiln Properly proportioned mixtures stand a very high heat without injury.

Underburning, as stated above, in the case of an over-clayed mixture, yields quick-setting and weak cement. Normal mixtures, when underburned, usually give cement which fails in soundness tests. Light burning is generally indicated by heating of the cement on mixing with water. This behavior generally accompanies quick setting, and may be so marked as to be quite apparent to the touch of the fingers. Some cements, though slow-setting when first made, become very quick-setting on storage. Cases are on record in which this change has taken place within a few days. After longer periods the original slow-setting quality may return. The cause of this phenomenon has not been determined; it may be said, however, that troubles of this class, including quick setting and heating with water, are especially characteristic of cements made from aluminous materials.

CHAPTER VII

STANDARD CEMENT TESTS

The tests which are regarded as most suitable for the selection and acceptance of cement for important concrete construction are as follows:

- Chemical analysis.
- Specific gravity.
- Fineness.
- Activity, or time of setting.
- Tensile strength of neat cement and sand mortars.
- Soundness or constancy of volume.

The French Commission* in 1893, in addition to these tests, gave standard rules for testing weight, homogeneity (with the microscope), compressive strength, bending strength, yield of paste and mortar (*rendement*), porosity, permeability, decomposition, and adhesion, one or more of which tests may be desirable under certain conditions. As these are usually of minor importance, however, special mention of them is reserved for the following chapter.

In unimportant construction it is often safe to use a first-class American Portland cement without testing, and in other cases the test for soundness is the only one which need be actually made. Under almost all circumstances, however, when purchasing cement, full specifications (see Chapter III, p. 28) are advisable, so that if the cement does not work satisfactorily it may be more carefully examined and unused portions rejected.

In this chapter are presented, in addition to the description of the methods of making cement tests, complete lists of apparatus for a large and a small laboratory (p. 80), formulas and tables for determining the quantity of water in cement mortars (p. 85), comparisons of American and European practice in cement testing, a discussion of the causes of unsoundness and the results of soundness tests (p. 101), curves showing the growth in strength of typical cements and cement mortars (p. 99), and other information with reference to the qualities and testing of Portland cement.

STANDARD METHODS OF CEMENT TESTING

The following recommendations for testing are reprinted, with comments by the authors, from the preliminary or Progress Report of Special Com-

*Commission des Méthodes d'Essai des Matériaux de Construction, 1894, Vol. 1, p. 235.