CRITICAL REVIEW OF THE SECOND SERIES OF ANALYSES OF MATERIALS FOR THE PORTLAND CEMENT IN- DUSTRY MADE UNDER THE AUSPICES OF THE NEW YORK SECTION OF THE SOCIETY OF CHEMICAL INDUSTRY.

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THE efforts of a committee of the New York Section of the Society of Chemical Industry, headed by Mr. Clifford Richardson, to improve the state of technical analysis in this country are doubtless known to many, if not most readers of this Journal. The subjects thus far taken up have been Portland cement and copper slag analysis, the latter initiated by Mr. Thorn Smith, of Isabella, Tennessee. Carefully prepared samples were sent to many chemists and the tabulated results of analysis were handed over to me for examination and criticism. A report on each sub- ject was rendered. The first, on Portland cement and raw lime- stone mixture, was published as a part of the Committee's report in the *Journal of the Society of Chemical Industry*, January 15, 1902.[1] In the number of October 15, 1902, there is a criticism of it by Messrs. Stanger and Blount, with attendant discussion by others. The report on copper slag analyses has not appeared in print, but in the *Engineering and Mining Journal*, **75**, 295, the list of analyses is given with extended comments by Mr. Thorn Smith, based upon this report, of which copies had been sent to the gentlemen who had made the analyses. Following the first cement report, which contained a tentative scheme for technical analysis by the committee, a second series of samples was dis- tributed for analysis in accordance with its directions. Upon the data thus secured, a second report was rendered by me to Mr. Richardson, and at his request I have prepared, for publication, the present paper, which contains the greater part of that report in practically its original form. In preparing the report, much chemical work was done in the laboratory of the United States Geological Survey, the results of which were tabulated and dis- cussed, but, however interesting they may be from some points of view, they are not all of sufficient importance to warrant the consumption of space required for their presentation herein.

1 This Journal, **25**, R 259.

A cursory glance over the tabulated results of the present series of analyses offers little encouragement to those who hoped for a decided improvement over the first series made in 1901.   But it requires no very critical examination to show that there is improvement in certain directions and that the outlook is not all dark.   It is unfortunate for the purposes of a satisfactory review of the data presented that the committee's provisional scheme of analysis allowed any discretion as to whether certain corrections throughout the analysis should be made or not ; for instance, the correction of silica by hydrofluoric and sulphuric acids, of alumina by potassium acid sulphate, and in the matter of double precipitation of alumina, lime, and magnesia.   Thus, while nearly all the chemists practiced double evaporation and filtration for silica and almost all of these blasted silica, but thirteen applied the hydrofluoric acid correction; fifteen precipitated lime twice, but only eleven took the same precaution with magnesia.   It would have been more satisfactory had the samples been sent only to those having adequate facilities and agreeing to faithfully carry out the analyses according to a strictly laid down procedure, from which no important deviation could be allowed.   Then, and then only, could the results be thoroughly comparable and admit of plain deductions.   As it is, so few have adhered throughout to the committee's recommendations that the task of sifting the data has been very arduous and the results by no means commensurate with the labor expended.

This last statement is strengthened by the fact, revealed by special inquiries during the last stages of the examination, that the water used by a number of chemists was so impure as to vitiate their analyses as to certain constituents.   Only a few gave quantitative data on the quality of the water used by them, although information on this point was requested of all, but from the replies received it is manifest that not a few of the poor results are directly attributable to this cause and that the quality of the water used is often shamefully bad.   One chemist, in fact, declined to undertake the analyses at all because of the poor quality of the only water that was at his service.   Another analyst (2), after sending in his report and finding that his water yielded, on evaporation, 16.7 mg. per liter of residue—chiefly magnesium chloride and sulphate—repeated his analysis in duplicate with pure water and reported the results under 2a, Tables II

and III. This showing makes it probable that his results in the
1901 series of analyses were affected by errors due to the same
cause. Other chemists report up to 11 mg. of residue per liter,
which, however, in some cases seems to be largely of organic
nature or to consist of ammonium salts, since it disappears wholly
or is reduced in weight after ignition. Some simply say the
water used by them is good, others "do not know."[1] Even in
the former case it may be questioned if, in lack of quantitative
determinations, the statements as to quantity can be always unre-
servedly accepted, for the technical chemist is often too prone to
dismiss, as negligible and unweighable amounts which may,
nevertheless, be of moment in work of the present character. In
illustration, I may mention that one or two, after evaporation of
a solution containing silica, iron, alumina, etc., to dryness, and
correction of the filtered silica by hydrofluoric acid, find "no
residue." To one who has had much experience in silicate
analysis, this is a wholly incredible statement, though it may be
admitted that in cement analysis, by the exercise of unusual care,
the amount of this residue may at times be very trifling.

The factor of the quality of the water and reagents has hitherto,
perhaps, received too little attention. It was assumed by myself
in my former report that the reagents used were of a degree of
purity such as to affect the analyses with no serious error.
Furthermore, perhaps their solvent action on the glassware em-
ployed for precipitations and evaporations was given insufficient
weight. Mr. Thorn Smith, in a communication addressed to Mr.
Richardson regarding a matter only indirectly connected with the
present, comments on the very large amount of silica introduced
into the iron precipitate from the beakers used by him in slag
analysis. Such sources of error no doubt show their effect in
the analyses of the present series, but it is in no case except No. 2
possible to indicate with certainty the analyses or parts of analyses
thus affected, and too often it is not apparent how any error
of this kind can be made an excuse for the wide variations ob-

[1] In this connection a paragraph from a report "The Examination of Foods, Drugs
and Public Water Supplies," from the laboratory of hygiene of the State of New Jersey,
by R. O. Brooks, recently published, is most pertinent "Fifty-seven samples of what pur-
ported to be distilled water were received and analyzed, only twelve of which were pure
and only twenty-two of which had any claim to the title 'distilled water.' The residues
ranged from 260 parts(!) per million to 8 parts, sixteen being above 100 parts and the
average being 82 parts. All the samples with the exception of the aforementioned
twenty-two gave tests for either chlorides, sulphates, calcium salts, carbonates or me-
tallic impurities, usually several of these being present in one sample."

served.   Total iron, for instance, should be susceptible of exact determination, yet the two series of cement analyses and the one of copper slag reported show a most lamentable state of affairs among chemists, which can, so far as I am able to see, be ascribed only to gross carelessness either in manipulation or preparation and care of standard solutions, for errors from the sources above mentioned would seem to be here excluded.   If such carelessness has been shown with reference to iron, the inference is literally forced upon us that some of the other wide variations from the standard are due to similar causes.   Some of these points will receive later consideration.

Because of the uncertainties above set forth, particularly as to the quality of the water, the labor expended in the preparation of this report has been in part wasted, but some of the observations made, are, as said earlier, not without value.   It is quite useless, however, to continue experiments of this kind with reagents of doubtful quality.

The slurry and cement were not analyzed by me upon receipt from the Sandusky Portland Cement Co., but only six months later, after arrival of the reports from other analysts, and when it became apparent that without a standard analysis for comparison no adequate discussion of the data was possible.

The samples were received in glass vessels secured by a metallic screw-top pressing upon a cork washer.   It does not seem probable that in the interim, during which the vessels remained unopened, there could have been a material absorption of carbon dioxide and water, though the ease with which such absorption can and does take place through apparently tight joints is too little appreciated.   This view was not at first held, but the following experiment on the rate of absorption by the cement is instructive.   A portion of the cement was placed in a platinum crucible and left in the balance case (which contained no drier) with the cover somewhat displaced.   The weight was taken at intervals and the contents of the crucible disturbed from time to time, so as to expose fresh surfaces.   The following are the results:

Weight of cement, 1.6853; weight of cement and crucible, 26.5515.

Weight after 1st day...... 26.5537	Weight after 11th day ... 26.5615
Weight after 2nd day 26.5548	Weight after 14th day ... 26.5631
Weight after 4th day 26.5573	Weight after 17th day ... 26.5633
Weight after 6th day 26.5592	Weight after 23d day.... 26.5637
Weight after 8th day 26.5602	Weight after 63d day. .. 26.5642

There is shown a total gain during two months of but 0.75 per cent. when nearly fully exposed to the air. Even though this gain took place almost wholly early in the time period, it is not probable that in the closed vessel an appreciable increase of weight occurred. This conclusion is important, for, if true, it excludes as a probable source of serious error in this series of analyses that due to unequal absorption of carbon dioxide and water by the different samples of cement analyzed. It will be remembered that in the first series of analyses this was held to be a not improbable cause of the wide differences in "ignition loss" on the cement, an opinion which has lost most of its force, in view of the experiment referred to later under *Ignition Loss* (p. 1198).

The analyses made as standards of comparison head the lists given below. Their values are usually the mean of several closely agreeing determinations for which not quite the same degree of accuracy is claimed as for those made in 1901. In addition, others were made to test the committee's analytical scheme and the effect of using glass and porcelain vessels. From the first it appears that the committee's scheme is well adapted to furnish results that afford entirely satisfactory agreement with the standard, a conclusion which is confirmed by the concurrent testimony of several of the analysts who participated in the first series and who have since reported to the committee their experience with the method.

In this connection it may be as well to note that in my subsequent discussion I shall take into consideration some of the criticisms offered by Messrs. Stanger and Blount in their paper already referred to, and to which I, in part, replied at the time of its presentation in New York. A few of the criticisms and suggestions are, in my opinion, valid and good, and may well be heeded, should it seem fit in the light of experience to modify the committee's analytical procedure. Here it is incumbent upon me to point out that Mr. Blount and a number of others have fallen into error in thinking that the committee's method was devised by myself. Although it was submitted to me for comment and criticism and most of my suggestions were adopted, others were not. I purposely refrained from assuming the responsibility of devising a procedure to be followed by a class of factory chemists with whose laboratory facilities and general environment I had

no acquaintance. The scheme having been submitted to me for criticism, I made certain suggestions on what seemed to me the line of improvement from the chemical side chiefly, and there my responsibility ends. This is not to say that in my estimation the procedure is incapable of affording exact results when carefully followed (pure water and chemicals being assumed), for the contrary has been proved by myself and others. It was, however, admittedly a tentative scheme of analysis, open to and probably susceptible of betterment, in the matter of time at least. Mr. Blount has done us all a service in pointing out, in part, the way thereto. In the proper place I, too, shall indicate wherein modifications may, with advantage, be made both in view of certain suggestions of Mr. Blount and as a result of numerous experiments by myself on the slurry and cement samples now under discussion.

The standard analyses were made in general accordance with the outline of procedure given by me in my first report of 1901, but without regard to most of the minor constituents, except to ascertain that they were not present in such amounts that neglect to determine them would introduce errors of importance. Phosphorus and titanium are both present, but are counted in the analysis as alumina. No distinction is made between the different conditions of iron, but all is given as ferric oxide. Manganese is present, but in amount not to exceed 0.05 per cent. Its effect on the lime and magnesia figures has been ignored. Sulphur exists in both slurry and cement as sulphate and sulphide, the latter passing by ignition into sulphate without any loss at all. if the heat is not too prolonged or too high. This last subject is discussed further on in connection with the ignition loss (p. 1198). The alkali percentages are given because these constituents have an important bearing in explaining some of the variations for "loss on ignition," as will appear later (p. 1200).

The slurry was converted, in not over fifteen minutes, by a good blast, into a cement yielding but 0.05 per cent. of matter insoluble in hydrochloric acid. The contrary experience of some of the analysts is due solely to an ineffective blast or an improper manner of applying it, as with the crucible uncovered. The cement, when briefly treated with hydrochloric acid, yielded only 0.09 per cent. of insoluble matter after freeing from some separated silica, which amount might have been lessened perhaps by longer

action of the acid. These slight amounts of insoluble matter from both slurry and cement have not been entered separately, but were weighed with the silica, and what may have been left of them after correction by hydrofluoric acid was carried over to the alumina and iron. The error due to the possible presence in them of lime or magnesia is very slight indeed.

TABLE I.—STANDARD ANALYSES OF SLURRY AND CEMENT.

SO_3	1.45 } 1.82 SO_3[1]	1.53 } 1.75 SO_3	
S	0.16 }	0.09 }	
SiO_2	13.51	21.93	
Al_2O_3	[2]3.50 } 4.93	[3]5.99 } 8.34	
Fe_2O_3	1.43 }	2.35 }	
CaO	40.84	62.92	
MgO	0.75	1.10	
K_2O	0.79	0.61	
Na_2O	0.22	0.29	
H_2O	4.20	1.40	
CO_2	...	1.73	
Ignition	. .	2.91[4]	

TABLE II.—ANALYSES OF SLURRY.

Standard.	SiO2. 13.51.	Al2O3- Fe2O3. 4.93.	Al2O3. 3.50.	Fe2O3. 1.43.	CaO. 40.84.	MgO. 0.75.	SO3. 1.43.	Ignition loss. 37.50.
I	(12.69)	(7.07)	.....	.....	(40.46)	(0.72)	.....	36.36*
2	(13.24)	(5.36)	(3.51)	(1.85)	(41.06)	(1.25)	(1.62)	39.62†
2a	{ 13.46	5.00	3.77	1.23	40.90	0.79	1.42	37.46
	{ 13.54	4.98	3.75	1.23	40.80	0.73	....	37.46
3	13.95	4.97	3.01	1.96	40.95	0.81	....	38.66
4a	13.78	4.94	3.28	1.66	41.42	0.62	....	38.84
4b	13.80	4.84	...	...	41.48	0.88	....	38.90
5	12.62	5.32	4.07	1.25	40.96	0.92	....	38.88
6	(12.96)	5.30	...	...	41.04	0.65	....	39.68
7	(15.00)	(4.61)	(2.58)	(2.03)	(42.13)	(1.25)	1.62	38.58
8	(15.54)	(4.90)	(3.76)	(1.14)	(42.27)	(1.50)	1.52	39.20
9	(12.76)	(5.51)	(4.13)	1.30	41.98	0.77	1.48‡	38.90
10a	13.39	5.22	...	...	40.96	0.88	...	37.32
10b	13.16	5.31	...	...	40.93	0.85	...	....
11	13.20	5.98	3.75	2.23	40.21	1.20	1.62	37.69
12	13.72	5.28	3.68	1.60	41.18	0.79	...	....
13	12.88	5.02	2.36	2.66	40.50	0.86	...	39.04
14⅔	12.10	5.10	...	...	41.00	0.90	1.75	37.38
15	13.55	5.02	...	...	41.40	0.79	...	....
16	12.78	6.22	...	...	41.18	1.07	...	37.48
17	13.38	5.14	...	...	42.17	0.82	1.43	37.32
18	12.61	5.53	3.77	1.76	41.26	1.33	1.54	37.78
19**	(14.91)	(4.20)	(3.02)	1.18	41.71	1.10	1.48	35.15

[1] By fusion, after slow ignition and subsequent extraction by HCl, there was found the same total — 1.82.

[2] TiO_2, 0.18.

[3] TiO_2, 0.31.

[4] Mean of many results. The calculated loss from H_2O, CO_2, and the difference between 2+eS and $Fe_2O_3.2SO_3$ is 2.99. The slight discrepancy between the calculated and determined values may well be due to errors in the H_2O and CO_2 rather than in the directly found value for loss.

4a. Committee's method. 4b. Analyst's method. 7 and 8. Different analysts at same works. 10a. Committee's method. 10b. Analyst's method. * Average of five determinations. † Including 1.03 SO_3. ‡ Also 0.10 S. § Also 0.77 K_2O and 0.45 Na_2O. ** The figures of 19 are not in the form reported by the analyst, who gave analyses of soluble and insoluble parts separately.

TABLE III.—ANALYSES OF CEMENT.

Standard.	SiO₂.	Al₂O₃-Fe₂O₃.	Al₂O₃.	Fe₂O₃.	CaO.	MgO.	SO₃.	Ignition. loss
Standard.	21.93.	8.34.	5.98.	2.35.	62.92.	1.10.	1.54.	2.91.
I	22.29	9.68	....	....	62.81	0.95	1.52*	2.37†
2	(22.38)	(9.54)	(6.46)	(3.08)	(62.98)	(1.60)	(1.73)	2.66
2a	22.08	8.44	6.18	2.26	62.90	1.11	1.54	....
	22.04	8.50	6.20	2.30	62.80	1.15	....	....
3	22.10	8.72	5.78	2.94	63.44	1.23	1.52	2.71
4a	21.70	8.60	6.06	2.54	63 56	1.37	1.51	2.84
4b	21.68	8.46	....	....	63.56	1.25	1.52	2.85
5	21.20	9.04	6.67	2.37	63.13	1.39	1.58	3.48
6	22.08	8.66	....	....	63.09	1.31	1.63	3.74
7	(22.86)	(9.21)	(6.15)	(3.06)	(63.96)	(2.82)	1.56	....
8	(22.02)	(9.25)	(6.64)	(2.61)	(64.43)	(2.62)	1.38	....
9	21.69	8.64	6.19	2.45	63.27	1.08	1.43‡	4.50
10a	21.86	8.83	6.35	2.48	63.49	1.19	1.59	2.96
10b	21.79	8.83	6.35	2.48	63.40	1.20	....	....
	21.71	8.89	6.36	2.53	63.40	1.21	....	....
11	22.27	8.83	6.24	2.59	62.53	1.21	1.57	3.30
12	22.32	8.64	6.19	2.45	63.40	1.64	1.55	....
13	21.88	9.18	4.88	4.30	63.01	1.38	1.61§	2.66
14**	20.50	8.41	....	....	62.60	1.20	2.26	4.20
15	22.44	8.62	....	....	62.14	1.02	1.55	2.32
16††	22.18	8.52	....	....	63.88	1.28	....	2.86
17	22.24	8.36	....	....	63.72	0.99	1.46	3.01
18	22.58	9.08	6.48	2.60	63.15	1.38	1.51	2.58
19	22.53‡‡	8.39	5.74	2.65	63.88	1.34	1.62	0.98

4a. Committee's method. 4b. Analyst's method. 7 and 8. Different analysts at same works. 10a. Committee's method. 10b. Analyst's method. * Also 0.06 S. † Mean of two concordant results. ‡ Also 0.10 S. § Also 0.19 S. ** Also 0.85 K_2O and 0.50 Na_2O. †† Mean of close duplicates. ‡‡ In addition 0.20 insoluble in HCl reported.

Examination of the data furnished by most of the chemists with their analyses shows that certain of the latter must be rejected, in part at least, as not made in accordance with the committee's specifications in essential details. Slight deviations which could hardly affect the results appreciably, if at all, have not been regarded as sufficient ground for exclusion. This rule affects certain of the slurry analyses, and the values which are

regarded as fitly thrown out appear bracketed in the accompanying tables. With fuller information it is likely that still other figures would be similarly treated.

The grounds for excluding from discussion the bracketed values are the following:

Nos. 1 and 16.—The chemists, being unable to secure complete conversion to a soluble state by ignition, treated the partially converted slurry with hydrochloric acid, and, instead of filtering and further handling the residue as directed by the committee, evaporated silica and insoluble as for silica alone and corrected by hydrofluoric and sulphuric acids. No. 1 then found, after ignition, a fixed residue of 2.37 per cent., and No. 16 one of 2.60 per cent., which was, in each case, deducted from the crude silica and added to the alumina and ferric oxide obtained by precipitation with ammonia. Hereby a serious error was committed, affecting not only the value for silica, but those for alumina. lime, and perhaps magnesia as well, for the residue consisted not simply of aluminum and iron oxides, but of a little magnesia and probably considerable calcium sulphate too. The silica is thus made to appear too low by the amount of SO_3 retained by the lime, for, in case of No. 1, at least, the blast temperature was insufficiently high to convert to oxide. The lime and magnesia are also too low, but the alumina too high by the extent of the calcium sulphate and magnesia in the residue from the silica. In this way the quite abnormally high values for alumina and ferric oxide can be, in part at least, accounted for, but it is singular that analyst No. 1 should be the one to report also the highest alumina and ferric iron in the cement. where the conditions were normal and his silica and lime are nearly correct.

No. 2.—This analyst, after reporting, found that his water carried 16.7 mg. of solid matter to the liter, in large part chloride and sulphate of magnesium. His silica and lime values, particularly the latter, do not seem to be materially affected by the impurity of the water, but it has been thought best to reject the entire analyses for both slurry and cement. The analyses under *2a* are the work of the same analyst when using pure water, but as they were made after seeing the standard analyses, it is not right to consider them in the discussion.

No. 6.—In this case the insoluble and silica were fused with sodium carbonate, but instead of adding the hydrochloric acid solution of this fusion to the original filtrate it was separately evaporated twice for silica, the first filtrate also, whereby a greater loss of silica was incurred than if the combined solutions had been treated together.

Nos. 7 and 8.—These chemists, attached to the same works, did not ignite the slurry, but dissolved directly in acid and fused the residue with alkali carbonate. Under ordinary circumstances this procedure should not have caused trouble, but the slurry contained considerable organic matter, soluble in acid, which may have affected the subsequent precipitation of iron and aluminum to a marked degree. It is quite impossible to account in this way for the extraordinary values reported for silica, or for the excessive percentages for lime and magnesia, which characterize both slurry and cement analyses by these chemists, and for alumina in their cement analyses. Especially impossible are the figures given for magnesia in the cement. The fact also that two chemists following the same procedure should be able to find 1.14 and 2.03 per cent. of Fe_2O_3, respectively, speaks for itself. Either the grossest incompetence marks these analyses or the reagents used were of phenomenally bad quality. The glassware can hardly be more at fault than in the other analyses, for it is asserted to be Bohemian and furnished by a well-known New York firm. The analyses are therefore excluded, not only in the case of the slurry but of the cement also, as unworthy of serious discussion.

No. 9.—Portions of this analysis are rejected for the same reason as 7 and 8, that is, the manner of effecting solution of the slurry. The iron determination, being made on a separate portion and possibly after solution in a different manner, is not excluded. The cement analysis of this chemist shows normal character, notwithstanding certain deviations from the committee's rules.

No. 19.—The residue from incomplete conversion of the slurry to a soluble state by ignition was fused with sodium carbonate and analyzed separately, not being united with the first filtrate. This introduced uncertainties in the subsequent determinations, the reality of which is sufficiently apparent from a comparison of the values for silica and alumina with those of the standard, and hence justifies exclusion in part.

In individual determinations, a few of the other analyses show lapses from proper care quite comparable with those of 7 and 8, as, for instance, the silica values of 14 and the iron values of 13 in both slurry and cement, and of 11 in the slurry, but the data afforded by the chemists as to the methods used and the internal evidence of the analyses themselves do not furnish sufficient grounds for exclusion wholly or even in great part. Wide variations of the alumina values from the standard are not taken account of when it is plain that this is the result of an erroneous iron determination.

Were space available, it would be of interest before discussing the foregoing analyses to reproduce certain tables and attendant comments of the full report, showing the results obtained by myself when closely following the committee's procedure (using platinum vessels), and also the effect of completing the analyses, after separation of silica, in glassware of different makes. The tables referred to also show not only the percentages derived from the first crude weights, but also those found by applying the corrections usual in exact analysis. It must suffice to summarize the net results.

(1) That with pure reagents and only ordinarily careful work no such variations should be possible as are shown by Tables II and III, even when glassware of good quality is employed instead of platinum. Analyses of the cement made in glass gave: SiO_2, 22.08, 22.10, 22.11, 22.02, 22.30, 22.04; Al_2O_3, Fe_2O_3, 8.39, 8.43, 8.39, 8.22, 8.41, 8.37; CaO, 63.18, 63.03, 63.01, 63.18, 63.17; MgO, 1.16, 1.21, 1.12.

(2) That the solubility of glassware should not make itself so apparent by an abnormally high magnesia result as might seem to be the case in certain of the analyses of Tables II and III, for in all the analyses of the omitted list silica was in solution—up to 8 mg.—but, in agreement with all my previous experience, it is precipitated but little, if at all, with the magnesium phosphate. It seems, therefore, probable that the very high magnesia results in the other cases may have been due to magnesium salts in the water used, as well as in No. 2.

(3) That with cements so completely soluble in acids as the present one, the correction of the silica by hydrofluoric acid and of the alumina by bisulphate ought to be for technical work, certainly for factory control, unnecessary, since they so nearly bal-

ance one another. Any one of my analyses made in glass would serve quite well for all practical purposes, but unfortunately very few of the analyses in Tables II and III conform throughout to the standard anywhere near so well. There is evidently something wrong with the manipulations or the reagents used by the several chemists, as a consequence of which few are able to secure results as good as the least satisfactory of those in the omitted table. They evidently do not work as I do, and, moreover, they do not work alike among themselves. The personal factor seems to be an important one.

(4) That while it might be safe under the conditions assumed above to neglect the corrections on silca and alumina (as was done by analyst 12), it is not safe to apply one and neglect the other. This the following illustration will make clear: The uncorrected values for SiO_2 and Al_2O_3 were 22.12 and 8.59, which became 22.00 and 8.71 when correction was applied to the former only; but the latter held 0.30 SiO_2, so that the true values were 22.30 and 8.41. The wholly uncorrected figures were nearer right than when but half corrected.

DETAILED DISCUSSION OF ANALYSES OF TABLES II AND III.

It is now in order to look at the analyses in greater detail, and because the determinations of silica and alumina are so closely connected, I will discuss under one heading the figures given for silica and the precipitate produced by ammonia.

Silica and the Alumina Precipitate.—The cause mentioned just above, namely, the application of the correction on the silica for alumina and not on the alumina for its contaminating silica, accounts for the chief discrepancies in Tables II and III after excluding the "rejected" values enumerated on pages 1188-1189. This is shown by the following tabulations, where Table IV*a* contains the analyses in which the double correction was made, while IV*b* shows those in which the correction was made only on the silica. The silica was blasted in all cases.

TABLE IV*a*.—SHOWING ANALYSES IN WHICH THE CRUDE SILICA AND ALUMINA WERE BOTH CORRECTED.

No.	Slurry.		Cement.	
	SiO_2.	$Al_2O_3Fe_2O_3$.	SiO_2.	$Al_2O_3Fe_2O_3$.
3	13.95[1]	4.97	22.10	8.72
4*a*	13.78	4.94	21.70	8.60
10*a*	13.39	5.22	21.86	8.83
11	13.20	5.98	22.27	8.83
17	13.38	5.14	22.24	8.36

[1] No hydrofluoric acid correction.

TABLE IV*b*.—SHOWING ANALYSES IN WHICH CRUDE SILICA BUT NOT THE CRUDE ALUMINA WAS CORRECTED.

No.	Slurry.		Cement.	
	SiO_2.	$Al_2O_3Fe_2O_3$.	SiO_2.	$Al_2O_3Fe_2O_3$.
1	....	...	22.29	9.68
5	12.62	5.32	21.20	9.04
13	12.88[1]	5.02	21.88	9.18
14	12.10	5.10	20.50	8.41
15	13.55[2]	5.02	22.44[2]	8.62
16	....	...	22.18[1]	8.52
18	12.61	5.53	22.58	9.08

In the first of the above tables, the four silica values for slurry, due to double correction, all fall within the limits 13.20 and 13.78, the standard being 13.51. Analysis 3 is included in this series, notwithstanding the omission of the hydrofluoric acid correction, because it is plain that with the correction made it would occupy an even more favorable place than it does with respect to silica.

The second table contains four of the eight markedly low silica results reported for the slurry— that is, below 13 per cent.— while only one is above 13 per cent. In this, the evaporation for silica was made in glass, while in the other cases porcelain was used, except platinum for the slurry in 13. The other four returns below 13 per cent., namely 1, 6, 9 and 16, are excluded from consideration for the reasons given on pages 1188-1189.

With respect to the silica values for the slurry in Table IV*b*, it seems singular that with such a low general average of uncorrected alumina for the five, the silica should not be much higher than it is. Assuming that the alumina is all accounted for in the values given, there must have been a marked loss of silica in four of the five analyses. Were the alumina considerably higher, the same cause might be assigned that was sufficient to exclude slurries Nos. 1 and 16 from the comparisons, but there is nothing in the data furnished by the chemists who made these analyses that throws any light upon this point. Were it not for the fact that similar deficiencies do not appear in their cement analyses, it might be thought that in some of the cases silica had adhered so tenaciously to the porcelain dish on evaporation as to escape complete removal. This is a cause of error quite likely to arise at times when using porcelain, because of the difficulty of seeing the adhering silica against the white surface. Analyst 16, who evaporated for silica twice in platinum, remarks that the glass

[1] In platinum.   [2] In glass.

used for subsequent operations was "easily attacked," which might account, in part, for his abnormal alumina in the slurry, were it not that for the cement it is nearly normal.

Notwithstanding that the results of Table IVa are, on the whole, most emphatically favorable to the appliction of the double correction, the fact remains that the general average of the alumina is still far in excess of the standard. This may be in part because the silica correction, as made by bisulphate, does not give the true correction, as I showed conclusively in my paper "Common Errors in the Determination of Silica,"[1] since a large, or even a major, portion of the silica contaminating the alumina goes into solution and can only be recovered by evaporating the dissolved product of fusion with excess of sulphuric acid, and heating till fumes of the acid are copiously evolved. Upon cooling, diluting, and digesting for a time, the whole of the silica collects in flocks and can be readily separated and determined. See, also, page 1205.

In all cases where alumina was twice precipitated (and this was done by all but 3 and 15), except under the conditions of treating the slurry followed by analyst 1, there is no reason to suppose that the high results for alumina are due to coprecipitation of calcium, even when the ammonia used contained carbonate and the liquid, during precipitation, was exposed to gases from the flame beneath. Therefore the variations in the lime and magnesia must be due, in the great majority of cases, to causes quite unconnected with the manner of getting the slurry and cement into solution and with the determining of the silica and alumina, except in the case of slurry No. 1, already alluded to, and possibly one or two others. This it would be impossible to assume, had but a single precipitation of alumina been made, for most chemists do find a little lime with the latter when they take the trouble to look for it, although of the present company 3 and 15, the only ones who tried it, seem to have made a good single separation, as Mr. Blount claims can always be done by the use of a sufficient amount of ammonium chloride. I must admit that a single trial, by myself, on the cement gave a result in accord with his statement, but then I use redistilled ammonia, which is almost free from carbonate, while that coming from the dealers contains a good deal at times and may thereby give rise to rather serious error.

[1] This Journal, **24**, 362.

The excessive value obtained by No. 1 for $Al_2O_3 + Fe_2O_3$ in the slurry has been shown to be due, in part, to the possible counting of considerable calcium sulphate and a little magnesia as alumina, but since an almost equal excess occurs in his cement analysis without the possibility of a similar cause acting, the explanation must lie, in part, in the application of too low a heat. If the alumina was heated with uncovered crucible, as seems to be this chemist's practice, the error may be accounted for.

To sum up the situation as regards silica by a review of all the data, regardless of just grounds for excluding some, it appears that there has been a decided elevation in the average. It is nearly that of the standard in the slurry (13.43 : 13.51) as against 14.37 to 15.18 of the 1901 series, showing an average deficiency of only 0.08 per cent. now, as against 0.81 then. In the cement there appears now an average excess of 0.10 per cent. (22.03 : 21.93), as against a deficiency of 0.81 in 1901 (20.50 : 21.31). It is thus apparent that, whereas two years ago the average error of a large number of chemists was a serious minus one. it is now, in both cases, practically wiped out. The variations from the truth are as likely to be found on one side as the other, though the extremes are as far apart as ever. This last would be a more discouraging feature than it is but for the fact that the returns from analyses 7, 8, 9, 14 and 19 are so abnormal on the slurry as to occupy a position by themselves. Excluding their results, the extreme differences show a marked improvement also, being for the slurry only 1.34 now, as against 2.97 in 1901, and for the cement (excluding here only 14 as utterly abnormal) 1.18 against 2.38.

A similar comparison of the precipitates by ammonia shows the following results: The general average for the slurry is now 0.35 in excess of the standard (5.28 : 4.93) as against an excess of 0.84 in 1901 (7.93 : 7.09), and for the cement 0.52 in excess (8.86 : 8.34) as against 0.90 (10.33 : 9.43) in 1901. The real showing is doubtless somewhat less favorable than it appears from the above, because the alumina precipitates are now smaller than in the earlier series of analyses, but there is nevertheless a manifest improvement.

Iron.—In the foregoing the ammonia precipitate has, for brevity's sake, been spoken of as alumina. The values for the latter constituent, being in all cases determined by difference. are,

of course, affected by any error attaching to the iron. As stated earlier, gross carelessness must have characterized some of the iron determinations. The gravimetric determinations (3 and 19), after separation from alumina by potassium hydroxide. were wide of the standard, as may be seen by reference to Tables II and III, but not to the same degree as some of those made volumetrically. It is of interest to know that the hydrogen sulphide method of reducing iron has given decidedly better results than reduction by hydrogen, though there is still room for improvement by those using the former method.

Aside from carelessness in one way or another, it seems probable that a not unimportant factor in some of the errors is the strength of volumetric solution used. In most cases it was too strong for safety in rapid work on low iron percentages, being from 0.0055 to 0.0105 Fe per cubic centimeter.

Lime.—Except as before mentioned for slurries 1 and 16, the determinations of lime seem to be unaffected by any of the variations from the committee's directions for the solution of the slurry and cement, and there are no data to throw light on the cause of the wide variations, not only from the standard, but among themselves as well. The errors due to solvent action on the glass beakers should affect chiefly the silica and lime, and a portion of all the plus errors in these determinations are to be ascribed to this source. But, as my own analyses made in glass go to show, the errors resulting herefrom are not great enough to account for the large variations reported, unless the glass is much poorer than any that was at my disposal. Neither does there seem to be any decided advantage in the gravimetric method for lime over the volumetric one involving the use of permanganate, except in the case of the cement, where the maximum difference is 1.35 in eleven determinations as CaO against 2.29 by permanganate. If, however, the grossly inaccurate analyses of 7 and 8 are excluded from consideration here as before, the advantage is found to lie slightly with the volumetric method for both slurry and cement, leaving out of account the discrepancy in numbers.

There is internal evidence in a few of the analyses that insufficient heat was employed to convert the oxalate wholly to oxide. For instance, 17 shows in all respects, except lime, a close agree-

ment with the standard, whereas in lime his results are far above the average on both slurry and cement. The last statement holds for 19 too, though the agreement with the standard is not otherwise good. No. 11, on the other hand, shows a marked loss in both cases, with especially high alumina in the slurry, which seems to be indicative of incomplete separation from the latter, notwithstanding that the separation was made twice.

With respect to the temperature required for the complete conversion of calcium oxalate to oxide, it will be well to introduce here a few remarks and an experiment to dispel the common impression that this is a difficult matter. Analyst 1 blasts for an hour or more, but when it is learned that this is done with crucible uncovered, the reason is apparent, especially if the blast is not a powerful one. The following test, made by myself, shows what may be accomplished over a good Bunsen burner only.

A crucible containing 2.9997 grams precipitated $CaCO_3$ weighed 24.4033 grams. The covered crucible was heated for several periods with the results that follow :

	Grams.
Weight after twenty minutes over burner	23.1628
Weight after further twenty minutes over burner	23.0817
Weight after further twenty minutes over burner	23.0801
Weight after inclined blast for twenty minutes	23.0790

The total loss was 44.12 per cent., instead of the 43.95 called for by theory, the slight excess being doubtless ascribable to hygroscopic moisture. It is seen that forty minutes' heating over the burner sufficed to effect almost the whole of this with 3 grams of calcium carbonate. For the amounts usually encountered in analysis, of which cements afford about the maximum, ten minutes' heat of the Bunsen burner is almost as effective as an additional five minutes' blasting, which latter is usually ample. Could the Bunsen heat be applied effectively with exclusion of the flame gases from the interior of the crucible, the blast would be quite unnecessary at the end. It is, however, assumed that the crucible rests in a triangle of platinum and not of clay. It is also my custom to use an inclined blast on almost all occasions requiring this mode of heat application, and usually without allowing the flame to envelop the lid of the crucible. Hereby flame gases are largely or altogether excluded, and, consequently, in the case of

cements and limestones, given an equal temperature, more rapid loss of their carbon dioxide results than is possible with a vertical blast.

One possible cause of error in the lime results remains to be mentioned. Unless the lime is weighed soon after ignition—say not later than half an hour—the result may be too high. It is not known to what extent, if at all, this error affects the results under discussion.

Magnesia.—Regarding the discrepancies in magnesia there is little that can be said. When averages for 1901 and 1902 are compared, the present are found to be even a little worse than the earlier ones, and that too with smaller amounts of magnesia to deal with. Even allowing for considerable solvent action of reagents on the glass, it is difficult to see how this should give rise to such extraordinary results as some analysts report. It seems not impossible that the abnormally high magnesia returns were, in all cases, due to impure water, as was found to be the case with those of analyst 2. Even where the ammonium salts have been removed by nitric acid (method of J. Lawrence Smith), as recommended by Mr. Blount, the results are still high, as in both analyses 19.

The influence of impurities in stock solutions is one that should not be lost sight of. The practice of using stock solutions of such reagents as ammonium oxalate and sodium phosphate is dangerous, unless the solutions are renewed at frequent intervals. It is my practice to use the solid salt and dissolve it as wanted.

Sulphur.—For all but No. 3, the figures for sulphur trioxide represent only the sulphate sulphur. No. 3 reports only total sulphur. The only point calling for special comment is the comparison of the results as they were obtained with or without removal of silica by evaporation before adding barium chloride. Even excluding the particularly abnormal results of 14, the advantage is still with those who do not remove silica (5, 6, 9, 10*a*, 12, 17), although the comparison is not altogether satisfactory, because of the difference in the numbers using the two procedures. I am inclined to ascribe the higher values in the one case largely to absorption of sulphuric acid during evaporation for removal of silica, especially where water-baths heated by gas were used. That this source of error is a very real one has been long since shown. Impure water may be a factor in other cases for the

deviations in excess of the standard recorded by both procedures. The high value reported by No. 2, in his original analysis, is known to have its origin in the above source, and it may very well be, in view of the poor quality of the water reported subsequently by others, that this explanation fits other cases. That Stoddart should have found[1] frequently more sulphur in coals when not separating silica than when doing so, is contrary to all my experience in silicate work, where duplicates agree usually exactly, and, if they differ, are as likely to be high by one way as by the other.

Ignition Loss.—The results for loss on ignition will not be discussed in detail because the experiments, referred to below, have shown clearly enough why the results vary, and must vary, unless a closely defined method for determining this loss is followed. Such precision is not to be found in the committee's directions for the determination of this factor; hence, no blame can attach to those who obtain results varying from the standard. Several of the chemists stated that in their results "loss on ignition" comprised not only water and carbon dioxide, but also more or less sulphur trioxide, depending on the temperature of the blast, besides organic matter and possibly one or two minor factors. In my own analyses, it was supposed to include all possible factors except loss of sulphur from either sulphates or sulphides, for, unless the heat passes a certain point, the sulphides are oxidized to sulphates and no sulphur is lost, being retained by the lime. This is the explanation asked for by Mr. Blount in his reply[2] to certain remarks of mine at the foot of page 1221.

Mr. Blount is perfectly justified in objecting to the blast for "loss on ignition" in cements and cement mixtures containing sulphur when applied in the manner prescribed by the committee, but, as described below, the method is accurate for all reasonable demands, and results agreeing within 0.1 or 0.2 per cent. can be obtained almost as often as desired. It happened that, without special study of the subject, I had employed the right condition; from the start, but Mr. Blount's inquiry led me to take up the matter in some detail, and the results I now communicate.

It may be said at once that the variations in "loss" are not attributable to absorption of carbon dioxide and water from the air, unless there was great lack of care, and even then this can be

[1] This Journal. **24**, 852.
[2] *J. Soc. Chem. Ind.*, **21**, 1223.

but a minor cause, as the data given on page 1183 show.   Hence, my own former doubts and those of S. F. Peckham[1] on this point were largely unfounded.

Trials in great number were made on both slurry and cement under varying conditions.   It was found, as above said, that the sulphides could be easily and quickly oxidized without any loss of sulphur and yet with complete removal of water, carbon dioxide, and organic matter.   The proof of this was repeatedly obtained by finding in the ignited product as sulphate soluble in hydrochloric acid exactly all the sulphur that the cement or mixture originally held in both sulphate and sulphide condition.   Such a complete change can be effected in a short time and without any need to be very cautious in applying the heat.   It may be turned on nearly full at the start.

In all my experiments, ignitions were effected in covered platinum crucibles of about 20 grams weight.   Chemist No. 1 followed the practice recommended by me of fitting the crucible in a hole in asbestos board, but removed the cover, and in this last fact lies the explanation of the excessive time required by him for securing constant weight, and the too low results when obtained. My experiments show that even without the protection afforded by the asbestos board there need be no great error with an inclined blast if only the precaution is taken not to let the flame envelop the whole crucible, but only to impinge strongly against the lower third.   In using asbestos board, particles tend to cling to the crucible and to remain attached when the latter is removed after ignition; hence, I prefer, as much cleaner and no more expensive in the end (for the same asbestos serves but a few times), a sheet-platinum disk with a hole for the crucible, the disk in its turn covering a larger hole in asbestos board.   A further advantage of this modification is that, because of the higher heat obtained than when the crucible is in contact with asbestos, the duration of the heating is shortened.   A muffle answers equally well, as claimed by Mr. Blount (for time required see page 1207).

I have assumed that the loss shown when none of the sulphur has as yet been expelled is to be taken as correct, since in no case was there the slightest effervescence on dissolving in hydrochloric acid, nor any trace of organic matter left.   That this assumption is entirely justified was shown by the close agreement

1 *J. Soc. Chem. Ind.*, **21**, 831.

(in case of the cement, for which alone could the calculation be made) of this value with that obtained as the algebraic sum of all factors entering into the loss. A similar agreement appeared in my discussion of the 1901 series of analyses. But, because of the unavoidable variations in the heat supply used by different chemists, each one should ascertain, once for all, the effectiveness of his burner, blast, or muffle, by ascertaining, as I did, the limit of time beyond which sulphur begins to be volatilized, as shown by the ignited "mix" or cement yielding less total sulphur than before ignition. This necessarily, however, involves rather more accurate determinations of sulphur than most of those reported either now or in 1901.

The temperature at which carbon dioxide escapes from calcium carbonate being so much lower than that causing dissociation of the sulphate, is the reason why comparatively brief application of heat under the above conditions effects complete loss of carbon dioxide and little or none of sulphur trioxide. But it is not the above mode of ignition that must be used to convert the slurry to a wholly soluble cement. No disk protection is then allowable.

It is apparent from my experiments that most chemists employed far too protracted ignition in determining "loss," and that in extreme cases all, or nearly all, the sulphur trioxide was included in the loss. But in many cases there was a further factor making itself felt, for long before the last of the sulphur trioxide is expelled alkali begins to volatilize, and it is easy to remove all, or nearly all, in this manner. The alkali is volatilized as oxide and may be collected in quantity on the under side of the crucible lid. At the intense temperature of the rotary cement furnace this action must play an important part, and to it is to be attributed the great loss of alkali, noted by me in the cement of 1901, as compared with the raw "mix" from which it was made, an observation which is repeated in the present case and must be general in cement burning.

PROPOSED MODIFICATIONS IN THE COMMITTEE'S DIRECTIONS FOR THE ANALYSIS OF CEMENTS.

From the foregoing it is apparent that the committee's method of procedure has, in many respects, not been subjected to a fair or exhaustive trial. Furthermore, because of the real uncertainty regarding the quality of much of the water used, the value of this

report is below what it would otherwise be. Nevertheless, certain facts have appeared from my experimental work in the light of which modifications of the committee's directions for the analysis of Portland cements and raw mixtures used in their making are in order. These I will now consider.

Rendering Raw Material Soluble.—The committee's direction, following my own recommendation, to ignite the "mix" at an intense heat in order to render it soluble in hydrochloric acid, are thoroughly sound in principle and in accord with the practice of Messrs. Stanger and Blount. By doing this, the material undecomposed by the acid should, in no case, probably, exceed o.1 per cent. of the sample, and it is sometimes much less. By this it is not meant that no insoluble matter appears other than undecomposed silicates, for a little silica is always separated in a flocculent, non-gelatinous, easily filterable state. The unattacked particles can always be detected by their gritty character when touched with a rod.

Under no circumstances may a large residue of undecomposed matter, found at this stage, be evaporated with the solution to dryness and treated as if it were silica (as two or three chemists have done in the present series of analyses), for it may, and probably does, contain lime in addition to alumina, ferric iron, etc. The error in silica and alumina, caused by this lime being weighed as sulphate, after the hydrofluoric acid correction, has been discussed on page 1188.

The point has been raised that the strongly ignited material dissolves very slowly, being dense and semifused. If, however, the lumps are gently pressed upon with the flattened tip of a rod from the moment the acid strikes them, solution becomes a matter of no difficulty at all. In spite of the ease with which this conversion to a soluble state can be reached in fifteen or twenty minutes, quite a number of chemists failed by lack of blast of sufficient intensity. The committee recommends in such cases to filter off any undissolved matter, to ignite, to fuse it with sodium carbonate, and to add its hydrochloric acid solution to the main filtrate. Had these directions been followed in certain cases, fewer analyses would have been thrown out of court.

In order to obviate the need for a filtration and fusion of a possible residue, one chemist, W. R. Oglesby, recommends to strongly ignite a mixture of the material with only enough sodium

carbonate to cause sintering. It is claimed that solution in hydro-
chloric acid is then complete, that the amount of alkali introduced
is so slight as to give rise to no appreciable error in subsequent
operations, and that the necessity for correcting silica by hydro-
fluoric acid is avoided. My own tests show that the first claim
is well grounded when even so little as 0.5 gram of the flux to
1 of "mix" is employed. But the reason for the third is not
obvious, for it has never been my fortune to see silica separated
by evaporation from a solution containing aluminum, iron, tita-
nium, and phosphorus, or even the first of these alone, which was
so pure that no contamination was revealed by the hydrofluoric acid
treatment. The residue is rarely under 1 mg. and may be twenty
to thirty times that amount in special cases (not cements). My
own limited experience with cements shows that it runs from 1
to 2 mg. after a single evaporation for silica and slightly more
after a double one. Still, no strong objection can be brought
against this method of attack of the raw mixture on the score of
accuracy, and if it on a general trial should meet with the ap-
proval of cement chemists, there may be no objection to its super-
seding the blast ignition without addition of flux. But the amount
of this flux should be rigidly kept down to the lowest limit, not
exceeding that given above.

Determination of Inert Constituents in Cement.—Mr. Oglesby
would also apply the above mode of attack to cements as well, but
this brings up the question whether the committee shall see fit to
take account of the existence of cements containing acid-soluble
constituents in appreciable amount. These undoubtedly do exist
here, as well as abroad, and it seems reasonable and proper that
inert constituents, when present, should be reported as such and
not help to swell the active components. But if the determina-
tion of these inert constituents is to be made, I cannot recommend
that the directions of Messrs. Stanger and Blount be followed,
for the reasons set forth in my criticism of certain features of
their paper,[1] but must adhere to the procedure there outlined by
myself. I do not agree with their statement that no foreign
matter is to be found with the silica separated from cements, nor,
do I think, will many others do so who look carefully into the
matter (see remarks relating to this point a few paragraphs
above, page 1201).

[1] *J. Soc. Chem. Ind.,* **21,** 1222.

Solution of Cement and Ignited "Mix."—The committee's directions for dissolving cements and ignited cement mixtures may very well be modified in the interest of time-saving by adopting the practice of Messrs. Stanger and Blount,[1] for to digest, and especially to dilute strongly, before evaporating causes quite unnecessary delay. Usually, in two or three minutes after pouring the acid upon the moistened cement, solution is effected and evaporation may begin.

Dehydration of Silica.—Messrs. Stanger and Blount's plan of baking on a hot plate, at a temperature of about 200°, is a very speedy way of rendering nearly all the silica insoluble and saves much time. It may be unhesitatingly recommended for a first evaporation. But at this point my approval of their procedure ceases. I can refer only to my experiments quoted on page 1221[2] in refutation of the claim that a single evaporation for silica suffices by their procedure. Their later results (p. 1223) only serve to confirm my objections instead of overturning them. If an error of over 0.2 per cent. in the alumina is negligible, then why do the authors regard it necessary to reject, as unfit for use, filter-paper which would introduce into an analysis an error of less than one-tenth of the above? But, in addition, the authors do not give us their way of analyzing the precipitates of Al_2O_3 and Fe_2O_3 in order to show that the amounts of silica they give were all that these precipitates contained. If it were done by solution of the Al_2O_3 and Fe_2O_3 in an alkali bisulphate, they obtained but a minor portion probably of the total silica. As I have shown elsewhere,[3] that method, as hitherto carried out, gives utterly fallacious results, and it is only by the exercise of a certain precaution that all silica can be recovered. Even after two evaporations, the iron-alumina precipitate contains usually from 1 to 3 mg. of silica. Nor is this silica "more likely to be due to dust and outside impurities than to residual silica in the cement itself,"[4] if the water and reagents were pure.

No change should therefore be made in respect to the double evaporation and filtration for silica. It is not important, except

[1] *J. Soc. Chem. Ind.*, **21**, 1217.
[2] *Loc. cit.*
[3] This Journal, **24**, 362.
[4] *J. Soc. Chem. Ind.*, **21**, 1223.

as a matter of time-saving, whether the heating of the separated silica be done at steam-bath temperature or at that of the hot plate.

Alumina, Iron Oxide, Lime, Magnesia.—I do not feel that any fundamental changes in the directions given by the committee for the determination of these constituents are called for either by the comments of different writers or by the testimony of the analyses themselves. The amount of bisulphate to be used for the solution of the ignited alumina, etc., should be reduced from 10 grams to 2 or 3. Care should be taken to make a blank experiment with the reagent to ascertain its silica contents, if it has any.

I agree with Messrs. Stanger and Blount that quite satisfactory separations *can* be made in cements and cement mixtures, of alumina and iron from lime, and of lime from magnesia, by one precipitation, separations which would satisfy all requirements of the cement trade, and I have made them myself. But this can only be accomplished by the employment of really good reagents and utensils. With the ammonia used by nearly every one, varying perhaps in quality originally, not redistilled over lime, and contaminated from the glass bottles, it is hardly possible that accurate results can be obtained by single precipitations. Probably most ammonia used contains carbonate. I have found this to be so with that which we buy as of good quality. Hence, unless carefully redistilled over lime, the aluminum and iron oxides must be contaminated by calcium carbonate. Mr. S. S. Voorhees, of the supervising architect's office of the United States Treasury, finds this contamination to be less than 0.25 per cent., but it may often be more in careless work, and it is to avoid the effect of variable errors like this that I would make double precipitations the rule.

In the numerous analyses made by myself for this report, I have thoroughly tested the time-limit for the settling of calcium oxalate after precipitation, and find that very little, indeed, is gained by allowing to stand for more than twenty minutes after removal from the source of heat. The lime in the first filtrate will hardly ever exceed 1 mg. when the quantities to be precipitated are so great as in limestones and cements.

In blasting lime, the crucible should be always covered, and it is advisable that the blast-flame impinge only against the lower part of the crucible, at an angle of about 45°. The flame should not envelop the lid of the crucible, because when it does the contents are ever in an atmosphere of carbon dioxide, and the complete reduction to oxide is retarded. The heat of a good blast-lamp is, however, so many hundred degrees above the temperature of decomposition of calcium carbonate that no difficulty need be experienced in getting an unchanging weight, even if this precaution is not observed. With it, however, no ignition should ever require over ten minutes, and a second heating is, indeed, rarely made by myself.

I now regard it as quite unnecessary to blast the relatively small amounts of magnesium pyrophosphate obtained in cement analysis. Indeed, if blast heat is prolonged beyond two or three minutes, loss may ensue. This is especially so, if the phosphate, after blasting, shows signs of fusion.

If the double precipitation of magnesium is to be retained, I do not deem it at all essential that the procedure given by the committee be followed. That procedure, of Wolcott Gibbs, is designed to give a precipitate of normal composition, but if a second precipitation is to follow, it is immaterial whether the first is of normal composition or not, so long as all is precipitated. Therefore, it does not seem logical to boil with the precipitant in an acid solution before rendering ammoniacal, when the object can be more simply attained. The amount of precipitant should be largely reduced if a single precipitation only is intended, and it is unnecessarily large, in any case.

Application of Corrections to the Foregoing Determinations.— With good work, little is gained in analyzing cements by correcting the ignited silica and alumina for the contaminations which they invariably contain, provided two evaporations and filtrations have been made for silica. It is also shown on page 1191, however, that the one correction should not be made without the other, for then the errors on the alumina may be large, especially where, as is most always the case, glass vessels are used for the precipitations.

The bisulphate correction for silica in the alumina must be made, not in the usual way, but, in order to avoid serious error, as follows: The bisulphate fusion is to be dissolved in water to which a good deal of sulphuric acid is added, and then evaporated

in platinum and heated till acid fumes are copiously given off.
When cool, the pasty mass is redissolved in water, digested till
all but the flocculent silica is in solution, then filtered. The ignited
and weighed silica is to be checked by hydrofluoric and sulphuric
acids, like the main silica.

I have recently followed J. Lawrence Smith's strong recom-
mendation to use the sodium acid-sulphate for this purpose in-
stead of the potassium salt, and with very good results. There is
then no difficultly soluble potassium-aluminum sulphate to dis-
solve before filtering off the silica, but solution is speedy, and,
furthermore, the action of the sodium salt on the ignited iron-
aluminum oxides is more energetic, so that much time is saved
by its use. There is, however, the disadvantage that the salt is
far more difficult to keep in fusion than the potassium salt, so that
the progress of solution of the oxides on the bottom of the crucible
cannot be so well followed.

Sulphur.—Notwithstanding some adverse testimony from
another source than the chemists who have participated in these
series of analyses, I am fully of the opinion that the practice of
not first removing silica where small quantities of sulphur are in
question is perfectly safe. The only condition is that the silica
must not be allowed to gelatinize, and this I never have the
slightest difficulty in maintaining, first by using not very strong
acid for effecting solution and then by diluting freely as soon as
solution is accomplished. The vessel may then be placed on the
steam-bath or even boiled on the iron plate without fear of gelati-
nization resulting. This mode of procedure avoids the contamina-
tion by sulphuric acid from the flame of a water-bath that is
heated by gas, which is certain to result if the silica is first dehy-
drated in the usual way. When an oxidizing fusion of the cement
or mixture is made, the asbestos or platinum-asbestos protection,
mentioned in the paragraph below, should be used.

Ignition Loss.—Instead of igniting over a free blast-flame, the
covered platinum crucible should be inserted about two-thirds of
its depth into a close-fitting hole in asbestos board, or, better, in
a disk of platinum foil which itself covers a large hole in asbestos
board. The flame should strike at an angle of about 45°, and,
when using the disk, for thirty minutes with 1 gram of slurry or
limestone mixture, and five to ten minutes with a cement. Even

with only a good Bunsen lamp (using the disk) practically the same result can be reached in sixty minutes on a slurry or lime-stone and in thirty minutes on a cement.   With a hot, closed muffle, ten minutes' time suffices with either raw mixture or ce-ment, the crucible being placed about two inches from the door.

But each chemist should ascertain for himself, by direct ex-periment, what his blast or muffle can do, and this he can best learn by experimenting with a standard material whose composi-tion is known.   It would be, in my opinion, of great advantage to all cement chemists if the committee would see to the prepara-tion of a large sample of limestone mixture, sufficiently large to last for many years, which could be issued to all applying for it. I select limestone instead of slurry or cement on account of its unchangeability under varying atmospheric conditions.

CONCLUDING RECOMMENDATIONS.

Probably the most fruitful plan for arriving at a method of procedure that would best suit the conditions prevailing in the majority of cement works would be through a subcommittee or a new committee of not more than three well-selected members, who should not only be analytical chemists, but men familiar with cement works.   Now that the conditions governing accurate work are understood, such a committee should be able, by actual experi-ment on a standard sample like that mentioned above, to work out a detailed scheme of analysis that would be a satisfactory compromise between the imperative demands of the factory for immediate results, on the one hand, and a proper regard for reasonable accuracy on the other.   Such a method might be known as the "factory control method," while for more precise work one of greater refinement might be given in detail and its employment strongly recommended, if not prescribed.   While I agree, in general, with Messrs. Stanger and Blount in thinking that the consulting chemist, at least, should be untrammeled in the choice of his methods, it is, nevertheless, unfortunately true that no general analytical chemist is or can be equally familiar with all lines of work, nor are all of equal judgment in the se-lection of methods.   Men of skill and judgment can often arrive at like results by diverse routes, but it is certain that this is not yet so with respect to all of the stages of a silicate analysis, even so simple a one as that of cement, and till this condition is

reached I think it were well to prescribe the procedure at certain stages.

But, after all, no amount of careful attention to any analytical process is of much avail unless the materials used are of good quality. Too many chemists, as appears from the replies furnished in the present case, assume, without positive knowledge, that those used by them are satisfactory; others report one or the other as of good quality without giving any quantitative data in support of such an assertion. No chemist can be said to do justice to his employers or patrons who does not *know* what order of error his results may include, arising from impurities in reagents and the solvent action of those reagents on his utensils, or from other causes either preventable or admitting of exact correction. Too often, beyond doubt, is a known contamination thoughtlessly excluded as negligible when, in fact, a quantitative test might have shown the falsity of the belief.

FOURTH SESSION OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS.

HELD IN BERLIN, GERMANY, JUNE 4, 1903.

The following were present:

Professor Dr. A. Herzfeld, chairman.

Privy councilor, Prof. Dr. Landolt, Berlin.

Baron von Donner, chairman of the *Verein der am Zuckerhandel betheiligten Firmen*, Hamburg.

Privy Councilor Koenig, chairman of the board of directors of the *Verein der Deutschen Zuckerindustrie*, Berlin.

Professor Dr. Brodhun, representative of the *Physikalisch-Technische Reichsanstalt*, Berlin.

Professor Dr. Schoenrock, *idem*, Berlin.

Privy Councilor Professor Dr. von Buchka, delegate of the *Kaiserliche Reichsschatzamt*, Berlin.

Government Councilor Weinstein, representative of the *Kaiserliche Normal Aichungsamt*, Berlin.

Government Councilor F. Strohmer, Vienna, Austria.