If, now, it be granted that the difference between the saccharimeters of these two classes is intentional—that certain of them were meant to be used with sugar solutions prepared in Mohr cubic centimeter flasks, and the others in conjunction with true cubic centimeter flasks—the writer's observations agree entirely with Landolt's statements. In the one class the extreme variation in the readings of the E plate on ten saccharimeters is 0.12° V.; in the other class, including five instruments, it is still smaller, only 0.08°.

If, on the other hand, it be denied that the instruments were graduated for two distinct standards, Schmidt and Haensch are confronted by an extreme variation of 0.35° V. at the 100° point among thirteen of their instruments—a variation far greater than any careful instrument-maker would ever have permitted. And furthermore, we have to explain the fact that between the readings of instruments Nos. 5045 and 2880, respectively 99.88° and 100.06°, there is a gap of 0.18°, to bridge which no instrument has been found.

It seems, therefore, as if there must exist a double standard of graduation among the saccharimeters of Schmidt and Haensch;—as if their earlier instruments were graduated for the true cubic centimeter, as if in time this standard had been abandoned for the more convenient and more popular Mohr cubic centimeter, and finally, as if the latter in turn had been abandoned in consideration of the growing feeling against the double standard of graduation for volumetric flasks. In view of the fact that 0.23 per cent. may make, at times, a material difference in the results of a saccharimetric determination, it seems desirable that the attention of chemists should be called to the foregoing facts.

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THE ANALYSIS OF PORTLAND CEMENT.

BY BERTRAM BLOUNT.

Received May 16, 1904.

A YEAR or two ago the New York Section of the Society of Chemical Industry suggested the establishment of a standard method for the analysis of Portland cement. Samples of cement were distributed to various chemists to be analyzed according to a method laid down by the committee. Dr. Hillebrand was good enough to undertake the analysis of these samples as a control. In May, 1902, I read a paper before the New York Section of the Society of Chemical Industry in which I demurred to the methods proposed by the committee on two chief grounds: (*a*) That standardization of strictly analytical processes was undesirable; and (*b*) that the methods proposed by the committee were erroneous.

In the course of this controversy I had the advantage of meeting and conferring with Dr. Hillebrand, and on many of the points which appeared to be at issue between us we found ourselves in substantial agreement. Dr. Hillebrand, in a paper lately read before the American Chemical Society,[1] has quite frankly intimated his concurrence. There remain a few matters of great moment to the manufacturers and users of Portland cement and to the chemists who control the quality of their output, which are still in doubt; as the question affects a large industry and is of much analytical interest it may be usefully discussed in detail.

Before passing to these matters it may be said that the inaccuracies occurring in the analyses of some of the chemists who examined the samples distributed by the committee, are so numerous and serious as to show that the training, skill and care of the operators are inadequate; this state of things calls loudly for a remedy; the provision of such a remedy appears to be of more pressing importance than the erection of a standard method of analysis.

One of the principal questions as to the proper method of analyzing Portland cement is that of the determination of its insoluble residue. The samples analyzed by Dr. Hillebrand and reported on in his paper appearing in this Journal, November, 1903, contained so little that it could reasonably be ignored. But usually the proportion is substantial, ranging from 0.5 to 1.5 per cent. in a properly mixed and burnt cement and exceeding the latter figure in one which has been poorly prepared. The determination of insoluble residue is of value because the figure obtained is an index of the care which has been used in manufacture; a cement containing 5 per cent. of added sand would be diluted to that extent only, whereas one containing 5 per cent.

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[1] This Journal, **25**, 1180.

of insoluble residue is not merely diluted, but has incontestably been badly made. The method which I devised and have used for nearly twenty years consists in dissolving the cement in hydrochloric acid, evaporating the solution to dryness, but not intentionally baking the evaporated material, re-dissolving in hydrochloric acid, filtering, washing, dissolving out the precipitated silica with sodium carbonate solution and collecting the final insoluble residue. It may be fairly assumed that a silicious residue, which has resisted this series of treatments, is inert and valueless as a cementitious material. I believe that I am not misinterpreting Dr. Hillebrand when I say that he agrees with this; but he goes further and suggests that the treatment is too drastic and that it would be better to determine the insoluble residue in such a way that it is not exposed to digestion with strong hydrochloric acid. The method he proposes is to dissolve in dilute hydrochloric acid, filter at once and to remove any precipitated silica by means of sodium carbonate. This suggestion is important and has been examined in the following maner. Four samples of cement were chosen and the insoluble residue determined in each, both by the method which Dr. Hillebrand has proposed and that which I ordinarily use. My analyses of these cements are as follows:

	1. Per cent.	2.[1] Per cent.	3. Per cent.	4. Per cent.
Silica (SiO_2)	21.90	16.64	22.26	21.18
Insoluble residue	1.12	1.62	1.32	0.52
Ferric oxide (Fe_2O_3) Alumina (Al_2O_3)	10.66	10.20	11.20	10.14
Lime (CaO)	61.66	62.90	61.68	63.86
Magnesia (MgO)	1.33	1.47	1.14	1.27
Sulphuric anhydride (SO_3)	1.08	1.58	1.10	1.10
Carbonic anhydride (CO_2)	1.40	3.05	0.70	1.02
Water (H_2O)		1.13		
Sulphur	...	0.08	...	...
		98.67		
Deduct oxygen equivalent to sulphur	...	0.04	....	....
	99.15	98.63	99.40	99.09
Alkalies and loss	0.85	1.37	0.60	0.91

Duplicate determinations of the insoluble residue in each were made by Dr. Hillebrand's method and my own:

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[1] Cement No. 2 is adulterated with limestone.

	Dr. Hillebrand.		Bertram Blount.	
	Per cent.	Per cent.	Per cent.	Per cent.
(1)	3.48	3.28	1.10	1.16
(2)	3.34	3.12	1.60	1.64
(3)	5.20	5.00	1.28	1.36
(4)	0.80	0.96	0.50	0.54

The results are fairly concordant for methods of this kind and show that both processes can be relied upon to yield consistent results. As might be expected, the difference between the two modes of procedure has led to their values differing widely. If we assume with Dr. Hillebrand that the insoluble residue obtained by his method is inert, evidently the determination of this material is of even greater importance than had been supposed; it is, however, not easy to obtain conclusive evidence on this point. The state of subdivision of the particles comprising cement has a great influence on their activity; unground clinker is scarcely more cementitions than so much limestone. Moderately fine particles, on the other hand, though setting slowly, will set eventually and it would be rash to assume that a material, apparently inert when tested for the short periods of time generally available in laboratory experiments, will not prove itself active at long dates, and in practice contribute to the strength of the concrete or mortar prepared with it. Bearing this in mind, one is not surprised to find that the insoluble residue obtained by Dr. Hillebrand's method is a cementitious material. This fact was ascertained in the following way: The insoluble matter from cement No. 1, isolated strictly according to Dr. Hillebrand's prescription, was finely ground and then treated again by Dr. Hillebrand's own method. The final insoluble residue thus obtained was 1.52 per cent. and 1.66 per cent. in duplicate experiments, as against a previous mean value of 3.38 per cent. on the unground substance. In point of fact the re-treatment reduces the insoluble residue to something closely approaching that found by my method of analysis, which, on the same cement, gave 1.10 per cent and 1.16 per cent. insoluble residue. It would appear from this that the chief difference between the two methods arises from the necessity of more finely grinding the cement if dilute acid is to be used; when fine grinding is substituted for the use of strong acid, similar results are obtained.

The nature of the insoluble residue, prepared by Dr. Hillebrand's method, was investigated. Two samples from cement No. I were analyzed, giving the following figures:

	Per cent.	Per cent.
Insoluble silicious matter	61.48	69.25
SiO_2	8.69	7.90
Al_2O_3 and Fe_2O_3	13.32	10.84
CaO	12.99	8.49
MgO	0.82	1.35
Alkalies and loss	2.70	2.17
	100.00	100.00

The samples are similar in composition. Such differences as they exhibit are not greater than might be expected, considering that the method of isolation is arbitrary and that small variations of condition will certainly influence the nature and extent of the decomposition of moderately refractory silicates.

From a study of these figures I thought it possible that this insoluble matter might be cementitious. Accordingly, a fairly large quantity of the material (about 25 grams) was isolated. This was ground and gauged with water in the manner of a cement. As might be predicted, it set feebly; it is, in fact, not a cement *per se,* but rather a puzzuolanic material. Its activity as a puzzuolana was proved by gauging it with one-third of its weight of quicklime; it set to a hard mass. As there is always an abundant quantity of lime set free from the decomposition of calcium silicates and aluminates in the process of the setting of cement, capable of acting with a puzzuolanic material, I conclude that the insoluble matter, isolated by Dr. Hillebrand's method, is not inert, but belongs in great part to the cement itself. The insoluble residue isolated by my own method is almost wholly silica in rather coarse fragments and is substantially inert. On these grounds I prefer my original method for determining insoluble residue.

Next, with regard to the determination of silica in cement, Dr. Hillebrand has done excellent service in promoting accuracy in mineral analysis by insisting on the necessity of a double evaporation. I agree that this double evaporation is necessary when the silica is set free in a mass of material such as is produced when a silicate is fused with sodium carbonate and the melt is decomposed with hydrochloric acid, but I consider that it is not requisite when the total quantity of material handled is small and the whole is well baked. It is perfectly practicable to obtain substantially the whole of the silica from Portland cement by a single evaporation.

Using the four cements, analyses of which are given below, the following figures were obtained, the correction for the small amount of matter other than silica being given in each case; the quantity of cement used was 0.5 gram.

Sample.		Total residue chiefly silica obtained by second evaporation.	Matter other than SiO_2 contained in this residue.	Actual SiO_2.
1	(*a*)	0.0010	0.0001	0.0009
	(*b*)	0.0012	0.0002	0.0010
2	(*a*)	0.0012	0.0002	0.0010
	(*b*)	0.0008	0.0001	0.0007
3	(*a*)	0.0016	0.0002	0.0014
	(*b*)	0.0014	0.0002	0.0012
4	Porcelain (*a*)	0.0015	0.0002	0.0013
	(*b*)	0.0016	0.0002	0.0014
	Platinum (*a*)	0.0009	0.0002	0.0007
	(*b*)	0.0010	0.0003	0.0007

The first three samples were evaporated in porcelain; Sample 4 was treated in both porcelain and platinum. It will be seen that even the largest of these quantities (0.0016 gram, equivalent to 0.32 per cent.) is insignificant and will in no way influence the opinion of the chemist on the quality of the cement analyzed. There is also ground for believing that a good part of the silica obtained by a second evaporation is of extraneous origin and is not derived from the cement. The lower result for Sample 4, which was treated in platinum, points this way, and evidence more direct than this is available. The filtrate from the second evaporation of Sample 4 was evaporated, filtered, and the process repeated until in all seven such operations had been performed. The experiment was made in duplicate and its results are instructive.

It is perfectly clear that a considerable part of the small quantity of silica, obtained by a second evaporation, is derived, not from the cement itself, but from the vessels used and from inevitable dust; when correction is made for this, the quantity of silica retrieved by a second evaporation properly conducted becomes negligible, certainly not more than 1 mg.

SAMPLE 4.

		Series A.		Series B.	
		Gram.	containing matter other than SiO_2. Gram.	Gram.	containing matter other than SiO_2. Gram.
SiO$_2$ +	Evap. 1.....	0.1073	.....	0.1075	.....
nsoluble	" 2.....	0.0015	0.0002	0.0016	0.0002
residue	" 3.....	0.0006	0.0002	0.0007	0.0003
	" 4.....	0.0006	0.0002	0.0006	0.0001
	" 5.....	0.0004	0.0001	0.0005	0.0001
	" 6.....	0.0005	0.0001	0.0005	0.0002
	" 7.....	0.0004	0.0001	0.0005	0.0002

The next matter in which there is a difference of view between Dr. Hillebrand and myself is whether silica, separated by the ordinary process of solution and evaporation, is pure or contains entangled in or associated with it sensible quantities of alumina and other bases. To examine this question I chose a cement (No. 4 of the series given above) containing a very small quantity of insoluble residue (*viz.*, 0.52 per cent.). In this insoluble residue there was almost nothing but silica; hence, any alumina or other metallic oxides found in the silica + insoluble residue, isolated from the cement in the ordinary process of analysis, must be derived from the cement itself. This cement was analyzed in the usual way, the silica and insoluble residue separated and treated with hydrofluoric acid. The total weight of matter other than silica in four successive determinations is stated below; for comparison, the quantity of matter other than silica found in the insoluble residue is also given.

ON 0.5 GRAM.

Matter other than silica in insoluble residue. Gram.	Matter other than silica in total silica + insoluble residue. Gram.
0.0008	0.0007
.....	0.0005
.....	0.0005
.....	0.0006

It is evident that when the solution, evaporation and re-solution of the cement are properly conducted, no alumina remains with the silica except that which is present in the insoluble residue.

One other point of some importance may be dealt with, namely, the possible presence of silica in the precipitate of ferric oxide and alumina. Dr. Hillebrand's view is that silica, remaining in the filtrate from a single evaporation for that substance, will appear in the ammonia precipitate in sensible amount; he also holds that the figures which I have previously advanced may not represent the whole of the silica present in the ammonia precipitate. To determine this question, experiments were made on the same four cements previously employed. The ammonia precipitate obtained after a single evaporation for silica and without special precaution of any kind, was analyzed for silica by the method of fusion with bisulphate, proposed by Dr. Hillebrand. The only deviation consisted in the addition of hydrochloric acid after evaporation with sulphuric acid to hasten the solution of aluminum sulphate. The quantity of cement used in each case was 0.5 gram and the experiments were made in duplicate, the evaporations being performed both in porcelain and platinum. The results are as follows:

	Sample 1.		Sample 2.		Sample 3.		Sample 4.	
	In porcelain.	In platinum.	In porcelain.	In platinum.	In porcelain.	In platinum.	In porcelain.	In platinum.
Total matter recovered	0.0017	0.0015	0.0018	0.0015	0.0021	0.0017	0.0017	0.0011
Matter other than SiO_2	0.0003	0.0002	0.0004	0.000	0.00063	0.0003	0.0004	0.0001
Silica from $KHSO_4$ ..	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Actual SiO_2 contained in the NH_3 precipit'e	0.0006	0.0005	0.0006	0.0004	0.0007	0.0006	0.0005	0.0002

It is evident, therefore, that the amount of silica contained in the ammonia precipitate from cement, analyzed in the customary manner and with only one evaporation for silica, is negligibly small.

Certain deductions may be drawn from the data given above and from those previously published.

Experiment has shown that in the analysis of cement, silica can be separated by a single evaporation with a maximum error of 0.32 per cent. and that this error is usually smaller; that the amount of silica appearing with the ferric oxide and alumina will not exceed 0.14 per cent., and is generally less; that a single precipitation suffices for the separation of ferric oxide and alumina from lime and of lime from magnesia.

I venture to believe in the light of the foregoing facts that the method laid down in the paper read by me before the New York Section of the Society of Chemical Industry in May, 1902, is satisfactory.

If errors occur, they are due to bad work and not imperfection in the methods of analytical separation.

I desire to thank Mr. W. Woodcock for his assistance.

LONDON, ENGLAND,
May 5, 1904.

A RAPID METHOD FOR THE DETERMINATION OF LIME IN CEMENT.[1]

BY BERNARD ENRIGHT.

Received June 7, 1904.

A RAPID determination of the lime in cement, a method by which the lime content can be accurately determined, in a brief space of time, without waiting for the lengthy evaporations and dehydration of the silica present, is frequently very desirable in the manufacture of the highest grade of Portland cement. For these reasons the following method has been devised; it has been thoroughly tested and has given very satisfactory agreement with accurate lime determinations made by lengthy methods in common use.

The method of procedure is as follows: Five-tenths of a gram of a cement, as a precautionary measure repulverized in an agate mortar, is weighed out, preferably into a casserole of about 12 ounces capacity. About 100 cc. of hot water are introduced in a stream from a wash-bottle in such a manner as to keep the cement in complete suspension, about 30 cc. of hydrochloric acid (1:1) then added, the rapid agitation of the liquid being continued during its introduction. After the addition of a few drops of bromine water the solution is rapidly brought to a boil and boiled a few minutes to effect complete solution of practically everything but a few flakes of silica and to expel the bromine. Dilute ammonia is now cautiously added with constant stirring until a faint excess is present, and the solution again brought to a boil for a minute. It is then filtered, preferably on an 11 cm. filter-paper,

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[1] Read before the Lehigh Valley Section of the American Chemical Society, June 1, 1904.