*(Paper No. 3034.)***"The Action of Sea-Water upon Hydraulic Cements."**

By Dr. WILHELM MICHAËLIS.

Translated and Abstracted by WALTER FRANCIS REID.

WHEN a saturated solution of lime acts upon the combined hydrates of silica, compounds of ferric oxide and alumina are formed, containing respectively, 3, 4 and 5 molecules of lime to 2 of the oxides, and these compounds are united with water in such proportion, that at least 1 equivalent of water is combined with 1 equivalent of lime. Hydraulic cements rich in lime must, therefore, during the hardening process, segregate the lime as hydrate. In Portland cement the hardened mass is completely permeated with crystals of calcic hydrate. The hydrate of the combined aluminate and sulphate of lime ($\text{Al}_2\text{O}_3, 3\text{CaO} + 3\text{CaOSO}_3 + 30\text{H}_2\text{O}$) has been observed when the compound was dried over sulphuric acid, and the following calculations are based upon this proportion of water although in practice it must be far greater. Each molecule of alumina present in hydraulic mortar as the hydro-aluminate of lime can form about 12 parts of this double salt and the hydro-ferrate of lime acts in the same way. The true Roman cements, containing 1 part by weight of silicate to 1.1 to 1.2 parts by weight of lime, are, from the chemical point of view, the best hydraulic mortars, because, during the hardening process, they form the most stable compounds, without unsaturated residues. Such cements are, however, burnt at so low a temperature that they are deficient in density, so that mortars made with them shrink considerably when exposed to the air through the evaporation of the water which they have absorbed. All water exceeding in quantity that required for the formation of calcic hydrate must be considered as water of expansion and is very loosely combined. Hydraulic limes, such as that of Teil, bear a close resemblance to Roman cements; but are even looser in texture. Of the 68.6 per cent. of lime in Teil lime, 36.48 per cent. only would combine with the other constituents during the setting process, leaving 32.12 per cent. of lime in an uncombined state.

Portland cement, having been burnt at a higher temperature, is denser than Roman cement in the ratio of 5 to 3; but from the chemical point of view this cement is also defective, because, even supposing the richest calcareous compounds are produced during the setting process, there still remains an excess of uncombined lime. A Portland cement containing 61·04 per cent. of lime would leave 13·79 per cent. of lime unsaturated, while one containing 68·379 per cent. would leave a similar residue of 29·1 per cent. In the case of a Portland cement of average composition, with 1 part of silicate to 2 parts of lime, 25 per cent. of lime or 33 per cent. of calcic hydrate would be segregated.

A body containing a substance of such strong chemical affinity as free lime cannot be regarded as stable. The free lime will continue to re-act until it forms a saturated compound. When the mortar hardens in the air or in water containing carbonic acid the lime is converted into carbonate; but in sea-water it is chiefly the sulphates which act upon the lime. In the first instance it is the free lime that is converted into carbonate or sulphate, then the very unstable compound with ferric oxide, then the aluminate, and finally the silicate. The formation of the sulphate with 2 equivalents of water causes a considerable increase of volume, and may destroy the cohesion of the mass. With this formation of gypsum the production of lime aluminate-sulphate goes hand in hand, and this causes an enormous increase of volume, and a total destruction of the cohesion, for this double compound crystallises with at least 30, probably with 60 equivalents of water, and in doing so converts the strongest mortar into a mud, the only parts of which retaining any cohesion being those protected by the formation of carbonate. Good Roman cements resist the action of sea-water well because they only contain enough sulphate of lime to form 16 parts of the double salt which finds sufficient space for expansion in the pores of the mortar. In such hydraulic limes as that of Teil there is little alumina, and consequently the chief increase of volume is due to the formation of calcic sulphate and not to the double salt. One of the reasons why Teil hydraulic lime has proved more successful for marine work than Portland cement is that the blocks made with it are allowed to harden in the air for a long time before immersion, while Portland cement is generally exposed to the action of the sea-water at once. Even if Portland-cement concrete blocks be exposed to the air until a protective skin of carbonate of lime is formed, such a skin cannot attain any considerable thickness, and the chemical reactions to which the destruction of the

cohesion must be attributed will eventually take place. In order to ascertain the action of carbonic acid and sea-water upon the strength of Portland cement, a series of experiments were carried out. Two sets of briquettes were made according to the German standard rules, one composed of 1 part by weight of Portland cement to 3 parts by weight of standard sand, and the other of 1 part cement to 5 parts of standard sand. These briquettes were allowed to harden for 24 hours in the air; but protected from carbonic acid, and were then placed in boiled distilled water for 56 days, the vessel in which they were kept being hermetically closed. Half of the briquettes were then treated with moist carbonic acid for 5 weeks, and were finally returned to the closed vessels in which they remained 4 weeks longer. When tested, the briquettes were therefore 120 days old. The 1 : 3 mortar protected from carbonic acid gave a tensile strength of 26.9 kilos. per square centimetre, while the briquettes treated with that gas gave 28.5 kilograms per square centimetre (405.3 lbs. per square inch). The crushing strength was 309 kilograms per square centimetre in the first case, and 338 kilograms per square centimetre (4,806.3 lbs. per square inch) in the second. The 1 : 5 mortar protected from carbonic acid broke at a tensile strain of 14 kilograms per square centimetre (199 lbs. per square inch), and, treated with carbonic acid, the strength increased to 16.8 kilograms per square centimetre (238.9 lbs. per square inch). The crushing tests gave 112 and 138 kilograms per square centimetre (1,592.6 and 1,962.0 lbs. per square inch) respectively.

In the 1 : 3 briquettes only 13.3 per cent. of the total lime, and in the 1 : 5 only 24.8 per cent. was converted into carbonate. These briquettes being very small, and the conditions for the absorption of carbonic acid favourable, it is evident that even a long exposure of concrete blocks to the air would only cause a very thin film of carbonate to be formed. The whole of the lime was not converted into carbonate until the mortar had been coarsely powdered and exposed to the action of carbonic acid for some time. Immersed in sea-water, or in a 2 per cent. solution of magnesium sulphate, the briquettes which had been protected from carbonic acid soon disintegrated, and even those which had been carbonated were strongly attacked in seven months, especially the 1 : 5 mortar, although this had absorbed more carbonic acid.

In fresh water the conditions are more favourable, for only the free lime can be dissolved or converted into carbonate. The more lime is dissolved out, the more insoluble are the residual silicates and aluminates. The whole of the lime can never pass into

solution, although this may be effected on a small scale when carbonic acid is excluded. A well mixed and burnt Portland cement may contain 70 per cent. of lime and yet resist the action of fresh water.

The magnesia which is deposited during the action of sea-water upon hydraulic mortar, is a preservative agent which tends to close the pores of the mass. It would be more correct to speak of the injurious action of the sulphates in sea-water, than to attribute such action to the magnesia salts, although it is true that magnesium sulphate is the special salt which acts in sea-water. The sulphates of lime or of the alkalis, in fact, any soluble sulphate, have the same destructive action; but do not act with the same degree of energy.

The Author finds, as the result of his investigations, that those cements which are richest in lime are those which offer the least resistance to sea-water. The addition of lime or of more calcareous cements to Portland cement mortar is therefore unsuitable, and modern Portland cements of high strength, but rich in lime, are less suitable for marine work than the older cements containing less lime. A mortar containing free caustic lime is as unstable from a physical as from a chemical point of view. By the reactions already explained, great internal strains are produced, and expansion and cracking continue, sometimes for many years. All these defects may be avoided by offering to the lime, which remains or becomes free during the hardening process, hydraulic silica or alumina with which it can form more stable compounds. The disadvantage of the efflorescence of caustic alkali cannot be avoided; but as the quantity is small, and it is easily soluble, this caustic alkali cannot endanger the stability of the mortar. In water the alkali is simply washed out; in the air it is only a temporary efflorescence which can be washed off.

The addition of milk of lime to Portland-cement mortars must be injurious, and hastens their destruction. Even in fresh water the advantages of such an addition are only apparent; the excess of lime is easily washed out and the mortar soon becomes porous. Even in two to three years a diminution in the strength of such cement-lime mortars takes place. The action of carbonic acid may come to the rescue, but the chief use of this addition is to make poor mortars more plastic.

In carrying out experiments on the action of sea-water upon cements, it is of importance that the test-pieces should be as porous as possible, otherwise the results would only be delayed. In carrying out a series of experiments with various mortars the

Author used artificial sea-water, and solutions of calcium sulphate, magnesium sulphate and sodium sulphate. The mortars were moulded in the form of prisms 10 centimetres long with a rectangular section of 5 cubic centimetres. For 24 hours the briquettes were allowed to harden in moist air, from which carbonic acid was excluded; they were then placed in the test solutions. The solutions were renewed daily for 14 days, weekly for 3 months, and then monthly. One of the mixtures which withstood the action of calcium sulphate best was Teil lime mixed with 5 parts of standard sand; but all mixtures containing hydraulic silica either as hydrate, or in the form of trass or burnt kaolin, were but slightly acted upon, and remained intact after the lapse of 2 years.

In a 1 per cent. magnesium sulphate solution similar results were obtained. Neat Portland-cement mixtures, without the addition of hydraulic substances, soon disintegrated, especially in the case of those cements rich in alumina. A Bavarian Roman cement containing 47·2 per cent. of lime stood well, while a Bosnian Roman cement with 49 per cent. of that substance began to show signs of deterioration. Long before there are visible signs of disintegration through the action of sea-water the tensile strength indicates whether an injurious action is taking place. As porous briquettes are more rapidly acted upon than impervious ones, it is advisable to use a mortar containing 1 part of cement to 5 parts of sand, rather than one composed of the 1 : 3 mixture. A number of experiments were carried out by the Author, in which the briquettes were composed of 1 part of cement mixed with 5 parts by weight of Berlin standard sand.

The cements used were:—A, a Stettin Portland cement; B, a Portland cement made by the dry process; C, Teil lime; D, a Bavarian Roman cement.

—	A.	B.	C.	D.
Silica	21·712	21·331	23·88	23·881
Alumina	5·805	8·918	2·57	9·709
Ferric oxide	2·949	2·695	0·88	4·052
Lime	64·851	63·776	69·15	44·263
Magnesia	1·030	0·805	1·60	3·992
Potash	0·748	0·777	0·14	..
Soda	0·160	0·101	0·07	..
Calcium sulphate	2·468	1·631	1·09	7·203
Residue	0·357	0·123	..	6·381
	100·080	100·157	99·38	99·481

Artificial sea-water was used, 1 litre of which contained 30 grams of sodium chloride, 12 grams of magnesium sulphate with 7 molecules of water, 3 grams of magnesium chloride, and 1 gram of calcium sulphate with 2 molecules of water (gypsum). The majority of the briquettes were kept for the first day in a closed space saturated with moisture; but in some cases, marked Ma, they were exposed to the air for 8 weeks in order to absorb carbonic acid, during which time they were sprinkled daily. Those marked M were kept in sea-water, those marked S in fresh water. The age of the briquettes is reckoned, not from the date of making, but from 1 day before immersion. The results are given in the following Table in kilograms per square centimetre :—

Age.	AS.	AM.	AMa.	BS.	BM.]	BMa.
7 days . .	7.23	6.00	15.93	10.50	7.86	17.05
28 „ . .	10.09	7.54	15.25	12.68	6.91	17.75
90 „ . .	11.60	10.40	15.28	15.00	9.10	15.89
1 year . .	16.00	16.00	{ 6.5 to 18.00 }	16.70	11.20	{ 2 to 15.00 }

Age.	CS.	CM.	CMa.	DS.	DM.	DM.
7 days . .	3.81	4.96	7.75	2.86	6.27	13.12
28 „ . .	5.17	6.50	6.97	5.11	9.22	13.50
90 „ . .	8.38	10.86	9.89	9.68	11.43	14.66
1 year . .	13.25	15.20	12.50	14.43	14.12	15.44

The cement A was then mixed with Plaidt trass, which left 41 per cent. residue upon a sieve with 2,500 meshes per square

COMPOSITION OF CEMENT A.

	Per cent.
Hygroscopic water	4.141
Water chemically combined	6.899
Loss at 900° C.	0.202
Silica	53.583
Alumina	19.008
Manganic oxide	0.115
Ferric oxide	4.193
Lime	1.736
Magnesia	1.652
Potash	4.147
Soda	4.242
Sulphuric acid	0.107
	<hr/> 100.025 <hr/>

centimetre. Heated for 10 hours upon a waterbath with 10 per cent. caustic soda solution, it yielded 15·543 per cent. hydraulic silica, and 4·810 per cent. hydraulic alumina. Heated for 24 hours under the same conditions the figures were 16·708 per cent. hydraulic silica, and 6·043 per cent. hydraulic alumina. Its composition is shown on p. 330.

Two mixtures were made; the first, E, was composed of 1 part by weight of cement A, 1 part of Plaidt trass, and 4 parts of standard sand; the second mortar, F, contained 1 part by weight of cement A, 0·5 part of Plaidt trass, and 4·5 parts of standard sand. In the following Table the letter S denotes immersion in fresh water and M in sea-water. The results are given in kilograms per square centimetre, each being the average of ten tests.

Age.	ES.	EM.	FS.	FM.
7 days . . .	9·80	11·80	11·05	10·10
28 „ . . .	19·15	28·00	16·90	19·55
90 „ . . .	26·70	35·70	21·80	23·65
1 year . . .	30·95	39·50	27·55	24·59

From a Portland cement with an average amount of lime about 33 parts by weight of calcium hydrate would be liberated. It is therefore probably advisable to add 125 or more parts by weight of trass to 100 parts of Portland cement. Of course, the higher the proportion of lime, the more trass should be added. In FM an injurious action of the sea-water becomes evident in one year; in this mixture 10 parts by weight of lime would remain free to react with the sulphates of the sea-water.

A further series of experiments was carried out with mixtures of Portland cement on Teil lime with trass and standard sand. The composition of the various mortars was as follows:—

G, Portland cement containing 9 per cent. of alumina—1 : 5 Berlin standard sand;

H, 1 part by weight of the same cement with 1 part by weight of trass and 6 parts by weight of Berlin standard sand;

I, 1 part by weight of the same cement with 1 part by weight of trass and 6·75 parts by weight of Berlin standard sand;

K, Teil lime, 1 : 5 Berlin standard sand;

L, 1 part by weight of the same lime, with 1 part by weight of trass and 5 parts by weight of Berlin standard sand;

M, 1 part by weight of the same lime, with 1 part by weight of trass and 6 parts by weight of Berlin standard sand.

K, L, and M were allowed to harden exposed to the air for 7 days in an enclosed moist space.

The experiments E to M are to be extended over a period of 3 years. After the lapse of 1 year the broken briquettes are placed partly in a 2 per cent. and partly in a 3 per cent. solution of magnesium sulphate, and are therefore exposed to a much more energetic attack than in the strongest sea-water.

The following are the results obtained so far in kilograms per square centimetre, each figure being the average of ten tests. Δ gives the density of 1 cubic centimetre immediately previous to testing.

Time of Immersion.	GS.	GM.	HS.	HM.	IS.	IM.	KM.	LM.	MM.
28 days. .	8.80	6.35	10.40	21.65	10.10	20.45	2.97	11.75	10.30
Δ . .							2.162	2.195	2.227
90 days. .	10.25	7.55	16.85	24.55	16.55	24.60	2.39 ¹	21.57	20.10
Δ . .	2.137	2.172	2.26	2.28	2.274	2.292	2.252	2.250	2.259

An examination of the above figures shows at once that the action of sea-water, in the case of all the mortars in which lime is liberated, is antagonistic to an increase in strength. Two processes, the hydraulic hardening process and that of crystallization, struggle for supremacy, and, as a rule, the latter is victorious and destroys the cohesion already attained.

One of the briquettes, BM, showed, in 90 days, signs of destruction; it was so disintegrated and cracked, that it broke while being placed in the clips of the testing-machine. The fracture showed a deposit of magnesia hydrate to a depth of several millimetres. In one year this deposit of magnesia was found to have penetrated as far as 5 millimetres; the same was observed with the BMa briquettes. It was remarkable that those briquettes which had been exposed to the action of carbonic acid were even more rapidly destroyed; the carbonated crust split off and curled up. All the D briquettes were perfectly sound and did not show the slightest deposit of magnesia on the fractured surface.

The addition of trass or of an efficient pozzuolana to hydraulic cement containing an excess of lime, such as Portland cements, can increase the strength of mortars twice or three times, and

¹ The 90-day tests of Teil lime without addition showed signs of swelling of the external crust in addition to the diminution in strength.

render them stable in sea-water. This is not surprising, because the best pozzuolanas contain at least as much active hydraulic material as the best Portland cement.

Hydraulic cements which contain more lime than is required to form stable hydrosilicates and hydroaluminates should not be used for marine work unless improved by the addition of substances such as those named. The proportion of pozzuolana or trass to be mixed with the cement can easily be calculated in each case. It would be preferable for the manufacturer of the cement, rather than the consumer, to add the necessary quantity of material, as the proportion would vary with the composition of the cement, which is best known to the manufacturer.

The Author suggests that the resistance of mortars to the action of sea-water should be tested by means of porous briquettes (1 : 5), whether for tensile, crushing, or elastic strength; the briquettes to be immersed in artificial or natural sea-water which should be renewed daily for the first twenty-eight days, and afterwards weekly. In order to maintain a uniform percentage of sulphuric acid in the water-rods of gypsum tied up in linen, they should be suspended in the artificial sea-water. A 2 per cent. solution of crystallized magnesium sulphate will give quicker results.