

NOTES ON HYDRAULIC LIME AND CEMENT.—BY FRANCIS H. MASON, F. C. S., *Metallurgist, Halifax.*

(Communicated by Dr. Poole, 11th April, 1904.)

SETTING OF HYDRAULIC LIME AND CEMENT.

It is generally accepted that the ingredients necessary to form hydraulic lime and cement are lime, silica, and alumina: while in all probability oxides of iron, and manganese and magnesia may, to a large extent, replace alumina without detrimental effect to the hydraulic properties of the lime or cement.

That it is not essential that the silica, oxide of iron and alumina shall be in chemical combination with the lime, is at once evident from the fact that the old Roman cement, described by Pliny, Vitruvius and others, consisted of a mixture of volcanic scoria and fat lime. Volcanic scoria is composed principally of silicates of peroxide of iron and alumina, with small quantities of magnesia, oxide of manganese and the alkalis. It is necessary that the scoria and the lime shall be in a fine state of division and in intimate contact with each other.

The initial setting of cement is undoubtedly due to hydration, while the hardening is, in all probability, due to chemical action.

Considerable attention has been given to the subject by a number of able chemists, which has resulted in a very great diversity of opinion. The results of the researches of Le Chatelier are probably the most generally accepted.

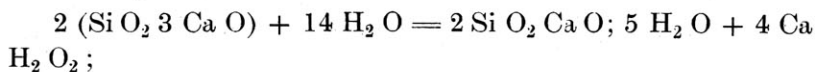
His method of procedure, namely that of examining thin plates of cement, at different stages of setting, under the microscope by the aid of polarized light, and then building up similar crystals synthetically to match, so to speak, does not carry with it that finality which analysis of those same crystals would have

done had it been possible to separate them mechanically for the purpose.

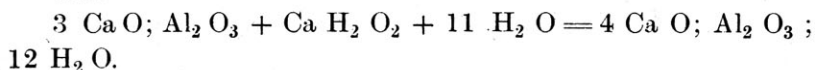
Le Chatelier claims that the setting of cement is due to the hydration of an aluminate of lime having the formula $4 \text{ Ca O}_3 \text{ Al}_2 \text{ O}_3$ which takes up 12 molecules of water; while the hydration of the silicate of lime Ca O Si O_2 which takes up 5 molecules of water, causes hardening.

The weakest point about La Chatelier's conclusions are that he finds the original cement contains the alumina in the form of a tri-calcic aluminate and the silica in the form of a tri-calcic ortho-silicate.

In order to get the tri-calcic aluminate, he has to first decompose the tri-calcic ortho-silicate, at the same time liberating free calcic hydrate, with which he forms his tetra-calcic aluminate thus:



then



Thus he has to bring about the reaction which he claims causes the hardening, before he can obtain the material causing the setting.

It has occurred to the writer that while the setting of limes and cements is evidently a process of hydration, the hardening may be due to the transferring of the silica from the alumina to the lime, leaving the alumina either in the free state or forming double silicates between it and the lime. In other words, that the function of the alumina in the setting of a lime or cement, is mainly that of a carrier of the silica to the lime. If such be the case, why should not other substances less basic than lime act equally well? The reply to this must take the form of another question; has it been proved that they do not?

The most likely substances occurring in limestone to act as conveyors of silica to the lime, are oxide of iron and manganese,

and magnesia. It is well known that highly silicious magnesian limestones almost invariably possess hydraulic properties, and if we examine the analyses of natural cements and hydraulic limes, we shall find that while the percentage of alumina is erratic, with certain notable exceptions the percentage of oxide of iron, alumina and magnesia together are a much more constant quantity.

Take four analysis by Knauss given in Thorpe's " Dictionary of Applied Chemistry " :—

Peroxide of iron	9.2	}	12.4	}	7.1	}	3.6			
Alumina	7.3		19.2		4.6		20.7	9.8	18.5	5.6
Magnesia	2.7				3.7			1.6		9.2
Lime	48.2				46.1			49.2		47.1

All these are reported to be good natural cements.

If, then, these substances only act as conveyors of silica to the lime, the question at once arises, would it not be possible to supply the silica in such a form, without the presence of these substances, that the lime would combine with it readily ?

Landrin, in his researches, throws some light upon this point. He found that while pure lime intimately mixed with fine sand or powdered quartz possessed no hydraulic properties, it did set when mixed with precipitated gelatinous or dialized silica and in time attained a strength equal to the best Portland cement. He further found that 30 parts of silica would take up 38 parts of lime, corresponding to the formula $4 \text{ Ca O } 3 \text{ Si O}_2$. In this we have a cement without alumina, oxide of iron or magnesia. If then, alumina, oxide of iron and magnesia act only as agents for holding the silica in a form in which it is readily attacked by the hydrate of lime, when that reaction has taken place they become inert and act as diluents and tend to weaken the final product, so that if it is possible to commercially prepare a cement free from these substances, pound for pound it should be of better quality than the highest grade Portland cement.

Unfortunately, where a quick-setting cement is demanded, alumina is necessary, for all these straight silica lime cements are slow setting under water, while they only attain their greatest strength if kept under water, owing to the lime being converted into carbonate by atmospheric carbonic acid when allowed to set in air.

The writer has repeated some of Landrin's experiments, using pure lime and native infusorial earth, after submitting the latter to gentle ignition, and obtained excellent products. Further, he finds that recently ignited infusorial earth slowly but surely takes up lime from lime-water when kept in a solution of the latter. The infusorial earth, which is perfectly friable after gentle ignition, becomes quite hard after an emersion in lime water for three months. The strength of the lime-water must be kept up during the experiment. 1.222 grammes of such earth in three months took up .549 grammes of lime.

LIMESTONE FROM BARRA HEAD, N. S.

The writer has for some time been experimenting with a limestone from Barra Head, near St. Peter's, Richmond Co., N. S. The first sample brought to him was composed of a single slab of highly carboniferous limestone, which, when burnt, gave the following analysis:—

Lime.....	70.10
Silica.....	16.30
Alumina.....	6.50
Peroxide of iron ..	1.36
Oxide of manganese.....	Traces
Magnesia.....	1.13
Soda and potash.....	.61
Sulphuric oxide.....	2.41

This lime set and hardened rapidly under water. The writer visited the property in the fall of 1902 and brought away two large samples of the quarried stone. Unfortunately other things intervened and only partial analyses were made

some time after the lime had been burnt and after it had taken up a certain amount of carbonic acid.

The following are the analyses :—

Lime.....	78.80	80.70
Silica.....	12.20	11.00
Alumina.....	1.74	1.76
Ferric oxide.....	1.56	1.14
Magnesia.....	.48	.53

Test pieces were made, and while they would not set under water, they set in two days in a covered jar over water and continued to harden under water. When thoroughly hard they were put out on the window sill of the laboratory and remained there the whole winter without in the slightest degree suffering from the continual freezing and thawing to which they were subjected. In the spring they had obtained a hardness almost equal to Portland cement similarly treated.

This was so encouraging that the writer interested other persons, and as soon as the hand diamond-drill was available four bore-holes were put down, three to a depth of 50 feet and one to 70 feet.

It was intended that eight holes should have been put down, but owing to the severity of the past winter and the difficulty of keeping the drill from freezing, only about half that amount of boring was accomplished.

The following are the analyses of average samples of each core after burning :—

	1.	2.	3.	4.
Silica.....	11.45	9.25	11.80	11.20
Alumina.....	3.57	3.25	3.19	3.11
Ferric oxide.....	1.48	1.14	1.28	1.29
Manganese oxides.....	0.08	0.10	0.63	0.70
Magnesia.....	0.25	0.25	0.43	0.52
Lime.....	81.25	83.55	79.60	80.00
Sulphuric oxide.....	0.44	0.42	1.61	1.71
Not determined and loss.....	1.58	2.04	1.42	1.47

The sulphur existed in the form of iron pyrites which, when burned in the oxidizing atmosphere of the muffle, was converted into sulphate of lime and peroxide of iron.

It will be noticed that the analyses show the deposit to be very homogeneous, and further, that the burnt stone has an analysis very similar to Portland cement with 50% of added lime.

Pats were made with varying proportions of quartz sand which set rapidly in a moist atmosphere and hardened under water.

Some of the lime was hydrated and mixed with twice its weight of quartz sand, allowed to set for two days in a moist atmosphere, then two months under water, then one month dry, when it gave a tensile breaking strength of 140 lbs. per cubic inch.

A briquette made from the samples taken of the quarried stone, burned, ground and mixed with twice its weight of gold ore tailings, was placed, mould and all, immediately in water for two months, then placed on the window-sill for twelve months, and on breaking, it gave a tensile breaking strength of 354 lbs. per cubic inch.

Mr. Fennell, manager of the Wouldham Cement Co., West Thurrock, Essex, England, reported as follows on the adaptability of this limestone from Barra Head for the manufacture of Portland cement :

THE WOULDHAM CEMENT COMPANY, 1900, LIMITED,
LION WORKS,
WEST THURROCK, ESSEX.

Established 1855.

29th Jan., 1904.

“ I beg to state that I have thoroughly investigated the sample of stone recently sent me for examination, and report as to its suitability as a material from which to produce Portland cement.

“ I have fortunately had considerable experience with the manufacture of high-class cement from materials practically

identical with that submitted, and may say that the sample
ent shows this stone to be most admirably adapted for the pur-
pose.

“ It is practically identical in composition with the limestones
from which some of the best cement in this country is produced,
viz., the Lias beds occurring in Warwickshire and South Wales,
The following is an analysis showing the average composition
of the stone :—

Carbonate of lime	84.82	per cent.
Total loss on ignition	39.00	“
Matter soluble in hydrochloric acid	89.48	“
Matter insoluble in “ “	10.52	“
Composition.		
Silica	9.94	“
Alumina	2.06	“
Ferric oxide89	“
Lime	47.14	“
Magnesia73	“
Sulphuric anhydride	Nil.	
Sulphur (as sulphides)34	“
Carbonic anhydride	38.57	“
Combined water09	“
Alkalies and loss24	“
	100.00	

“ It will be noticed that the analysis, although more detailed
shows the stone to be practically of the same composition as the
English Lias stones above referred to, the composition of which
is as follows :—

Moisture and organic matter	1.60	per cent.
Silica	11.15	“
Alumina	1.97	“
Ferric oxide36	“
Carbonate of lime	84.55	“
Loss37	
	100.00	

“ It will be noted from the analysis that the stone contains 84.82 per cent. of lime, which is too high for a natural cement. It therefore becomes necessary to employ with it clay of a suitable character, and there should be, occurring between the layers of this stone, five or six clays of the requisite composition. This material, in common with the British Lias limestones, varies in composition in piece and piece, in this case the variation being, on the sample submitted, from 4 to 5 per cent. of carbonate of lime.

“ In dealing with the production of cement from this material, therefore, it will be necessary to employ great care in the adjustment of the proportions of the stone and clay, which could only be done by the employment of a skilled chemist.

“ The stone is readily pulverized, and it may be as well to point out that owing to the natural inter-mixture with it of a proportion of silicates of iron and alumina, or clay, it is not necessary to reduce it to nearly the same fineness as when dealing with Thames or Medway chalk, which is practically pure carbonate of lime.

“ For the purpose of practically demonstrating the value of the stone as a material suitable for cement making, I have prepared some samples of cement from it, with the admixture of the necessary proportion of Medway clay. The following represents the composition of the clay used :—

Loss at red heat (organic)	5.39	per cent.
Silica	62.41	“
Alumina	18.09	“
Ferric oxide	10.35	“
Carbonate of lime	1.63	“
Alkalies	2.10	“
Loss03	“
	<hr/>	
	100.00	
	<hr/>	

“ In the preparation of these samples, the clay was dried and ground with stone to such fineness as practically to leave no residue when sifted through a sieve of 10,000 mesh per square inch. The raw material thus obtained was mixed with water and allowed to dry into cakes which were burned to a clinker, coke being the fuel used in the burning. The clinker produced was then ground to the same fineness and the cement resulting gave the following analysis:—

Silica	22.80	per cent.
Insoluble residue	1.10	“
Ferric oxide)	12.30	“
Alumina)		
Lime	60.46	“
Magnesia	1.04	“
Sulphuric anhydride	1.30	“
Carbonic anhydride and water50	“
Alkalies and loss50	“
	<u>100.00</u>	

“ An examination of this cement showed it to be a true Portland in every respect. It was burned to a s. g. of 3.175. Briquettes were moulded, to be broken at 2, 4 and 7 days old, and the following results were obtained. Unfortunately, I have not obtained the results for the 28 days:

2 days.	4 days.	7 days.	
185	345	450	lbs. per sq. inch
185	340	470	“ “
210	410	485	“ “

“ It will be seen from the breaking strains obtained, that the cement is one which shows a steady growth in tensile strength, which is one of the most important and desirable features of a good Portland cement. The sample was also tested for soundness, and neither under the boiling water test or under the Le Châtelier test did it show the slightest sign of expansion or

blowing. The last named test is most searching in character, and is one which only a high class Portland cement would be capable of withstanding.

“Pats of the cement which were guaged and placed under cold water a few minutes after guaging, set hard and showed no sign of cracking or buckling.

“Accompanying this are samples of the ground limestone, ground clay, the raw material (admixture of stone and clay), cement clinker, and the finished cement. In addition are pats which have been subjected to the boiling water test, together with the broken briquettes and also the mould of cement which has been subjected to the Le Châtelier test.

“It may be borne in mind that in preparing small samples of cement, the maximum results are never realized, and cement made on a large scale with this material would give much higher results under test.

“In conclusion I beg to state that this limestone is one of the best possible materials from which to produce really high class Portland cement.”

(Sgd.) WM. FENNELL.

I am inclined to think that there is a mistake in Mr. Fennell's analysis of the stone. It will be observed that no possible mixture of the limestone and clay of the analysis given can produce a cement of the composition given by his analysis.

There can, however, be no possible doubt that given a suitable clay for mixing, this limestone is admirably suited for the manufacture of Portland cement; and further, that the burnt stone by itself makes an excellent hydraulic lime.

The writer is now experimenting with two clays and a soft clay slate found in close proximity to the limestone for mixing purposes, and he hopes at a future date to prepare a paper on the cement industry at St. Peter's, Richmond County.

The following figures of the amount of cement made in and imported into Canada will be interesting. They are from the "*Canadian Mining Review*," for November, 1903 :—

"During the year ending June 30th last (1903) the Canadian imports of Portland cement as given by the Department of Customs in the Trade and Navigation returns, amounted to 2,316,853 cwt., valued at \$868,131, divided as follows :—

From Great Britain	516,796 cwt.	\$187,572
" United States	610,445	305,775
" Belgium	814,252	244,633
" Other countries	375,360	130,151
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Total	2,316,853 cwt.	\$868,131

'This would amount, taking the weight of a barrel of foreign cement as 400 pounds, to an importation of 579,213 barrels of an average value of \$1.50 per barrel; to this cost must be added a duty of 12½ cents per hundred pounds, amounting, at the average weight taken, to 50 cents a barrel. Now add to these importations the amount of the Canadian production and we have the following :—

	Bbls.	Value.
Imports of foreign cement	579,213	\$1,157,737
Production of Canadian cement	594,594	1,028,618
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Total	1,173,807	\$2,186,355