indicates that the vanadium is reduced the solution is boiled and a rapid current of carbon dioxide passed through the boiling solution to expel the last traces of the sulphur dioxide. The titration is made on the hot solution with permanganate of a strength not to exceed twentieth-normal. The iron precipitate can be dissolved and the iron estimated in the usual way if desired.

The volume at this point can not conveniently be more than 75 cc. if the reduction with the spiral is to be carried on in one tube.

If the ore is quite rich it is well to divide the solution here and carry the reduction on in two test-tubes. The two solutions may be combined by pouring into the Erlenmeyer flask near the end of the titration and the titration completed as if the reduction had been carried on in one tube. From this point on the procedure is the same as in the reduction of the mixtures of the pure salts described above. The number of cubic centimeters of standard permanganate used in the titration of the reduced solutions in the test-tube minus three times the number of cubic centimeters used in the titration after reduction with sulphur dioxide gives the number of cc. needed to reoxidize the uranium alone from UO_2 to UO_3 .

Four samples of carnotite thus treated gave for uranium, 15.92, 15.66, 15.26, 15.46 per cent.; for vanadium, 8.47, 8.57, 8.44, 8.44 per cent.

Edgar used a Jones reductor filled with zinc in the differential reduction of iron and vanadium and of molybdenum and vanadium. In a number of experiments in this laboratory, where a zinc reductor was used for the reduction of the uranyl and vanadyl solutions, the results obtained were not so satisfactory as those obtained with the apparatus above described. If it be true that the uranium is reduced below the UO_2 state, as Pullman and others suggest, then to pass it into a solution of ferric alum at once would give too high results, as far as uranium alone is concerned, but since some provision of this kind is necessary to prevent the reoxidation of the highly reduced vanadium it appears that an error is likely to occur in one direction or the other whether the ferric alum be used or whether it be omitted.

The method above described furnishes a convenient means of separating uranium and vanadium without the necessity of gravimetrically separating these two elements and of determining each with a degree of accuracy fully equal to that which

can be obtained by any of the methods heretofore published.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, June 14, 1909.

ON THE INFLUENCE OF THE TEMPERATURE OF BURNING ON THE RATE OF HYDRATION OF MAGNESIUM OXIDE.

By EDWARD DE MILLE CAMPBELL.

Received July 1, 1909.

In 1885 a court-house in Kassel, Germany, was seriously injured by expansion of the cement used in its construction. An investigation of the cause of this expansion was made by a government commission, of which Rudolph Dyckerhoff, Dr. Ing. h. c., was Chairman. The cement used in the construction of the court-house was found to contain from 18–20 per cent. magnesium oxide. This led to a series of experiments to determine the influence of magnesia on Portland cement, and particularly the maximum amount which could be present without causing dangerous expansion. After more than twenty years of experimental work in Germany, France, England and the United States, different investigators have failed to come to complete unanimity regarding the maximum allowable per cent. of magnesia in Portland cement.

In an article entitled "Some Conditions Influencing Constancy of Volume in Portland Cements"¹ which appeared in 1906, the author, in conjunction with A. H. White, gave the results of a series of experiments extending over a period of four years, which showed that the expansion of Portland cement caused by magnesia was due to the slow hydration of free magnesium oxide, and that combined magnesia is without effect so far as expansion is concerned. The fact that the amount of expansion caused by the presence of magnesia is due more to the form in which the magnesia exists than to the total amount present offers a simple explanation for the differences in opinion of different investigators concerning the maximum allowable per cent. The expansion bars made from neat Portland cement containing free magnesia show that when kept in water the bar containing 1 per cent. of free magnesia has ceased to expand at the end of three years, that with 2 per cent. at the end of six years, while those with 3 per cent. and 4 per cent. have apparently not ceased expanding after eight years' immersion.

¹ *J. Am. Chem. Soc.*, **28**, 1273, Oct., 1906.

For many years it has been well known that certain natural cements, which are burned at a comparatively low temperature, but which often contain as much as 28 per cent. of magnesia, will give mortar or concrete as constant in volume as that made with good Portland cement. At the same time such natural cements cannot be depended upon, as not infrequently concrete made from such material will slowly expand and occasionally completely disintegrate from excessive expansion. Since these natural cements, high in free magnesia and yet giving satisfactory results, are burned at a much lower temperature than Portland cements, it would seem natural to expect that since the expansion is due to the hydration of magnesium oxide there must be some close relation between the temperature of burning and the rate of hydration.

In a special publication by Rudolph Dyckerhoff, Dr. Ing. h. c., entitled "Ueber die Wirkung der Magnesia in gebranntem Zement," published

44.40 per cent., loss on ignition 51.06 per cent., total 99.95 per cent. The composition of the burnt magnesite from such materials would be by calculation: silica 2.53 per cent., alumina and ferric oxide 2.70 per cent., calcium oxide 3.96 per cent., magnesium oxide 90.78 per cent. If there was no combination of magnesium oxide after dissociation of the carbonate with silica, alumina or ferric oxide, the amount of water required to completely hydrate the magnesia according to the equation

would be 40.51 per cent. of the weight of the burnt magnesite. Under the same conditions, the amount of water which would be required to satisfy the equation

would be 1.27 per cent. of the weight of the burnt magnesite.

In burning the various samples the method of procedure was substantially the same in all the

TABLE I.

Length Hydr.	500°.	600°	700°.	800°.	900°.	1000°.	1100°.	1200°.	1300°	1400°.	1450°.
1 day.....	24.83	36.61	36.51	36.52	23.40	18.00	7.61	0.43	0.46	0.58	0.34
3 days.....	25.45	37.63	37.92	38.65	41.00	41.93	22.84	2.05	1.25	1.24	0.93
7 days.....	25.64	37.93	38.30	38.51	42.26	42.38	39.22	4.85	2.17	1.85	1.55
14 days.....	25.89	38.21	38.55	38.72	42.59	42.73	41.65	15.28	3.32	2.74	2.43
21 days.....	26.09	38.38	38.69	38.89	42.75	43.06	42.34	32.23	4.43	3.56	3.29
28 days.....	25.48	38.03	38.45	38.64	42.05	42.73	42.13	36.15	5.75	4.11	3.35
2 months.....	30.58	40.63	40.61	40.41	44.46	44.39	43.97	38.92	17.36	13.24	10.64
3 months.....	30.51	40.38	40.47	40.33	44.51	44.57	44.69	39.12	20.29	17.55	14.81
4 months.....	30.66	40.38	40.47	40.29	44.58	44.57	44.69	40.02	22.55	20.48	17.55
6 months.....	30.59	40.35	40.45	40.29	44.64	44.70	44.86	40.48	24.54	24.12	20.45
9 months.....	30.39	40.35	40.39	39.94	44.72	44.85	45.18	41.19	27.48	27.60	22.59
12 months.....	30.34	40.34	40.53	40.32	44.88	44.92	45.33	41.34	28.99	28.12	23.31
18 months.....	29.99	40.03	40.14	40.03	44.63	44.54	45.34	41.74	31.22	30.31	24.85

in 1908, the author summarizes the results of his own experiments extending over a period of more than twenty years, and assumes that magnesium oxide burned at a low temperature hydrates readily and completely when immersed in water, but shows that the same oxide, when burned in a wind furnace at a temperature such as is employed for sintering Portland cement, combined with only about 3.5 per cent. of water during each of two evaporations to dryness.

The object of the experiments here described was to determine the quantitative relation existing between the temperature at which magnesium oxide from magnesite was burned and the rate at which such magnesium oxide would combine with water at ordinary temperature to form the hydroxide. The magnesite used for the work had the following composition: Silica 1.24 per cent., alumina and ferric oxide 1.32 per cent., calcium oxide 1.94 per cent., magnesium oxide

cases. For temperatures up to 1000° C. 16-18 grams of the finely ground magnesite, contained in a magnesium oxide crucible, were placed in a Heraeus platinum resistance furnace. Two standardized platinum-rhodium thermocouples were used for measuring the temperature. One couple was placed in the annular space between the crucible and the side of the furnace, while the other was embedded in the center of the finely ground magnesite. The temperature of the furnace was gradually raised until the thermocouple inside the crucible containing the magnesite had reached the desired temperature, and after this had been reached the temperature was maintained for one hour. The furnace was then allowed to cool and the burnt magnesite removed, ground to pass a 100-mesh sieve, and quickly stoppered. For samples burned above 1000° C. the magnesite was first subjected to burning at a low red heat in order to completely remove carbonaceous matter and so prevent de-

Hydration of MgO.

Table II.

terioration of the thermocouple embedded in the magnesite when a high temperature was reached. These samples were burned in a specially designed platinum resistance furnace which was capable of maintaining a temperature of 1450°C . for a good many hours without volatilization of the platinum and consequent burning out. The control of the temperature was such that in no case did the thermocouple inside the crucible containing the magnesite vary more than four degrees in the hour during which the material was being held at constant temperature.

Samples of one gram each of the burnt magnesite, ground to pass a 100-mesh sieve, were placed in a series of weighed porcelain crucibles. Sufficient distilled water was then placed in each crucible to completely cover the sample. As soon as the samples were covered the crucibles were placed in a vacuum desiccator containing concentrated sulphuric acid, and the water was allowed to evaporate. Samples which were covered with water one day and placed in a vacuum desiccator over sulphuric acid appeared dry the following day. The rack containing the set of crucibles was then placed in a drying-oven at from 102° – 105°C . and allowed to remain over night. After cooling, the crucibles were weighed, and the gain in weight taken as the one-day hydration. After the one-day hydration water was again added, and the samples allowed to stand in a closed desiccator containing some water for two days, after which they were again dried *in vacuo* over sulphuric acid for one day, and again in a steam drying-oven over night. This second gain in weight was taken as the hydration after a total of three days. A similar method of hydrating and drying—first *in vacuo*, followed by steam drying-oven—was used for the hydrations up to and including the twenty-eight day test. Through an oversight the samples in this last case were left in the drying-oven two days before weighing. The fact that the samples dried in the drying-oven lost appreciably after prolonged drying led to a change in the method of drying after the twenty-eight day test. Beginning with the two-month test the samples, after allowing to stand covered with water at room temperature, were placed in a vacuum desiccator over sulphuric acid and allowed to remain until the weight had become practically constant. This usually required from seven to nine days. The percentage gain in weight of the various samples, after the different periods of hydration, is given in Table I.

The table shows clearly that at 500°C . the magnesite was not completely dissociated in one hour. Experiments made in this laboratory upon calcite showed very slight dissociation at 600°C . after an hour's heating. Since magnesium oxide alone probably exists as such in the sample burned at 600°C ., and since such magnesium oxide, as stated in the earlier part of this paper, would require 40.51 per cent. of the weight of the burnt magnesite for complete hydration, this amount has been taken as the basis for computing the curves given in Table II, which shows graphically the progress of the hydration.

A study of the curves, considered in connection with the fact that samples after hydration lose some of their water when dried in a steam-oven, seems to indicate the following conclusions:

1. That magnesite is not completely dissociated at 500°C . in one hour under the conditions used in the experiments.
2. That dissociation of the magnesium carbonate is complete at 600° , while that of calcium carbonate is not.
3. That the hydration of magnesium oxide burned at 600° , 700° or 800°C . is practically complete in three days.
4. That between 800° and 900°C . the calcium carbonate is dissociated, and that combination takes place between basic and acidic oxides, resulting in the formation of silicates or aluminates. The silicates or aluminates so formed combined with more water than would be required for the complete hydration of the basic oxides alone.
5. That a change in the constitution of the magnesium oxide sets in between 1000° and 1100°C . resulting in a marked decrease in the rate of hydration, and that this change becomes more marked with rise of temperature of burning, until at 1450°C ., or nearly the temperature required for burning Portland cement, the magnesium oxide after eighteen months' immersion in water has combined with only 61.4 per cent. of the water required for complete hydration.

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June 18, 1909.

FREE LIME IN PORTLAND CEMENT. A MILL STUDY.

By ARTHUR G. SMITH.
Received July 17, 1909.

The purpose of this paper is to present actual results obtained by testing for free lime both the night and day runs of portland cement as manu-