THE EFFICIENCY OF PORTLAND CEMENT RAW MATERIALS FROM NAGA, CEBU

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Two plates

INTRODUCTION

In the interest of certain prospective manufacturers, the most promising of the raw materials from Naga, Cebu, were collected by Mr. Wallace E. Pratt, a geologist of the Bureau of Science, and submitted to as comprehensive an investigation as was necessary definitely to establish the relative merits and suitability for the commercial manufacture of Portland cement. Before presenting our experimental work, we shall discuss a few considerations which appear to be generally misunderstood or overlooked.

Most of the materials had already been tested by two laboratories in the United States, and they reported results which, with a few exceptions, were satisfactory. However, the few unsatisfactory features involved considerations of such vital importance that the prospective manufacturers could not accept the data obtained as sufficient evidence to justify further steps toward the establishment of a plant. Finally, they submitted the reports to the Bureau of Science, and requested our interpretation of their significance.

The laboratories in question did the work which they were requested and paid to do in a very honest and painstaking manner, and while we criticize certain of their methods and conclusions this is not done in an attempt to cast reflections on their work and reputation. Their methods compare favorably with those of most laboratories, and their conclusions are based upon generally accepted theories and practices, some of which are of doubtful value. We shall make specific reference to their reports, because their data stand as official records against many of our own conclusions on the merits of these raw materials.

We fail to find much significance or usefulness in results obtained, as in this instance, by submitting each combination of different raw materials to only one burning test. A burning test may produce excellent cement, but the results obtained might be so seriously affected by unavoidable variations in factory conditions as to exclude the possibility of their successful commercial use. On the other hand, a burning test may give very unsatisfactory results, and yet a thorough study of the raw materials used may reveal commercially practicable conditions of manufacture which will produce extremely good results.

Slight variations in composition, degree of burning, and pulverization are unavoidable both in laboratory and manufacturing practices, and such changes modify the quality of the product more or less according to the nature of the raw materials. Therefore, it is necessary to ascertain the effects produced by reasonable modifications in the hydraulic index, degree of vitrification, fineness, etc. This is especially true if, as in this instance, we desire to know the relative merits of available raw materials and the conditions of manufacture which will produce the best results from the standpoint of manufacturing efficiency. The changes brought about by well-planned modifications in the conditions of manufacture will be the more significant the more closely the experimental conditions approach those of the best commercial practices. This is especially true with respect to the degree of vitrification.

A very objectionable feature of many reports is that the results were obtained with underburned or unsound cement. Such products have no definite characteristics in setting or hardening properties. They may develop considerable strength in seven or twenty-eight days only to disintegrate entirely after a few months, and both their set and strength may change from a satisfactory to an unsatisfactory one, or vice versa, overnight. In reality they are not true Portland cements but a mixture of lime; hydraulic limes; and Roman, slag, and Portland cements. Obviously, it is misleading to judge the efficiency of raw materials from results obtained by improper burning. It is much more logical to ascertain the possibilities of well-sintered mixtures, to observe whether good burning would be practicable under commercial conditions, and then to take into consideration such allowance as must be made for unavoidable variations and imperfections in commercial manufacture.

If the clinker is allowed to cool slowly with the experimental kiln, the results obtained may be characteristic only of the set-kiln products. In the rotary kiln process the clinker is cooled much more rapidly, and if, as in this instance, the prospective manufacturers intend to install rotaries the clinker from the experimental burnings should be cooled accordingly. It was for this reason that we designed a furnace which enables us to dump the clinker and cool it as rapidly or as slowly as desired.

The necessity of testing the resulting cements in a thorough and comprehensive manner is also imperative. This is especially true of the "time of setting." The extent and manner in which the setting properties of cements may change owing to the influence of slight variations in the quantity of retarder or degree of seasoning, the means whereby it is possible to ascertain if the set is capable of being kept within desirable limits during storage, and the minimum amount of retarder required have been fully described.[1] Yet, it is the common practice of many laboratories to add 2 or 2.5 per cent of plaster to the cement and submit the result obtained as characterizing its setting properties. Nothing is apt to be more misleading, as the following incident will serve to show.

One of the reports submitted to our inspection showed that the tester had added 2 per cent of calcined gypsum and obtained a cement which required an excessively high percentage of water for normal consistency and gained its initial and final sets in about five and one-half and nine hours, respectively. These and other similar results made it appear that the manufacturers would have considerable difficulty in producing Portland cement from these raw materials which would set and harden with sufficient rapidity.

However, for reasons which we have already thoroughly discussed,[2] the opinion was expressed that these cements really set so quickly that they became partially regauged and consequently abnormally slow setting during the mixing process. The commonness of errors of this kind has been pointed out. In fact, so far as our experience goes, the regauging of extremely quick-setting cements is the main cause of the serious discrepancies which occasionally occur between the reports of the set from the manufacturer and those of the consumer. Nine-tenths of the cements which, when tested in the cement laboratory of the Bureau of Science, failed to pass our standard specifications did so only because they set with abnormal quickness. Fully

[1] *This Journal, Sec. A* (1912), **7**, 207–252.
[2] *Ibid.* (1911), **6**, 248.

one-half of these could not have produced a slow-setting paste before they were packed, unless regauging had taken place to a considerable extent during the process of mixing.

We also disputed the correctness of the assumption that the cements obtained from these raw materials would set and harden slowly, because the value of the ratio of silica to alumina was high. Apparently many experts believe that the early hardening properties of Portland cement are due to the aluminates. If this were true, we could not account for the rapid development of great strength and quick-setting properties of many well-burned, highly siliceous Portland cements which have come under observation. Our own extensive researches verify the work of Dr. O. Schott [2] that the quick-hardening compounds of Portland cement are formed at a high temperature and that with the silicates the strength increases as the lime increases while with the aluminates the opposite is true; and as the high silicates and the low aluminates require the greatest heat it is evident that high temperatures produce high strength.

We further expressed the opinion that a high silica cement should carry more calcareous material than one with less silica and more alumina and that in several instances the hydraulic moduli of mixtures prepared in the United States were too low. We realized that an increase in the calcareous constituents would raise the clinkering temperature, but believed that there was sufficient iron oxide in the raw materials to permit higher liming. For the same reasons, the use of less siliceous materials did not seem desirable, much less, necessary.

While many of the problems involved in the successful and economic manufacture of Portland cement cannot be solved by laboratory experiments, we believe that an investigation such as is outlined and described in the following pages will establish the relative merits of different raw materials and point out the most important of the conditions of manufacture which will produce the most desirable results.

EXPERIMENTAL WORK

The geology, field relations, and physical characteristics of the raw materials are discussed by Mr. Pratt on pages 151 to 161. The chemical characteristics of each of the 8 samples of raw materials examined are made apparently by the data in Table I.

[2] *Cement & Eng. News* (1910), 22, Nos. 9-13.

TABLE I.—*Ultimate chemical composition of the raw materials.*

Constituent.	Sample No.								
	35.	37.	39.	46.	47.	48.	49.	50.	51.
Loss by ignition	35.90	36.70	38.92	41.90	8.60	8.07	8.44	40.55	19.45
Total silica (SiO_2)	14.87	8.94	8.25	3.80	70.28	60.29	58.59	3.20	41.97
Alumina (Al_2O_3)	2.18	0.48	2.37	2.18	11.89	15.04	18.53	0.35	8.66
Ferric oxide (Fe_2O_3)	2.20	3.09	0.61		2.36	12.05	7.58	1.39	9.54
Calcium oxide (CaO)	43.12	47.40	46.52	51.59	2.55	1.37	2.69	53.16	16.12
Magnesia (MgO)	0.87	0.82	0.82	1.44	0.91	2.29	2.25	0.59	2.16
Sulphur oxide (SO_3)	trace	trace	trace	none	trace	trace	0.11	0.10	0.32
Free silica	2.82	3.51	none	trace	9.34	8.24	5.12	1.76	2.12
Total alkalies (Na_2O, K_2O)	0.84	0.66	0.62	0.46	3.73	1.18	2.10	0.36	2.31

It was thought advisable to combine samples 35, 37, and 39 into one mixture composed of equal parts of each. Mr. Pratt states that such a mixture represents the probable average output of the most feasible quarry site, although if desirable it would be almost as convenient to confine operations to the beds represented by 37 and 39.

The first mixtures prepared for burning were combined so that the hydraulic modulus

$$\left(\frac{\text{per cent CaO}+\text{per cent MgO}}{\text{per cent SiO}_2+\text{per cent R}_2\text{O}_3}\right)$$

of each of the resulting cements would approximate 2. The calcareous material represented by the mixture of 35, 37, and 39 was given the most consideration, because these limestones are said to be the most conveniently located and most easily quarried of the available calcareous supplies. The essential characteristics of the four mixtures prepared for the first burning tests are given in Table II.

TABLE II.—*Characteristics of the first four cement mixtures.*

Mixture No.	Material.	Parts by weight.	Fineness through the 100-mesh sieve.
			Per cent.
1	Limestone 50	100	92
	Clay 48	27	
2	Limestones 35, 37, and 39	100	95
	Clay 47	9	
3	Limestones 35, 37, and 39	100	94
	Clay 51	18	
4	Limestones 35, 37, and 39	100	93
	Clay 49	10	

TABLE II.—*Characteristics of the first four cement mixtures*—Continued.

PRINCIPAL ULTIMATE CONSTITUENTS AFTER VITRIFICATION (BY CALCULATION).

Constituent.	Mixture No. 1.	2.	3.	4.
Silica (SiO_2)	23.10	23.90	23.55	23.00
Alumina (Al_2O_3)	5.22	3.14	4.15	4.87
Ferric oxide (Fe_2O_3)	5.80	3.05	4.34	3.76
Calcium oxide (CaO)	63.60	64.70	62.60	63.70
Magnesia (MgO)	1.43	1.28	1.57	1.46
Hydraulic modulus$\left(\frac{\%CaO+\%MgO}{\%SiO_2+\%R_2O_3}\right)$	1.92	2.15	1.97	2.10

REFRACTORY PROPERTIES.

Mixture No.	Observations.
1	Easily sintered into well-burned clinker at a temperature considerably below the melting point, and no tendency of product to dust.
2	Similar to 1, but a little more refractory.
3	Similar to 1, but if fused the clinker dusted completely while cooling.
4	Ideal refractory properties, and no tendency to dust when cooling.

Throughout this work the various materials and products were not ground to a greater degree of fineness than is customary in commercial manufacture, although in most instances better results could have been obtained by so doing.

After the addition of sufficient water, each mixture was molded into briquettes and burned practically without contamination to the point of incipient fusion, the accepted product being analogous to well-burned rotary clinker. The clinkers were crushed in a jaw crusher, mixed with 1 per cent plaster, and ground by means of a tube mill employing manganese-iron balls, to the degree of fineness demanded by our cement specifications. The finished products were then subjected to preliminary tests for soundness.

As shown by the attached photographs in Plate I, all of the steamed pats remained perfectly sound. They all adhered firmly to the glass plates, and showed excellent color and texture. As the cements had not been seasoned, their soundness proved conclusively that the clinker had been well burned. Furthermore, observations during the process of burning showed that the mixtures would meet the requirements of commercial kilns.

The briquettes vitrified at a comparatively low temperature, slightly lower than the raw meal used for the manufacture of "Green Island" Portland cement, but sustained such a considerable increase in temperature without fusing that no difficulty was experienced in producing good, thoroughly sintered clinker without melting part of the charge. There also was practically no "dusting" when the well-sintered, uncontaminated clinker cooled.

We were prepared to make a thorough study of the setting properties of these cements under different conditions of seasoning, grinding, and plastering, but a few tests showed that there need be no difficulty in controlling their setting properties and that the amount of plaster or gypsum required could be maintained at a low figure.

The results obtained with the nonseasoned cement are recorded in Table III.

TABLE III.—*Essential characteristics of the nonseasoned cements produced from the first four mixtures.*

Test.	Mixture No.			
	1.	2.	3.	4.
Fineness:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Through the 100-mesh sieve	98.8	97.8	98.2	97.8
Through the 200-mesh sieve	79.4	77.6	77.8	77.6
Soundness, 5-hour steam test	sound	sound	sound	sound

Setting properties.

Mixture No.	Plaster added.	Water required for normal consistency.	Initial set.	Final set.
	Per cent.	*Per cent.*	*Hrs. min.*	*Hrs. min.*
1	1	21	3 00	5 55
2	1	22	1 10	6 10
3	1	[a]27	Flash set.[a]	
4	1	21	35	5 25
1	2	20.5	2 30	5 00
2	2	21	3 50	5 50
3	2	21	1 30	5 30
4	2	20	3 00	5 00

[a] The set was almost instantaneous, but when the cement was manipulated according to specification an extremely slow-setting paste resulted which, in reality, was a regauged cement. [Cf. *This Journal, Sec. A* (1911), **6**, 207-252.]

All commercial cements season more or less during the process of manufacture. The cements under consideration required no seasoning, but it was thought advisable to aërate[4] them in the laboratory for twenty-one hours spread out in layers about 2.5 centimeters in thickness, after which they were subjected to all specified tests. The results obtained, together with the requirements of the standard specifications now in operation, are given in Table IV.

TABLE IV.—*Physical properties of the Portland cements obtained from the first four mixtures.*[a]

Test.	No. 1.	No. 2.	No. 3.	No. 4.	Specified requirements.
Fineness:					
Per cent through the 100-mesh sieve	98.9	98	98.4	98.2	92
Per cent through the 200-mesh sieve	78	78.6	78.8	78.4	75
Specific gravity (dried at 110° C.)	3.16	3.15	3.16	3.16	3.1
Water required for normal consistency	20	21	20	20	none
Soundness, air, water, and steam	sound	sound	sound	sound	sound
Time of setting in hours:					
Initial set	2.8	3.3	0.9	3.2	(b)
Final set	5.5	4.8	2	4.6	(c)
Tensile strength in pounds per square inch:					
1-day, neat mortar	507	404	370	420	none
7-day, neat mortar	860	740	520	755	500
28-day, neat mortar	840	780	605	780	600
7-day, 1:3, Ottawa-sand mortar	315	298	258	275	200
28-day, 1:3, Ottawa-sand mortar	410	360	320	360	275
PRINCIPAL CONSTITUENTS OF THE NONPLASTERED CEMENTS (BY ANALYSES).					
Silica (SiO_2)	22.65	23.95	23.80	23.10	----------
Alumina (Al_2O_3) and ferric oxide (Fe_2O_3)	10.70	7.54	9.65	10.07	----------
Calcium oxide (CaO)	64.70	65.35	62.60	63.95	----------
Magnesia (MgO)	1.60	1.16	1.44	1.33	(d)
Hydraulic modulus	1.98	2.11	1.86	1.97	----------

[a] Content of plaster = 2 per cent. [b] Not less than 0.75. [c] Within 10. [d] Less than 4.

Each of the cements passed well above all of the requirements, optional or otherwise, of the United States Government specifications for Portland cement as adopted by the Government of the Philippine Islands. They also pass the requirements of the present cement specification of the American Society for Testing Materials. The good results obtained from mixture 2 are of

[4] We regard aëration as the least efficient, practical method of seasoning Portland cement, and recommend grinding in the presence of steam or, better, quenching the hot clinker thoroughly with, or in, water.

special significance, because the materials represented by samples 35, 37, 39 (combined), and 47 are most desirable from the point of view of field relations.

A second series of tests was made which included mixtures similar to 1, 2, and 3, but somewhat modified in composition, and mixture 5 for which limestone 46 was combined with clay 47. The essential characteristics of these four mixtures are given in Table V.

TABLE V.—*Characteristics of second four cement mixtures.*

Mixture No.	Material.	Parts of weight.	Fineness through the 100-mesh sieve.
			Per cent.
5	Limestone 46	100	93
	Clay 47	25	
1a	Limestone 50	100	94
	Clay 48	28.4	
2a	Limestones 35, 37, and 39	100	91.2
	Clay 47	11	
3a	Limestone 35, 37, and 39	100	95
	Clay 51	14	

ULTIMATE CHEMICAL COMPOSITION OF THE VITRIFIED MIXTURES (BY CALCULATION).

Constituent.	Mixture No. 5.	1a.	2a.	3a.
Silica (SiO_2)	25.40	23.36	25.30	22.30
Alumina (Al_2O_3)	7.10	5.29	4.06	3.87
Ferric oxide (Fe_2O_3)		5.52	3.04	4.44
Calcium oxide (CaO)	64.50	62.23	63.00	64.40
Magnesium oxide (MgO)	2.06	1.42	1.27	1.52
Hydraulic modulus	2.04	1.86	1.90	2.16

REFRACTORY PROPERTIES.

Mixture No.	Observations.
5	Highest temperature obtainable required to produce well-burned clinker; no fusing and no dusting.
1a	Easily sintered; slight tendency to dust if cooled slowly.
2a	Similar to No. 1 and a little less refractory than No. 2.
3a	Refractory properties better than No. 3, and no tendency to melt or fuse on cooling.

The data in Table V show that in this second series of tests the calculated percentage of calcium oxide was reduced from 63.60 in mixture 1 to 62.23 in mixture 1a and from 64.70 in mixture 2 to 63.00 in mixture 2a and was increased from 62.50 in mixture 3 to 64.40 in mixture 3a. The object of making these modifications has already been stated in the introduction, and the necessity of it will be verified in the discussion of the results obtained.

The essential characteristics of the nonseasoned cements obtained from well-burned clinkers of these mixtures are given in Table VI.

TABLE VI.—*Characteristics of nonseasoned cements obtained from the second series of mixtures.*

Test.	Mixture No.			
	5.	1a.	2a.	3a.
Fineness:	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Through the 100-mesh sieve	97.4	98.4	98.4	94.8
Through the 200-mesh sieve	86.7	77.8	76.4	75.8
Soundness, in air, water, and steam	sound	sound	sound	sound

SETTING PROPERTIES.

Mixture No.	Plaster added.	Water required for normal consistency.	Initial set.		Final set.	
	Per cent.	*Per cent.*	*Hrs.*	*min.*	*Hrs.*	*min.*
5	1	21	1		3	
1a	1	21		45	6	15
2a	1	25	Flash set.[a]			
3a	1	27	Flash set.[a]			
5	2	20	2	20	4	20
1a	2	20	2	55	5	55
2a	2	21		30	1	45
3a	2	21	2	35	6	35

[a] See note to Table III.

Experiments on the setting properties of No. 2a showed that the compounds which caused the cement to set were so active and abundant that 3 per cent of plaster and twenty-four hours of thorough aëration were required to produce satisfactory results. The physical properties of No. 2a treated in this manner, and of cements 5, 1a, and 3a, mixed with 2 per cent of plaster and aërated one day, are given in Table VII.

TABLE VII.—*Physical properties of plastered and seasoned cements 5, 1a, 2a, and 3a.*

Test.	No. 5.	No. 1a.	No. 2a.	No. 3a.
Fineness:				
Per cent through the 100-mesh sieve	97.4	98.7	98.8	98
Per cent through the 200-mesh sieve	88.7	78.4	77.2	77
Specific gravity (dried at 100 °C.)	3.13	3.13	3.19	3.16
Per cent water required for normal consistency	21	21	21	21
Soundness in air, water, and steam	[a]sound	[a]sound	[a]sound	[a]sound
Time of setting in hours:				
Initial set	4	3.4	3.2	2.7
Final set	6	6.5	5.4	5.9
Tensile strength in pounds per square inch:				
1-day, neat mortar	505	396	393	477
7-day, neat mortar	650	675	540	735
28-day, neat mortar	695	795	640	765
7-day, 1:3, Ottawa-sand mortar	310	268	232	300
28 day, 1:3, Ottawa-sand mortar	340	320	390	355

[a] The perfect soundness of the steamed pats is shown in Plate I.

The results obtained with No. 5 are as satisfactory in general as those obtained with the first four mixtures. The modified mixtures also produced cements which passed all of the requirements of our standard specifications for Portland cement.

The principal object in testing these modified mixtures was to ascertain the effects of the changes in the hydraulic moduli, and therefore the other conditions of manufacture and testing were maintained as nearly constant as possible. Slight deviations might be expected on account of the unavoidable variations in mixing, burning, and grinding and the personal equation in testing. However, the results showed only slight differences between the physical properties of cements 1 and 1a or between 3 and 3a, and as these were all very good cements the four experiments show that the raw materials used are capable of producing good Portland cement regardless of considerable variation in the hydraulic moduli and unavoidable changes in the conditions of manufacture.

On the other hand, there is a very marked difference between the setting properties of cement 2, which was very satisfactory, and cement 2a, which required 3 per cent of plaster and considerable seasoning. Additional experiments showed that cement 2a, containing 2 per cent of plaster, failed to become desirably slow setting while undergoing thorough aëration for a period of seven days, although the specific gravity fell to 3.09.

Also, the addition of slaked lime in quantities up to 2 per cent failed to retard the set.

The object of adding slaked lime was to ascertain the possible effects of free lime, small amounts of which are present even in the best burned commercial products. It is known that if this lime remains unslaked until the cement is used the heat generated when the water is added will tend to quicken the set. Since, in this instance, small quantities of slaked lime did not retard the set, the presence of free lime could only serve to quicken the setting properties. Consequently, we believe that it would be impossible to control the set of well-burned cements made from the same mixture as cement 2a so that it would remain within desirable limits until used.

We believe that this change from normal to quick-setting properties was due entirely to the reduction in the content of calcareous materials. This conclusion is warranted to some extent by the fact that the same raw materials were used in both instances and by the normal setting properties of the cements (3, 3a, 4, and 5), which were made with either similar limestone or similar clay. However, it required additional data either to verify this conclusion or to prove that good results were dependent upon the conditions of manufacture which produced cement 2. Owing to this and the importance of the raw materials under consideration, we prepared and tested a third mixture (2b) which contained more of the calcareous material than either 2 or 2a.

Mixture 2b was calculated so that the resulting cement would contain about 66 per cent of calcium oxide, thus increasing the hydraulic modulus from 1.86 and 2.15 to 2.31. No difficulty was experienced in burning this high-limed mixture properly, and the well-sintered clinker, pulverized with 1 per cent of plaster to about the same fineness as cements 2 and 2a, gave the excellent results recorded in Table VIII.

TABLE VIII.—*Composition and setting properties of cement 2b.*

Material.	Parts.
Composition of mixture:	
Limestone, equal parts of Nos. 35, 37, and 39	100
Clay 47	7

TABLE VIII.—*Composition and setting properties of cement 2b*—Continued.

Material.	Per cent.
Composition of clinker (calculated):	
Silica (SiO_2)	22.54
Alumina (Al_2O_3)	8.53
Ferric oxide (Fe_2O_3)	3.06
Calcium oxide (CaO)	66.20
Magnesium oxide (MgO)	1.28
Hydraulic index	2.31
Fineness of the cement:	
Per cent residue on the 100-mesh sieve	93.6
Per cent residue on the 200-mesh sieve	78.2
Soundness, 5-hour steam test	sound

SETTING PROPERTIES.

Cement.	Plaster added.	Water required for normal consistency.	Initial set.	Final set.
	Per cent.	*Per cent.*	*Hrs. min.*	*Hrs. min.*
Nonseasoned (sp. gr. = 3.14)	1	21	15	4 00
Do	2	21	2 40	4 50
Aërated for 19 hours (sp. gr. = 3.11)	1	21	3	5
Do	1.5	21	2 00	4 50
Do	2	21	3 35	6

As the setting properties of this higher limed cement proved entirely satisfactory and easy to control, the results obtained with mixtures 2, 2a, and 2b showed that it is necessary to keep the hydraulic modulus within the upper rather than the lower limits if quick-setting products are to be avoided. The combined results also show that the range of permissible variations in the upper limits is sufficiently wide to permit satisfactory factory control in composition.

FINENESS

In Tables III and VII it is recorded that with the exception of 5 the cements were not pulverized nearly as fine as modern grinding machinery has made practicable. The finest ground commercial cements which have come under our observation show about the same residue on the 100- and 200-mesh sieves as No. 5—namely, 2 and 13 per cent, respectively—and our work on the physical and chemical properties of Portland cement proved very conclusively that such fine grinding is very beneficial because it increases the sand-carrying capacity, permits better seasoning, and increases the constancy in volume after induration. As stated in a previous publication, we believe "that the influence of fineness on the rate of set introduces no new or insurmountable factors into the problem of the control of the set." However, as our conclusions in this respect have not been generally accepted, we reground all of the cements except No. 5, and then subjected them to physical tests, the results of which are recorded in Tables IX and X.

TABLE IX.—*Characteristics of the reground cements.*[a]

Test.	Results.						
	No. 1.	No. 2.	No. 3.	No. 4.	No. 1a.	No. 2a.	No. 3a.
Fineness in per cent:							
Through the 100-mesh sieve	98.6	99.4	99.6	99.6	99.3	99.6	99.6
Through the 200-mesh sieve	86	84.6	85	85.4	85	85.6	85.4[c]
Soundness:							
5-hour steam test	sound	sound	sound	sound	sound	sound	sound
Normal consistency:							
Per cent water required	21	21	20	21	21	[b]28	21
Setting properties:							
Initial set in hours	3	2.60	0.25	1.75	3.20	[b]flash	1.75
Final set in hours	4.25	4.35	1.45	2.45	4.15	[b]flash	4
Tensile strength in pounds per square inch:							
7-day, 1:3, Ottawa-sand mortar	303	317	[c]250	307	320	[c]200	343
28-day, 1:3, Ottawa-sand mortar	366	360	[c]283	335	350	[c]225	369
3-month, 1:3, Ottawa-sand mortar	447	421	[c]392	440	385	[c]330	380

[a] Content of plaster = 2 per cent, except for cement 2a which contained 3 per cent.
[b] See footnote (a) to Table III.
[c] Very erratic development of strength on account of quick-setting properties.

TABLE X.—*Setting properties of cement 3, reground.*[a]

Seasoning.	Per cent plaster added.	Per cent water required for normal consistency.	Soundness (steam test).	Time of setting, in hours.	
				Initial set.	Final set.
None	0.5	21	sound	1.60	3.00
Do	1.0	21	sound	1.75	3.75
Aërated 4 hours	none	20	sound	1.00	5.00

[a] Content of plaster = 2 per cent.

Regrinding caused no undesirable characteristics to develop in cements 1, 2, 4, 1a, and 3a. Cement 3 became quick setting, but as is shown by the data in Table X its quick-setting properties were easily remedied by either a little additional seasoning or plaster.

Cement 2a became extremely quick setting, but as already stated its setting properties were not satisfactory when it had been pulverized only to an ordinary degree of fineness.

AUTOCLAVE TESTS

It is not thought probable that an autoclave test such as is described in the "specifications for Portland cement" of the Delaware, Lackawanna and Western Railroad Company will be adopted by the United States Government or by the American Society for Testing Materials. However, the data in Table XI make it evident that these raw materials are capable of producing Portland cement which will pass even such severe requirements.

TABLE XI.—*Autoclave tests*[a] *of cements*[b] *1, 2, 4, and 5.*

Test.	Requirements of the D., L. and W. R. R. Co.	Results obtained.			
		No. 1.	No. 2.	No. 4.	No. 5.
Tensile strength in pounds per square inch:					
Neat mortar after 24 hours in moist air.	Not less than 200	507	404	420	505
Neat mortar after autoclave test.	Not less than 500	580	700	596	573
Expansion of neat mortar in per cent.	Not greater than 0.5	0.127	0.104	0.160	0.062

[a] Steam pressure = 295 pounds per square inch.

[b] Not reground. The fineness is recorded in Tables III and V.

RELATIVE MERITS OF AVAILABLE RAW MATERIALS

Other conditions being the same, the suitability of a limestone for the manufacture of good Portland cement increases as its chemical composition approaches that of the cement clinker. "Cement rock," which requires little or no additional calcareous or siliceous material, is ideal in this respect, as nature already has prepared a more or less intimately mixed and partially combined mixture which must be produced by artificial means when the limestone is purer. Furthermore, the particles of comparatively pure limestone which fail to combine with siliceous material remain as free lime,[5] whereas the coarse or underburned particles of cement rock are more apt to possess the more desirable properties of such products as hydraulic limes and Roman cements. However, it should be borne in mind that, as an impure limestone requires less siliceous material than a purer one, the relative cost of quarrying, crushing, and grinding the different raw materials might make it advisable, from an economic standpoint, to use the purest available limestone in spite of these advantages of impurity.

The data in Table I show that the available crystalline limestones 46 and 50 contain only 3.91 and 6.44 per cent, respectively, of clay substance and fluxing materials. Such pure limestones are practically nonfusible, and they must be ground to extreme fineness to enable them to unite thoroughly with the pulverized siliceous materials at cement-kiln temperatures. On the other hand, the coralliferous limestones 35, 37, and 39 are more closely related to cement rock. They contain on the average about 13.2 per cent of clay substance and fluxes, and combine so much more readily with siliceous material that their use is advantageous and involves less danger from free lime and kiln troubles. In addition, they are the most conveniently located and the most easily quarried and pulverized of the calcareous materials. These advantages are especially significant here, because clay 47 is the most conveniently located and desirable of the available siliceous resources.

Clay 47 has the highest content of free silica. Ordinarily, this would be disadvantageous, but in this instance the grain is so fine and the content of total silica so high (70.28 per cent) that, as a whole, the silica content is very satisfactory. Iron in quantities above that required for fluxing purposes is not desirable. Clay 47 contains the least iron, but sufficient to produce, without excessive treatment, a well-burned cement (2b) with a hydraulic index as high as 2.31. Clay 47 can be combined with limestones 46 and 50 to produce good cement, but much more satisfactory results are obtained by combining it with the coralliferous limestones. This is more or less apparent from the data given in Table XII.

[5] The evil effects of free lime and the manner in which it affects the physical and chemical properties of Portland and other hydraulic cements have been thoroughly discussed in previous publications. Cf. Reibling, W. C., and Reyes, F. D., *This Journal, Sec. A* (1910), **5**, 117–142; *ibid.* (1911), **6**, 207–252; *ibid.* (1912), **7**, 135–191.

TABLE XII.—*A comparison of characteristics of cement mixtures, 2, 2a, and 2b with 5 and 5b.*

Mixture No.	Materials.			Fineness.[a]	Hydraulic modulus.	Clinkering properties.	Characteristics of cement		
	Limestone No.	Clay No.	Parts by weight.				Soundness.[b]	Setting properties.	Relative weight.[c]
2	35, 37, and 39		100	95	2.15	More refractory than 2a, but easily sintered into well-burned clinker. No tendency to melt, and no dusting when the clinker cooled.	Sound	Very satisfactory	360
		47	9						
2a	35, 37, and 39		100	91.2	1.90	Easily sintered into well-burned clinker at a temperature considerably below the melting point, and practically no tendency to dust.	do	Inclined to be quick setting and rather difficult to control.	390
		47	11						
2b	35, 37, and 39		100	91	2.31	Sintered into well-burned clinker without difficulty, and no tendency to melt or dust.	do	Very satisfactory	[d]280
		47	7						
5	46		100	93	2.04	Highest temperature obtainable required to produce well-burned clinker. No tendency to melt or dust.	do	do	340
		47	25						
5a	46		100	93.2	1.87	Less refractory than 5, but still rather difficult to burn properly. Clinker dusted considerably even when cooled rather rapidly.	do	Very quick setting and impossible to retard.	([e])
		47	29						
5b	46		100	92.1	2.17	So refractory that we were not able to obtain a well-sintered product.	Warped and cracked[f]	Satisfactory, but a little erratic.	[g]245
		47	23						

[a] Per cent through the 100-mesh sieve.
[b] 5-hour steaming test.
[c] 28-day, 1:3, Ottawa-sand mortar.
[d] Nonseasoned.
[e] Very erratic on account of quick setting.
[f] Exposed to the atmosphere in a thin layer for 48 hours before the steamed pat remained sound.
[g] Seasoned until sound.

With the crystalline limestone, a hydraulic index of 2.04 gave satisfactory results although some difficulty was experienced in obtaining a sufficiently high temperature. However, when the index was lowered to 1.87, the clinker dusted and the cement became extremely quick setting, and when the index was raised to 2.17 the mixture became too refractory.

With the coralline limestones, no difficulty was experienced in obtaining good cement from mixtures having hydraulic indices of 1.90, 2.11, and 2.31, and even the last was easier to sinter than 5a, the least refractory of the mixtures, prepared with the crystalline limestone.

In this connection, it is only fair to note that results were obtained with limestone 50 and clay 48 (mixtures 1 and 1a). However, this clay contains 12.05 per cent of iron oxide, 15.04 of alumina, 1.18 of alkalies, and only 52.05 of soluble silica. It is very fusible, and if utilized for the rotary process is apt to cause trouble similar to that described in the following extract of an article by J. G. Dean:[8]

* * * the clay used in manufacturing was low in silica and high in iron oxide and alumina. The Silica-Alumina Ratio

$$\frac{\text{per cent } SiO_2}{\text{per cent } Al_2O_3 + \text{per cent } Fe_2O_3}$$

would average a trifle less than 2.

When pure limestone was used with this clay it was nearly impossible to produce a cement that could be depended on for setting time and tensile strength, and if the lime content of the mix was high enough to burn properly in the kilns the cement would seldom pass the "boiling test."

In order to overcome this defect in the clay, it was necessary to mix the limestone from the upper strata of the deposit, which was siliceous in itself and carried in addition the sand and silt that filtered into it, to the purer stone from the bottom of the quarry. By this haphazard method we were able to keep the Silica-Alumina Ratio high enough to produce a high grade cement.

This method required very careful mixing and grinding, as with cements having a low Silica-Alumina Ratio the limits of variation are extremely narrow. If the lime content is lowered the cement becomes erratic in setting qualities and other peculiarities of over clayed cement. If the lime content is raised the cement will fail on constancy of volume tests and will require "air slaking."

These peculiarities become very complicated with such materials when they have been properly proportioned but improperly ground before burning. * * * The burner will complain of its being "soft" or over clayed. The boiling test on the cement will reveal "free lime" and the tests for setting time and strength will indicate an excess of clay, while the

[8] *Chem. Eng.* (1909), 10, 52.

chemical analysis will reveal nothing out of the ordinary. * * * [The sieve test] will show that that portion of the mix which was capable of combination was over clayed and the coarse particles of limestone in the mix were burned to "quick lime," consequently the resulting cement displayed the double characteristics of being over clayed and over limed.

No such difficulties would be experienced with a proper mixture of the coralliferous limestones and clay material 47, which latter has a silica-alumina ratio

$$\frac{\text{per cent } SiO_2}{\text{per cent } Al_2O_3 + \text{per cent } Fe_2O_3}$$

which averages a trifle less than 5 and is sufficiently low in lime and alkalies to possess desirable refractory properties.

ROTARY VERSUS STATIONARY KILNS

Provided that financial considerations permit, we strongly favor the installation of rotary, rather than stationary, kilns. Underburning is fatal to the efficiency of Portland cement, and while with these raw materials there would be no necessity of producing soft-burned clinker if the rotary process was used the best stationary kilns would yield a considerable amount of underburned cement. In fact, the product of a set kiln, unless well sorted at considerable expense, would not be true Portland cement but a mixture of seasoned, underburned, and well-burned cements containing sintered, nonsintered, and hydrated free lime and fused and sintered compounds of many kinds.

However, we made a few tests of underburned clinkers obtained from some of the mixtures already described, and the results obtained are recorded in Table XIII.

TABLE XIII.—*Characteristics of decidedly underburned cements seasoned until sound.*

Test.	Results.			
	No. 2.	No. 2b.	No. 3a.	Average.
Specific gravity	2.94	2.95	2.95	2.95
Time of setting in hours:				
Initial set	1.25	1.85	0.85	1.30
Final set	6.75	8.45	6.90	7.40
Tensile strength in pounds per square inch:				
7-day, 1 : 3, Ottawa-sand mortar	212	189	177	193
28-day, 1 : 3, Ottawa-sand mortar	220	170	180	190
3-month, 1 : 3, Ottawa-sand mortar	325	315	322	321

It is evident[7] that the well-burned clinkers could be mixed with considerable of the underburned product, and yet, if properly seasoned, produce Portland cement which would pass all the requirements of our standard specifications.

NATURAL (OR ROMAN) CEMENT

In a previous publication of the Bureau of Science[8] we called attention to the possibility that the present and near future resources and the commercial and economic conditions of these Islands might favor the manufacture of what may be called an artificial natural, or Roman,[9] cement.

Natural cements are largely used in America because of their cheapness. They harden more rapidly in air or water than hydraulic lime, but generally speaking they lack uniformity in strength, setting properties, and constancy of volume to a much greater extent than Portland cements. This is due largely to the present universal practice of burning cement rock in set kilns under which conditions considerable variations in chemical composition and both under- and overburning are unavoidable.

To produce a more desirable cement of this class in the Philippines, we advocate the method of producing an *artificial* Roman cement by blending ground calcareous and siliceous materials in the proper proportion and then burning the mixture in a rotary kiln at a temperature of about 1,000° C. By this method the chemical composition and the degree of burning could be uniformly regulated and a cement of definite physical properties produced. It might not be a feasible method in countries where the cost of the production of Portland cement is low, but the high cost of imported coal and Portland cement in the Philippines would overcome this objection and especially since local coals could be utilized for burning the natural cement.

We prepared and burned several of such artificial Roman cement mixtures, and the results obtained showed conclusively that the method could be adopted with good results. We had time and opportunity to make only a very preliminary study of the possibilities of the raw materials in this respect, but even so obtained several cements which passed all of the requirements of the American Society for Testing Materials for natural cement, even though we used heavily clayed and, consequently, easily burned mixtures. The data in Table XIV show that these

[7] Cf. *This Journal, Sec. A* (1910), **5**, 117–142.

[8] *This Journal, Sec. A* (1913), **8**, 135–195.

[9] Bleininger, A. V., *Bull. Geol. Surv. Ohio* (1904), **4**, 186.

raw materials are capable of producing natural cement with a cementation index as high as 2.47 and still pass the requirements of specifications in spite of the fact that such products become feebler as this index rises above 2.

TABLE XIV.—*Characteristics of artificial Roman cement "I" obtained from Naga raw materials.*

MIXTURE BURNED AT 1,000° C.							
Material.	Parts by weight.	SiO_2.	R_2O_3.	CaO.	MgO.	Loss by ignition.	Cementation index.
Coralline limestone	100	9.34	2.94	47.38	0.89	35.90	
Clay 51	100	41.97	18.20	15.12	2.16	19.45	
Mixture	200	51.31	21.14	62.50	3.05	55.35	
Per cent	100	25.65	10.57	31.25	1.52	27.68	[a] 2.47

CEMENT.

Test.	Result.	Requirement of specifications.[b]
Time of setting:		
Initial set in minutes	30	([c])
Final set in hours	3	([d])
Tensile strength in pounds per square inch:		
Neat mortar, 7 days	167	150
Neat mortar, 28 days	262	250
Neat mortar, 3 months	300	([e])
7-day, 1 : 3, Ottawa-sand mortar	148	50
28-day, 1 : 3, Ottawa-sand mortar	330	125
3-month, 1 : 3, Ottawa-sand mortar	385	([e])

[a] $\frac{2.8 \times \%SiO_2 + 1.1 \times \%Al_2O_3 + 0.7 \times \%Fe_2O_3}{\%CaO + 1.4 \times \%MgO}$

[b] *Am. Soc. Test. Materials* (1912).

[c] Not less than 10.

[d] Not more than 3.

[e] Not given.

CONCLUSION

The results obtained by this investigation are regarded as conclusive proof of the following:

1. The raw materials which are available in the vicinity of Naga, Cebu, are eminently suitable for the commercial manufacture of high-grade Portland cement.[10]

[10] Plate II, figs. 1 and 2, are photographs of raw materials from Naga, Cebu, and samples of Portland and Roman cement and concrete which they produced. These products formed part of the exhibit of the Bureau of Science of local calcareous-siliceous resources at the 1914 Philippine Exposition.

2. The raw materials represented by coralline limestones 35, 37, and 39 and tuff 47 constitute the most desirable of the available resources. This is especially true as, in addition to their high merits with respect to manufacturing efficiency, their use would reduce the cost of quarrying, transportation, and grinding to a minimum.

3. Proper mixtures of these two raw materials produce cements which are comparatively high in silica and low in alumina, and for best results the hydraulic modulus

$$\frac{\text{per cent CaO} + \text{per cent MgO}}{\text{per cent SiO}_2 + \text{per cent R}_2\text{O}_3}$$

should be kept within the higher (2 to 2.3) rather than the lower (1.8 to 2) limits. Owing to the presence of a very desirable quantity of fluxing materials, the high-limed mixtures have ideal sintering properties and the use of less siliceous materials is not desirable, much less necessary.

4. Contrary to a somewhat general belief, it is not characteristic of Portland cements as high in silica and low in alumina as proper mixtures of these raw materials to harden too slowly. On the contrary, they are very apt to be extremely quick setting if the hydraulic modulus is low.

5. These raw materials are capable of producing satisfactory, *artificial* natural (or Roman) cement, and as the clay content can be carried very high with good results the commercial production could be accomplished at a minimum expense.

Incidentally, this work demonstrates many important principles involved in testing raw materials, and the results obtained add corroborative evidence to our published observations and conclusions concerning the physical and chemical properties of Portland cement and specifications and methods for their purchase.[11]

[11] Reibling, W. C., *This Journal, Sec. A* (1913), 8, 107–124.

ILLUSTRATIONS

Plate I

Steamed pats of nonseasoned cements 1, 2, 3, 4 (Table IV), 5, 1a, 2a, and 3a (Table VII), showing perfect soundness.

Plate II

Fig. 1. Naga, Cebu, raw materials, and the resulting Portland clinker, cement, and concrete exhibited at the 1914 Philippine Exposition. ⅛ actual size.

2. Naga, Cebu, raw materials and the resulting Roman clinker, cement, and concrete exhibited at the 1914 Philippine Exposition. ⅛ actual size.