

down in the channels, they projected so slightly that a block could be set close to the last one placed, and the hook removed without disturbing it.

As early as 1873, concrete blocks ranging in size from 13 to 60 tons in weight were used by the Department of Docks in New York City,* and in 1900 this method of construction was still in operation in that city.

In Belgium in 1899, for breakwater construction,† blocks about 25 feet square and 82 feet long, weighing 3 000 tons, were formed by building on the shore metal caissons of the required size, lining them with concrete, then floating to place, and removing plugs in the bottom so as to allow them to sink. The remainder of the concrete to fill the caisson was deposited in the interior.

Depositing Dry Concrete under Water. By dry concrete is meant in this case a mixture of aggregates and cement without water. This method, although occasionally practised, is undoubtedly one of the worst to employ in laying concrete under water. No matter how carefully the concrete is placed, more or less of the cement is carried off by the water. Experiments by Mr. B. B. Stoney‡ show, as one would expect, that a wall laid in this way is honeycombed, and is not nearly so dense as that formed of concrete mixed with water in the usual way before placing.

Plastic Concrete. Plastic or, as it is termed by Mr. Faija, "reset" concrete was once employed in England.§ The concrete was mixed on land with the smallest possible quantity of water, and allowed to set there about three to five hours, or until it attained the consistency of wet clay, before being deposited in the water. Mr. Kinniple claimed that setting eight hours on land before placing did not reduce the ultimate strength of the concrete, and that less of the cement was washed away.

Concrete in Sea Water. In the United States several instances have been noted where concrete has been disintegrated to the depth of 2 or 3 inches and sometimes more. The injury in all cases is limited to the space between high and low water mark, and frequently appears to be caused in part by frost action. Since other concrete close by is often intact, the chief cause for the defects seems to be in the character of the concrete. From the many cases of structures in good condition after many years, notably the docks in New York Harbor, the conclusion is drawn that concrete can be used with confidence in sea-water construction provided it is proportioned and laid with the best materials so as to form a dense impervious concrete. A still further precaution is to keep the concrete from immediate contact with sea-water by leaving the forms in place for several weeks.

*"Fabrication of Beton Blocks by Manual Labor," by Schuyler Hamilton, Transactions American Society of Civil Engineers, Vol. IV, p. 93.

†See paper by L. Vernon Harcourt in Proceedings Institution of Civil Engineers, Vol. CXII, p. 2

‡Proceedings Institution of Civil Engineers, Vol. LXXXVII, p. 230.

§W. R. Kinniple, Proceedings Institution of Civil Engineers, Vol. LXXXVII, p. 65.

CHAPTER XVI

EFFECT OF SEA WATER UPON CONCRETE AND MORTAR*

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The principal conclusions which have been reached by the author of this chapter, as discussed in the following pages, may be summarized as follows:

(1) No cement or other hydraulic product has yet been found which presents absolute security against the decomposing action of sea water. (See p. 309.)

(2) The most injurious compound of sea water is the acid of the dissolved sulphates, sulphuric acid being the principal agent in the decomposition of cement. (See p. 310.)

(3) Portland cement for sea water should be low in aluminum (see p. 312), and as low as possible in lime. (See p. 311.)

(4) Puzzolanic material is a valuable addition to cement for sea water construction. (See p. 313.)

(5) As little gypsum as possible should be added, for regulating the time of setting, to cements which are to be used in sea water. (See p. 310.)

(6) *Sand containing a large proportion of fine grains must never be used in concrete or mortar for sea water construction.* (See p. 316.)

(7) The proportions of the cement and aggregate for sea water construction must be such as will produce a dense and impervious concrete. (See p. 316.)

EXTERNAL PHENOMENA

At present there is no hydraulic product which is known to be capable of resisting absolutely the decomposing influence of sea water. It is true that some concrete masonry has remained intact for a very long time in salt water, but with our present knowledge it is impossible to say why these structures have resisted so well, and there is little doubt that the cements from which they were made might have decomposed rapidly if they had been used under different conditions. In some cases, on the other hand, similar large structures subject to the action of sea water were

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

ruined in a few years and were torn down and completely rebuilt. Notable instances of this kind are the failures which occurred in the ports of Aberdeen,* Dunkerque, and Ymuiden.

Such occurrences have aroused great interest in the subject of the action of sea water upon mortars, and but few questions have received more careful study. In spite of this, however, it cannot be said that any sure means of preventing these failures have been found.

The decomposition manifests itself in various ways: sometimes the mortar softens, and little by little becomes disintegrated; sometimes the mortar becomes covered with a crust which finally cracks off; more often fine white veins develop on the surface of the mortar, these gradually grow large and open, the mortar swells, cracks, and falls off in small pieces or collapses in a pulp-like mass. Almost always the interior of the decomposed mortar is found to contain a soft white material which may be easily separated from it. The chemical composition of this substance is not, however, constant.† Generally, the more advanced the state of decomposition, the more readily the white material can be extracted from the mortar and the richer it is in magnesia. The proportion of sulphuric acid in it also increases with the degree of decomposition, though less uniformly.

ACTION OF SULPHATE WATERS

For several years the injurious action of sea water upon hydraulic compounds was attributed chiefly to the magnesia in the water. It is noteworthy, however, that chloride of magnesia is almost without action, while sulphate of magnesia acts very energetically upon cement, and it has now been ascertained that magnesia plays only a secondary part, while in fact it is the sulphuric acid combined as a soluble sulphate which is the real cause of the decomposition.

This has been confirmed in practise by the destruction of masonry washed by water which has traversed earth containing gypsum, or built from mortar made with sand which has been extracted from strata containing sulphate of lime.‡ A consideration of this fact makes it apparent how dangerous it is to use, in concrete or masonry subject to the action of sea water, cements to which gypsum has been added for the purpose of regulating the rate of their setting or of increasing their initial strength.§

There are numerous instances in which brick masonry has rapidly de-

*Smith, Proceedings Institution Civil Engineers, Vol. CVII, 1891-92.

†Ferret, Annales des Ponts et Chaussées, 1892, II, p. 93.

‡Bied, Annales des Ponts et Chaussées, 1902, III, p. 95.

§Ferret, Annales des Ponts et Chaussées, 1890, I, p. 375.

composed because the bricks, burned with coal, contained alkaline sulphates which when drawn out by water attacked the mortar of the joints.*

These practical observations combined with certain laboratory experiments intelligently conducted have demonstrated that sulphuric acid is the principal agent in causing decomposition.

CHEMICAL PROCESSES OF DECOMPOSITION

Messrs. Candlot,† Michaelis,‡ and Deval§ have discovered successively by different methods that aluminate of lime $Al_2 O_3 \cdot 3 CaO$, which exists in cements in company with other calcareous salts, such as silicates, possesses the property of combining with sulphate of lime so as to give a double salt $Al_2 O_3 \cdot 3 CaO \cdot 3 (SO_3 CaO)$ combined with a large quantity of water with great increase in volume. This substance, moreover, has no firm coherence. It is soluble in pure water, but insoluble in lime water, a fact that explains its existence in a solid state in mortars.

On the other hand, even if the cements do not contain free lime when they are anhydrous, their setting under the action of water frees a part of the lime which was combined with the acid elements, principally with silica. If a soluble sulphate other than sulphate of lime is placed in contact with a hydraulic binding material during hardening or after having set, it produces, with the freed lime, sulphate of lime, which in turn combines with the aluminate, giving "sulpho-aluminate," and produces the swelling which causes the disintegration of the mortar. The same reactions would be produced, moreover, without the intervention of free lime as a result of the reaction of the sulphuric acid of the salt dissolved by the water upon a part of the lime of the binding material.

Although the formation of the sulpho-aluminate of lime seems to be the principal cause of the decomposition of cement by sea water and sulphate waters, it may not be the only one: the setting and the hardening of the cement in contact with water result in the separation of compounds rich in lime, in salts less calcareous, and in free lime. According to the nature of the medium and the conditions affecting its preservation, this reaction may be modified or counteracted in such manner that the hardening cannot follow its regular course; likewise, the lime set at liberty may be dissolved little by little in the water which penetrates the mortars, and may disappear by exosmose, giving place to other more or less injurious compounds.

*Zamboni, Industria, October 15, 1899.

†Ciments et Chaux Hydrauliques, Paris, 1891, p. 257.

‡Der Cement-Bacillus, Berlin, 1892.

§Bulletin de la Société d'Encouragement pour l'Industrie Nationale, 1900, I, p. 49.

These various phenomena are yet far from being satisfactorily explained; nevertheless, it appears that those cements which are richest in lime are the most quickly decomposed.

SEARCH FOR BINDING MATERIALS CAPABLE OF RESISTING THE ACTION OF SEA WATER

For a long time the efforts of experimenters have been directed toward finding a cement of such composition that it cannot be decomposed by sea water. Thinking at first that the destructive action of the water resulted from the substitution of the magnesia which it contained, for the lime of the cement, the idea was conceived of making cement by burning dolomitic limestone which consequently was composed largely of salts of magnesia. But it was found that the magnesia which this contained, since it was burned necessarily at a very high temperature, was slaked with great difficulty, and by its tardy hydration caused the mortar to swell. Cements were also made experimentally of baryta, a laboratory product whose high price does not permit its introduction into regular practice.*

After the discovery of the sulpho-aluminate of lime, the question changed its aspect, and alumina was considered a dangerous element in cement, the proportion of which ought to be reduced as much as possible. At present the specifications adopted by the Administration of Public Works in France limit to 8% the maximum amount of alumina allowed in cement intended for use in sea water, and this limit would be placed much lower were it not for the fact that in many localities it would be very difficult to obtain products containing less alumina. On the other hand, the percentage of alumina cannot be greatly reduced without at the same time rendering more difficult the burning of the cement, in which operation this element acts as a flux. Accordingly, it was suggested that the alumina be replaced by iron oxide. Cements have been made in the laboratory which were absolutely free from alumina and rich in iron, and these resisted sea water very well.† The various hydraulic cements and limes produced by the works of Teil, whose reputation is world-wide, contain not more than 2% of alumina, and some of them usually last much better in sea water than most of the Portland cements which contain between 7% and 8% of alumina. These too, however, become decomposed under certain conditions, but with this peculiarity — that their disintegration is not usually accompanied by any increase of volume.

*Le Chatelier, *Annales des Mines*, May and June, 1887.

†Le Chatelier, *Congrès International des Matériaux de Construction, held at Paris in 1900*, Vol II, Part 2, p. 65.

It has been noted that the cements which are the richest in lime decompose the most quickly in sea water. Based upon this observation, the experiment was also tried of making cements for marine use by burning mixtures less rich in carbonate of lime than the ordinary Portland cements. This diminished the strength of the cement, but the falling off in strength was only of secondary importance. The principal difficulty lay in the process of manufacture. In burning cements of this class there was produced in the kilns a considerable quantity of powder possessing only a comparatively feeble hydraulic power, which obstructed the draught. This difficulty was lessened by mixing ferruginous materials (ore, etc.), or even sulphate of lime,* with the raw materials before burning. Also, the use of rotary furnaces prevents the choking of the draught. As has just been said, cements low in lime do not attain as great strength as the ordinary Portland cements, but they generally resist the decomposing action of sea water better.

When the proportion of limestone is small, the burning can be done only at a very low temperature, and the cement obtained sets very quickly. Some of these low lime cements appear to resist chemical decomposition satisfactorily, while others resist no better than most of the Portland cements, a difference which has not yet been explained. In any case, on account of the rapidity of set, this class of cements cannot readily be used on large work, and, in fact, their use is mainly limited to special cases.

Another means of neutralizing the bad effects of the excess of lime liberated by the setting of Portland cement consists in mixing with the latter, before using, materials capable of combining with this lime so as to produce insoluble compounds. Puzzolans have been found to be the most useful material for this purpose. Laboratory tests, verified by experiments on a larger scale,† have shown that mortars made in this way generally resist sea water better than if they had been made from similar cements without puzzolanic material. Sometimes, too, their strength is increased by this mixture. It is conceivable, however, that the substances which in the Puzzolans appear as acids are less energetic in their action upon the lime of the cement than the sulphuric acids of sea water or of water containing gypsum, and that therefore in the end they will be displaced by the latter with the consequent decomposition of the mortar. This method cannot then be looked upon as giving absolute security against deterioration although it has been proved to be useful.

*Candlot, paper delivered at the meeting of the French and Belgian members of the International Association of the Materials of Construction, on April 25, 1903.

†Ferret, *Annales des Ponts et Chaussées*, 1901, IV, p. 191.

METHOD OF DETERMINING THE ABILITY OF A BINDING MATERIAL TO RESIST THE CHEMICAL ACTION OF SULPHATE WATERS

One method is to gage the cement to be tested with sufficient water to obtain a plastic paste, spread this paste on glass plates so as to form cakes or pats with thin edges, immerse the pats in sea water, and observe them from time to time. But with this method the amount of deformation in the pats depends to a large extent upon the hardness of the paste at the time of immersion, so that a cement which cracks when immersed before setting may stand a long time without showing any trace or alteration if the pat is not placed in contact with the water until twenty-four hours after gaging. Further, the surface of the pat is quickly covered by a crust more or less thick resulting from the partial carbonization of the freed lime, so that the substitution of magnesia for a part of this lime and the presence of this crust may influence the decomposition of the underlying cement.

Another and more exact method consists in molding a block of cement or of mortar of a sufficient thickness; for example, a briquette such as is used for a tensile test. Allow this to harden in the usual way, say for twenty-eight days, then cut out from the center of this block a small solid disc with sharp edges, and immerse it in sea water or in a sulphate solution (saturated gypsum, sulphate of magnesia, etc.). In order to prevent all new superficial carbonization of the specimen, carbonic acid should not be allowed to come in contact with or be present in this liquid. When decomposition occurs in the cement it is indicated by cracks which appear at the edge of the disc after a lapse of a variable time.

As a third test, sea water under pressure can be made to filter continuously through mortars made with fine sand. The author of the present chapter uses for this test mortars containing from 250 to 450 kilograms (551 to 991 lb.) of cement per cubic meter (35.3 cu. ft.) of sand (corresponding approximately to proportions 1:6 to 1:3 by weight) which he gages to a plastic consistency and molds into cubes 50 square centimeters (7.74 sq. in.) on a face, with a tube of brass penetrating to the center of the block. After a few days the brass tubes are attached with India rubber tubes to a vessel containing sea water under a head of 2 meters (6.52 ft.). The amount of water which flows through each cube in a given time is accurately measured from time to time, the cube being immersed in sea water in a glass receptacle, where the state of preservation of the mortar can be closely observed.

Finally, the following quite rapid method is used in the laboratory at Boulogne. A mixture is made consisting of 100 parts of cement to be

tested and 300 parts marble ground to a fine powder. To this is added gypsum in the form of a very fine powder, varying progressively from 0% to 20% of the weight of the cement. Plastic mortars are then made from each of these mixtures, which are molded into prisms 2 by 2 by 12.5 centimeters (0.8 by 0.8 by 4.9 in.), allowed to harden for seven days in moist air, and then immersed in fresh water after the length of each has been exactly measured. The water is frequently renewed and at stated periods the lengths of the prisms are again measured, at which time their state of preservation is also examined.

The ability of the cement to resist decomposition by sulphates is indicated by the time taken for the prisms to expand abnormally and to develop cracks, and also by the quantity of gypsum which the binding material is able to bear for a given time without deterioration.

As a result of a long series of experiments, especially of those made by the last two methods, the conclusion has been reached that no binding material has as yet been found which will not be decomposed sooner or later when subjected to these tests, so that at present no cement can be looked upon as absolutely safe from the action of sea water.

MECHANICAL PROCESSES OF DISINTEGRATION

It seems possible to divide the phenomena of disintegration into two classes according as the destruction of the mortar is produced by a sort of progressive dissolution of its elements without appreciable change in volume, or as the products of decomposition, collecting in the pores, enlarge them and produce a scaling off and a weakening of the mortar. This second class of phenomena is much the more frequent and serious.

In both cases decomposition may be produced when the mortar is simply immersed, because of the penetration of the water into its pores and its renewal by the double phenomenon of endosmose and exosmose. But when the masonry is subjected to different degrees of pressure upon its opposite faces, as is usually the case, this tends to establish a current of water through it and the replacement of the dissolving elements goes on more actively. However, disintegration may, under these conditions, proceed more slowly if the current of water is strong enough to carry away the solid products of decomposition as they are formed. The writer has cited in a former paper* experiments which plainly show the difference between these two methods of decomposition: if lean mortars, made with the same cement and sands of different granulometric compositions, are kept in absolutely quiet sea water, those which disintegrate most rapidly are the ones

*Annales des Ponts et Chaussées, 1892, II, pp. 106 to 116.

into whose composition there enters no fine sand, but only medium sand or, and above all, coarse sand. These latter are the mortars that contain the voids of largest size. On the contrary, if a series of similar mortars are subjected to a continuous filtration of sea water, those made from coarse sand remain intact, while decomposition is more and more active for mortars containing more and more fine sand. *In practise this latter is the most frequent case, and, in fact, it has been verified that the destruction of concrete or mortar by sea water has in most cases been due to the use of too fine sands.*

This is a point which cannot be too strongly insisted upon, and experiments show that a rather lean mortar of coarse sand is much preferable to a mortar of fine sand, even when a very large quantity of cement is introduced into the latter. Fine sands ought to be banished relentlessly from sea water construction even when the cost of coarse sand is very high.* When stone is at hand, an excellent sand can be obtained economically by crushing it.

PROPORTIONS FOR MORTARS AND CONCRETES

From the preceding it is evident that the best means of fighting against sea water is to prevent as far as possible its penetration into the mortars and concretes, and accordingly to make those of great density. The authors of this volume have suggested in a preceding chapter (Chapter IX) with what size of sand and what quantity of cement this result can best be attained in mortars: the maximum density is obtained with a mortar containing sand composed of material having about two parts of very coarse grains to one of fine grains, including cement. Usually, natural sands, even the coarsest, contain a proportion of relatively fine sand sufficient to make it useless to add more with the cement. If a sand is used from which the fine grains have been screened, and this is mixed with about one-half of its weight of cement, a mortar is obtained at once very dense and of great strength, but whose use would often be too costly. In such cases the cement can be replaced by a mixture of sand and cement prepared in advance, such as the product known as "sand-cement," for the making of which a few factories have been built in Europe and also in America. It must be borne in mind, however, that this solution, excellent for mortars destined to remain in the air or to come in contact only with fresh water, would be poor to use in sea water, for very fine sand intimately mixed with cement separates its grains and increases the surface of attack, and various experiments have shown that this kind of mortar suffers severely in sea water.

*See also, Feret, Baumaterialienkunde, 1896, p. 139, and "Le Ciment," 1896, p. 212.

For use in sea water, on the contrary, if a good puzzolanic material can be procured on favorable terms, it is advantageous to grind this with the cement to take the place of the fine sand, so that in the mortar it may play both a mechanical and a chemical role, assuring to it a great density, and at the same time forming, with the lime freed by the setting, compounds which tend to harden the mortar and render it impermeable.

For concretes the law of greatest density is not the same as for mortars, and it has not yet been possible to express a general law. It is necessary to see that the concrete does not contain voids, and above all that the cement is not diluted by an excess of fine sand, which must always be considered as the greatest enemy of masonry in sea water.

In every case the sea water should be prevented from coming in contact with the work for as long a time as possible, so that the setting of the cement may be already considerably advanced. Yet it must not be forgotten that when the mortar contains a puzzolanic material its hardening can be properly effected only in the presence of moisture.

MIXTURES OF PUZZOLAN AND SLAG WITH CEMENTS

Tests by M. Vetillart and the writer, described in detail in a paper published in *Annales des Ponts et Chaussées*, 1908, I, page 121, indicate that Puzzolanic material may be of great value when mixed with Portland cement for concrete construction in sea-water, materially increasing the durability of the concrete without increasing its cost.

The conclusions reached in these tests are as follows:

The use of Puzzolan in hydraulic mortars in combination with the cement increases the strength, and in a great many cases appreciably retards disintegration by sea-water. It should be employed then, at least experimentally, in accordance with the following recommendations:

Grind the Puzzolan to the fineness of Portland cement.

Mix it mechanically with the cement so as to obtain an absolutely thorough mixture.

For Portland cement and a good natural Puzzolan, take two parts by weight of cement to one part of Puzzolan.

Select only Puzzolan of known good quality; the use of gaize slightly roasted is especially recommended.

If other kinds of cement or limes are used with Puzzolan, or if the Puzzolan is of doubtful quality,—especially if it is obtained from granulated slag or a similar industrial by-product,—determine the proportions of the mixture by means of preliminary trials based on tests of strength.

Add to the sand the mixture of cement and Puzzolan as pure cement would be added, and in the same proportions; mix and place the mortar in the usual manner.

Always use for comparison with the Puzzolan mortar, specimens of mortar, of the same proportions and made under identical conditions, in

which the mixture of cement and Puzzolan is replaced by the same weight of pure cement.

Allow the Puzzolan mortar to harden in the presence of moisture.

It is as yet impossible to suggest detail rules for the acceptance and control of Puzzolan cements. The recommendation is made, however, that their ability to resist the decomposing action of the salts in sea-water be compared to the resistance of pure cements by means of the test with sulphate magnesia already referred to.*

VARIOUS PLASTERS AND COATINGS

Various methods have been tried to prevent sea water from wetting masonry too soon, either by coating the work with materials designed to obstruct the pores, or by covering it with a layer more or less thick and more or less impermeable, consisting usually of a rich mortar, clay, bituminous materials, etc.

This method of protecting the work is generally rather costly and is not applicable to all kinds of construction. Besides, it presents this disadvantage, that if by accident there is any break in the continuity of the covering, the sea water finds a passage towards the heart of the masonry and creeps in from one place to another, so that often the coating offers only an illusory security.

In certain cases, a coating is formed spontaneously by the carbonization of the lime in the parts of the mortar near the free surface, and this action is aided by the development of sea organisms such as sea-weed and shell-fish. This cause, together with the differences in the saltiness and the temperature of the water, and the course of the ocean currents, is the one which is most often called upon to explain why mortars decompose more quickly in some regions than in others.

* See also *Annales des Ponts et Chaussées*, 1908, I, p. 107.

CHAPTER XVII

LAYING CONCRETE AND MORTAR IN FREEZING WEATHER

The results of practise and experiment with cements exposed to frost, which are discussed more in detail in the following pages, may be summarized as follows:

- (1) Most Natural cements are completely ruined by freezing. (See p. 320.)
- (2) The setting and hardening of Portland cement in concrete or mortar is retarded, and the strength at short periods is lowered, by freezing, but the ultimate strength appears to be but slightly, if at all, affected. (See p. 321.)
- (3) A thin scale is apt to crack from the surface of concrete walks or walls which have been frozen before the cement in them has hardened. (See p. 320.)
- (4) Frost expands Natural cement masonry and settlement results with the thawing. (See p. 320.)
- (5) Heating the materials hastens setting and retards the action of frost. (See p. 323.)
- (6) Salt lowers the freezing point of water, and in quantities up to 10% of the weight of the water does not appear to affect the ultimate strength of the concrete or mortar. (See p. 324.)
- (7) In practise concrete work should be avoided if possible in freezing weather, because of the difficulty and expense of attaining perfect results. (See p. 320.)

EFFECT OF FREEZING

Numerous experimental tests have been made, chiefly in the United States, where the effect of frost is a more serious question than in England, France, or Germany, to determine the effect of freezing temperatures upon hydraulic cements. Although the conclusions of different experimenters are not in perfect accord, it is the generally accepted belief, corroborated by tests under the most practical conditions and by the appearance of concrete and mortar in masonry construction, that the ultimate effect of freezing upon Portland cement concrete and mortar is to produce only surface injury.

In their practise and research the authors have never discovered a case,