

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

A METHOD FOR DETERMINING CALCIUM OXIDE IN QUICKLIME.

BY W. E. STONE AND F. C. SCHEUCH.

Received September 1, 1894.

THE value of quicklime is based upon the amount of calcium oxide which it contains. This value may be diminished by the presence of other substances originally present in the limestone, consisting usually of magnesia, alumina, silica, and iron; by incomplete ignition in the lime-kiln, on account of which some calcium carbonate fails to be converted into calcium oxide; and lastly, by a partial "slaking," by which a portion of the calcium oxide reverts to calcium carbonate.

An analysis of quicklime, therefore, should show not only the amount of calcium present in distinction from other elements, but should distinguish between the calcium as oxide and other forms of combination. The customary gravimetric method, based upon solution of the calcium compounds in acids, precipitation as calcium oxalate, ignition, etc., attains only the first of these requirements and affords no data for judging of the original condition of the calcium thus found. Consequently this method may furnish erroneous conclusions with regard to the commercial value of the material examined.

The method here proposed enables one to determine with a high degree of accuracy and rapidity the actual amount of calcium oxide in quicklime. It is based upon the well-known fact that

the alkaline earths form definite compounds with sucrose, called saccharates. Several such compounds are known with barium and strontium. With calcium oxide, sucrose forms at least three compounds, the mono-, di- and tricalcium saccharates, containing respectively one, two, and three molecules of calcium oxide to one of sucrose. The two first are formed when quicklime is dissolved in the cold in a sucrose solution. On heating this to boiling, a precipitate is thrown down consisting in the main of the tricalcium saccharate.

Numerous authorities may be quoted with regard to the solubility of calcium oxide in sucrose solutions of which the two following will suffice for citation.

Berthelot¹ gives the maximum solubility in solutions of sucrose of varying strength.

Grams sugar in 100 cc...	0.096	0.400	1.058	1.386	2.000	4.850
CaO dissolved.....	0.154	0.194	0.281	0.326	0.433	1.031

The following data are from Schatten.²

In ten grams of sugar solution of different percentages:

Per cent.....	1.	4.	8.	12.	16.
Grams CaO dissolved,	0.029	0.080	0.160	0.271	0.394

Numerous other references indicate the ready solubility of calcium oxide in sucrose solutions, and the apparent possibility of applying this fact to the separation of the actual calcium oxide from the other constituents of quicklime, led us to make the following studies:

1. The conditions under which calcium oxide is dissolved in sucrose solutions:

Lamy³ has shown that solubility varies inversely with the temperature. Ten liters of ten per cent. sucrose solution, at the given temperatures, dissolved the stated amounts of calcium oxide.

Temperature C°.....	0°	15°	30°	50°	70°	100°
Grams CaO dissolved.....	250	215	120	53	23	15.5

For our experiments, pure calcium oxide was prepared by igniting pure calcium carbonate to a constant weight. It was

¹ *Ann. Chim. phys.*, [3], 46, 176.

² Von Lippmann, *Die Zucker-Arten*, 109.

³ *La Sucrierie indigene et Coloniale*, 11, 19.

found by repeated experiment that one gram of this material was easily soluble in 150 cc. of a ten per cent. sucrose solution after agitating fifteen to twenty minutes at ordinary temperature. To accomplish perfect solution it was necessary that the material be finely pulverized. If heat were employed, the lime was converted into a pasty, insoluble mass which, however, dissolved on cooling.

2. The degree of solubility of calcium oxide in sucrose solution. Repeated experiments gave the following results :

One gram of pure CaO was only partly dissolved in 100 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 150 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 100 cc. of a ten per cent. sugar solution.

One gram of pure CaO was completely dissolved in 150 cc. of a ten per cent. sugar solution.

From these results it appears that not less than 150 cc. of a ten per cent. solution of sucrose could be safely employed to dissolve the calcium oxide in one gram of quicklime.

3. Behavior of other constituents of quicklime toward sucrose solutions :

Besides calcium oxide, quicklime usually contains more or less iron, alumina, magnesia, and silica. In addition to these, calcium carbonate may also be present. The behavior of these toward sucrose solutions was studied in detail with the following results :

Magnesia. Pure magnesium oxide, specially prepared, was treated with a ten per cent. solution of sucrose. One hundred and fifty cc. of the latter, after shaking with one gram of magnesium oxide for thirty minutes, were filtered and treated with ammonia and sodium phosphate, but only the faintest turbidity resulted. Again, one gram of magnesium oxide was shaken with 150 cc. of sucrose solution, filtered, and the filtrate titrated with standardized hydrochloric acid, and an equivalent of 0.001 gram of magnesia was found, or one-tenth of one per cent. These results show that magnesia is not appreciably soluble under the given conditions. Indeed, the existence of a com-

pound between magnesia and sucrose is doubted. On the other hand, magnesia is said to be freely soluble in a solution of calcium oxide in sucrose.¹ To test this point, mixtures of pure magnesium and calcium oxides were treated with sugar solutions as follows: One-half gram of each were mixed and shaken with 150 cc. of sugar solution. A considerable portion of the material was insoluble. We filtered and titrated the filtrate with standardized acid, the result being an exact equivalent of the calcium oxide employed. Again, one-half gram of each were mixed and treated with sugar solution as before. We filtered and precipitated the calcium from the filtrate by means of ammonium oxalate. The filtrate from this showed only slight turbidity when treated with ammonium and sodium phosphate. These results show that magnesium oxide is not soluble to an appreciable degree in sucrose solution containing calcium oxide, under the stated conditions.

Alumina was found quite insoluble, no appreciable amount being found in the filtered sucrose solution.

Calcium carbonate was also insoluble to any appreciable degree in the ten per cent. sucrose solution under the stated conditions.

Ferric oxide shaken with ten per cent. sugar solution was also insoluble. Schachtrup and Spunt² mention that ferric oxide inverts sucrose but not in an alkaline solution. We have verified this by heating a small quantity of ferric oxide with a sugar solution; the latter soon acquired the power of reducing Fehling's solution. But when the same experiment was repeated with the addition of some calcium oxide no inversion occurred. It is evident, therefore, that the iron contained in quicklime would not be affected by sucrose solution.

4. The determination of calcium oxide when dissolved in sucrose solution:

Calcium oxide when dissolved under the preceding conditions admits of determination, either gravimetrically by precipitation as calcium oxalate or volumetrically by titration with hydrochloric acid. Several comparisons of the two methods were made, using known amounts of pure calcium oxide and while

¹ Von Lippmann, *Die Zucker-Arten*, 148.

² *Pharm. Cent. Halle*, 34, 148.

each were accurate to the extent of yielding the theoretical numbers, the volumetric method was found preferable on account of its greater rapidity. For the latter method, standardized hydrochloric acid of about fifth-normal strength was employed, using tropaeolin or rosolic acid as an indicator.

5. Application of the preceding data to the analysis of quicklime.

Following the conclusions derived from the preceding tests, several samples of quicklime were analyzed for calcium oxide. They were all in a fresh state and contained little calcium carbonate.

In each case, approximately one gram of the finely pulverized material was shaken with 150 cc. of a ten per cent. sucrose solution during twenty minutes, the solution filtered and the clear filtrate titrated with standardized hydrochloric acid. At the same time other portions of the same samples were dissolved in hydrochloric acid and the calcium determined in the usual way by precipitation as calcium oxalate. Following are the results:

Sample.	Weight of quicklime taken, grams.	Volume of ten per cent. solution of sucrose taken, cc.	Per cent. CaO by titration method.	Per cent. CaO by gravimetric method.	Variation of volumetric method.
No. 1	1.020	150	92.12	93.00	-0.88
" 2	1.090	150	91.90	92.28	-0.38
" 3	1.006	150	92.15	93.10	-0.95
" 4	1.108	150	95.01	95.90	-0.89
" 5	1.023	150	87.30	87.70	-0.40
" 6	1.232	150	91.70	92.30	-0.60

The results by the sucrose method were in each case slightly lower than by the gravimetric method discrepancy which may be ascribed to a small amount of calcium carbonate present in the sample.

In quicklime which had become partially slaked, this discrepancy would be still greater since the sucrose method would indicate only the actual calcium oxide. Aside from this, the greater ease and rapidity of the latter recommends it in cases where the total calcium is present in the form of the oxide. An entire determination may thus be made in a half-hour with a degree of accuracy quite sufficient for all ordinary purposes.