THE TECHNICAL ANALYSIS OF CEMENTS.

BY S. F. PECKHAM.

Received October 1, 1904.

THE recent publication of the paper, by Mr. Bertram Blount, on "The Analysis of Portland Cement,"[1] again brings to the attention of chemists this important question that had been allowed to slumber for some months.

The very satisfactory results and conclusions reached by Mr. Blount, with which I almost wholly agree, led me to a reperusal of the papers read by Dr. Hillebrand, and to a reconsideration of the subject. The practical value of the conclusions reached by Mr. Blount cannot be overestimated, and I say this without any intention of underestimating the intrinsic value of all the work done by Dr. Hillebrand,[2] and Mr. Richardson's committee. Whether or no it is desirable to formulate a process of analysis that all chemists may be expected to follow, the indirect results that have followed the work of this committee and the discussion that has proceeded from it, have proved to be of such value as to wholly justify all that has been done by all the parties concerned.

I think, however, that in the presentation up to this date, several very important aspects of the general subject have been lost sight of or overlooked. The discussion has proceeded as if there was little or no variation in the quality of cements, also as if there was one invariable purpose in the analysis of cements, and further, the analysis of the slurry and other substances used in the manufacture of cement has been mixed up with the analysis of cements, as if the sole object of the committee had been to devise the best scheme for the analysis of a uniform material for a uniform purpose.

Now I think it is quite clear that the problems presented to a chemist in a cement manufactory, and the problems presented in a city laboratory, and the problems presented to Dr. Hillebrand, are wholly different and require for their solution consideration of wholly different methods of procedure. The problems presented to Dr. Hillebrand were wholly scientific and have been treated by him in a manner that leaves nothing to be desired. If

---

[1] This Journal, **26**, 995.

[2] *Ibid.*, **25**, 1180.

I understood him correctly, in a conversation, he said that the technical aspects of the subject had not been presented to him and had not been considered by him. Such a conclusion is to be reached from a perusal of his papers. A further conclusion is to be reached by their perusal, *viz.*, that such methods of manipulation as he recommends, intrinsically valuable as they are, can be used to very little purpose by the class of manipulators that he describes.

It is to be presumed that a majority of these men who work with dirty water and impure reagents have passed scores of examinations successfully, and have worked up with the aid of their intructors, a thesis for a doctor's degree, cramming themselves full of information about things without the slightest appreciation of the temperamental and psychological qualities essential to the solution of chemical problems. I once remarked to a young professor of chemistry that a successful chemist must be a creator. He stared at me in open-eyed wonder and asked me where I could find one. What more striking demonstration could be found of the truth of Sir William Ramsay's strictures on technical education, that present methods develop memory and leave the inventive faculties dormant; that they show only what a man knows and not at all what he can do.

To return to our subject, it seems to me that while the strictly scientific aspects of the subject have been discussed in a masterly and well-nigh exhaustive manner, resulting in the presentation of a large amount of analytical data of the greatest value, the questions have been left wholly undetermined whether or no ultimate methods of analysis are to be applied indiscriminately to the solution of the three classes of problems mentioned above; or, if proximate methods are preferable, in what cases are they preferable?

Those engaged in the manufacture of cement can best decide what method of analysis will best solve the problems presented to them.

So, too, those who use cement and those who control the use of cement can best decide what methods are best suited to the time, place, conditions and identity of the problems presented to them for solution. For illustration: In a laboratory where determinations of lime are of daily occurrence, the use of permanganate solution may be both convenient and expeditious; but in a laboratory where the work is very varied and the aggregate of lime determinations does not occupy more than six weeks in a year, more time is lost in adjusting the permanganate solution than is saved by its use. There are a multitude of reasons, too numerous to mention, why the judgment of Mr. Blount is sound, that each chemist should be left free to decide for himself what analytical methods he will use, for if the analyst is not capable of making this decision, he is like a general in the field, subject to the dictation of a bureau.

Instead of having a number of uniform problems presented to this laboratory relating to cements, scarcely two of them have been exactly alike. To treat them uniformly by the most elaborate method of ultimate analysis, even as faultlessly arranged as that of Dr. Hillebrand, with determinations of titanium and phosphates, carried to a thousandth of a per cent., and with silica twice evaporated, and all the other refinements, would be a waste of time to little or no purpose. First-class cements containing a minimum of insoluble matter are rarely brought to this laboratory. The first determination I make is for "matter volatile at a red heat." For this purpose we, some time ago, installed an electrical muffle that with a current of given intensity, controlled by a rheostat, gives a uniform low red heat. Using two half-ounce platinum crucibles, duplicate determinations can be made with great accuracy.

I then weigh out 5 grams of the cement, just as it is received. To dry or pulverize it would make another and different sample of it. I use 5 grams instead of 0.5 gram for the reason that I have found, by considerable experience with students, that the number of human beings who are endowed by nature with the capacity to manipulate successfully and accurately very minute quantities, is, as a rule, very small. If 5 grams are taken, on an average there will be left enough insoluble residue for examination by fusion, if desired. True, there is more silica dissolved on an average than is necessary; but, generally, when a reasonably large amount is taken, the errors are compensated by a smaller proportional personal equation and smaller loss. All of the *cement* is decomposed by 10 per cent. hydrochloric acid. If the solution is made slowly and with care, no soluble silica is rendered insoluble, hence there is no need of the use of sodium carbonate. No process for the manufacture of cement is practically perfect, hence a small percentage of overburned or underburned slurry is to be expected in an average sample of even the best cement, along with an always present percentage of the ash of the coal that is blown into the rotary kiln. None of this material is cement and no method of analysis should be used, such as the use of strong acid that will decompose the ash, or of sodium carbonate that may dissolve part of the silica that is not in combination as cement, and thereby increase the percentage of silica apparently present as a constituent of the cement. While in this particular I do not agree with Mr. Blount, I do not question his conclusions concerning coarse cements that dissolve slowly. The solution cannot be hurried. A great deal of work has been done in this laboratory upon several hundred samples of cements of very differing quality. In no case, that has been tested, has any lime been found in the residue from 10 per cent. hydrochloric acid. An attempt was made to secure an acid that would decompose calcium carbonate and leave the cement intact, but wholly without success. Organic acids that were strong enough to decompose carbonates invariably decomposed the cement and sometimes rendered the silica insoluble.

Applied to several hundred problems, now for several years, the method that I recommend for bringing the silica that forms a part of the cement into solution, has been found to be wholly satisfactory for technical purposes. I, therefore, insist that it is neither "puzzolanic material" nor ashes that should be decomposed, but cement. When Mr. Blount admits that by the use of either supplementary grinding or strong acid, other silica than that constituting cement is brought into solution along with that contained in the cement, he yields all that for which I have been so long contending and which Dr. Hillebrand recommends. I evaporate the silica solution over night over a water-bath heated by an electrical stove. Morning usually finds the residue dry at a temperature below the boiling-point of water. Heating to a temperature of about 250° F., on an electrical stove, completes the dehydration at a uniform and low temperature. I am not prepared to say that small quantities of silica do not remain in solution on a single evaporation, but for technical purposes it is a negligible proportion of that contained in 5 grams.

The filtrate from the silica is made up to a liter and two portions, of 100 cc. each, are measured into two Becher glasses. The average technical analyst has no time to redistil ammonium hydroxide. It is much more economical of time to assume a contamination with ammonium carbonate and reprecipitate. This is not a long operation, especially with a filter pump, and is *always* safe. For technical purposes the lime and magnesia are easily determined with one precipitation each, although each may be contaminated with a trace of the other.

It is rare that for technical purposes a determination of carbon dioxide or alkalies is necessary.

While thanking Dr. Hillebrand and Mr. Blount for all the good things they have said and done, I am confident that the scheme above set forth will be found to furnish all the information necessary for the solution of a great number of technical problems, for which the elaborate niceties of Dr. Hillebrand's scheme were never intended, and for which they should never be recommended.

LABORATORY OF THE COMMISSIONERS OF ACCOUNTS,
NEW YORK, September 30, 1904.

[CONTRIBUTION FROM THE UNIVERSITY OF ILLINOIS AGRICULTURAL EXPERIMENT STATION NO. 12.]

THE DETERMINATION OF ORGANIC CARBON IN SOILS.

BY J. H. PETTIT AND I. O. SCHAUB.

Received September 16, 1904.

IN CONNECTION with the chemical side of the soil investigations now being carried on at this Station, it was desirable to know the organic carbon content of a large number of soils. The copper oxide combustion method was too long and tedious, and the wet combustion method, using potassium dichromate and concentrated sulphuric acid, did not give complete combustion on chemically pure organic compounds like sugar. Accordingly, Parr's[1] method for carbon in coal was tried for soils. After some modifications this method gave results which compare very favorably with the copper oxide combustion method, and it has the advantage of being much more rapid than other methods used.

---

[1] This Journal, 26, 294.