[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PORTLAND CEMENT ASSOCIATION]

The Reactions between Silica and Calcium Oxide in Aqueous Solutions and their Relation to Pozzolanic Action

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Our modern conception of pozzolanas defines them as materials which, though not cementitious in themselves, contain constituents which will combine with calcium oxide at ordinary temperatures in the presence of water to form stable insoluble compounds possessing cementitious properties. Most natural or artificial pozzolanic materials are generally composed of silica, alumina, iron oxide, and calcium oxide. There may also be present magnesia, potassium, and sodium oxides, and possibly other elements in very small quantities. In contrast to portland cement, no definite chemical composition can be ascribed to pozzolanas; the type of oxides present and their percentages vary within wide limits. They are materials of very complex mineralogic aspects, and complete petrographic researches are still lacking. Only one thing is common to all pozzolanas, and that is their ability to harden under water or in air in the presence of moisture when mixed with calcium oxide or a material which liberates calcium oxide.

Many investigations have failed to produce fundamental data because of the complexities of the systems studied. From previous work it has been established that the presence of water, silica, and calcium oxide is important for the development of pozzolanic action. It was decided, therefore, to confine the present study to the reactions between silica and calcium oxide in aqueous solutions, thus eliminating many complicating factors.

Experimental Part

Apparatus and Procedure.—An electrical conductivity method was selected, since this gave promise of providing a ready means of following continuously the reactions taking place. All experiments were carried out at a constant temperature of 30 ± 0.01° in a thermostatically controlled water-bath. For measuring the electrical conductivity, a precision slide wire Wheatstone bridge hookup was employed with a conductivity cell of the dip type. The constant of the cell was determined at 30° with 0.01 N potassium chloride solution and was found to be 0.1191. Conductivity water, prepared in a specially designed Pyrex still which produced a satisfactory water with a specific conductivity of less than 1.2×10^{-6} mho, was used in all experiments.

It was necessary to determine the conductivities of calcium oxide solutions at various concentrations, which was done over the range of from very dilute solutions to the saturation point. The stock solution with an excess of the oxide to ensure constant saturation was stored in a paraffin-lined glass bottle. The concentration of the solution was determined gravimetrically and by titration with standardized hydrochloric acid.

For the conductivity measurements mentioned above, measured quantities of the stock solution were diluted with conductivity water so as to provide the desired range of concentration. The results were plotted on large-scale coördinate paper in terms of grams of calcium oxide per liter and the corresponding electrical conductivities of the solutions. With this graph it was possible to determine accurately and rapidly the concentration of any calcium oxide solution by determining its electrical conductivity.

The silica used in this study was C. P. silicic acid, containing 80.00% SiO_2, ground to pass a 300-mesh sieve. In the first series of experiments, which were necessary to obtain information on the general nature and rate of reaction and the best manner of proportioning the three reacting agents (silica, calcium oxide, and water), the reaction chamber consisted of a 3-necked Pyrex flask. One liter of calcium oxide solution of the desired concentration was transferred to the flask immersed in the water-bath. The center tubulature was provided with a mercury seal stirrer rotating at a speed of 1000 r. p. m. Extreme care was taken to protect all calcium oxide solutions from exposure to air. The conductivity of the solution was determined after the solution had reached the bath temperature. Then a weighed amount of silica was introduced and conductivity readings again taken immediately. While the solution was being agitated continuously, measurements were made at short intervals until equilibrium was reached.

The conductivity method for determining the rate of combination of calcium oxide with silica proved very convenient and successful. The procedure permitted following accurately the reactions from the very earliest stages to final equilibrium without disturbing the system by the withdrawal of portions of the solution. The time required for one measurement was only thirty seconds. The method is distinguished by perfect reproducibility, and the entire course of the reactions can be plotted in small intervals over the entire range.

The amount of silica per liter of calcium oxide solution was kept constant at 0.8954 g. in this series of tests, and the concentration of the solutions ranged from 0.025 to 1.191 g. of calcium oxide per liter. In all cases the measurements showed a decided drop in electrical conductivity during the first few minutes of contact of the reacting agents, indicating a lowering of the calcium oxide content of the solution. As the time of agitation progressed, the rate of drop in conductivity became less, and finally a state was approached asymptotically in which there was no more

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change in conductivity. The more concentrated the initial calcium oxide solution was, the more slowly the final state of equilibrium was reached, requiring agitation periods of several months. Because of this slowness of reaction and to enable several tests to be run at the same time, a shaker was installed in which eight Erlenmeyer flasks of 500-cc. capacity were agitated simultaneously. To facilitate the interpretation of the results, silica and calcium oxide in the suspensions were proportioned on a molecular basis rather than on the gram basis used in earlier experiments.

The second series included thirty-four samples in which the molecular ratios of CaO to SiO_2 at the beginning of the experiment (initial ratios) were varied from 0.05 to 3.75. The amount of calcium oxide ranged from 1.0 to 75.0 milliequivalents (m. e.). The amount of silicon dioxide was 20.0 m. e. in most cases, although some samples contained 10.0 and 30.0 m. e. of silicon dioxide in order to broaden the field of investigation. In the range of high calcium oxide, above the point of saturation, solid calcium oxide was added, together with the silicon dioxide, to the saturated calcium oxide solution.

Equilibria in the System Calcium Oxide–Silica–Water.—The data on equilibria secured in this system are best explained by means of Table I and Fig. 1. In the first two columns of Table I are recorded the amounts of calcium oxide and silica which were allowed to react in water until equilibrium had been reached. The term equilibrium in this report refers to an apparently steady state in which there is practically no further change in conductivity with time. It is understood that such a state does not represent a true equilibrium, but the latter is attained exceedingly slowly at the temperature of the experiment, and the differences between apparent and true equilibria can be neglected without affecting the findings of this investigation. The initial ratios of CaO to SiO_2 are recorded in the third column. The conductivities of the solutions when equilibrium has been reached are given in the fourth column, and the amounts of uncombined calcium oxide remaining in solution at equilibrium (which were calculated from the conductivity data) are listed in the fifth column. The last column shows the ratio of combined CaO to SiO_2 at equilibrium.

Interpretation of Results.—An attempt was made to establish the nature of the combination of calcium oxide with silica, the question being whether it is a chemical reaction or an adsorption, or both. It was sought to determine whether the removal of calcium oxide from solution by the silica follows the Freundlich adsorption isotherm, which is generally taken as characteristic of a surface adsorption, or whether the observed data would suggest a different interpretation. Since the Freundlich adsorption isotherm is usually expressed by the equation

$$X = aC^{1/n} \text{ or } \log X = \log a + 1/n \log C \quad (1)$$

a straight line should result if the logarithms of the adsorbed quantities are plotted against the logarithms of the corresponding concentrations.

TABLE I

EQUILIBRIUM DATA OF THE CaO–SiO_2 REACTIONS

M. e. per liter CaO	M. e. per liter SiO_2	Ratio of CaO to SiO_2 at start	Conductivity of soln. at equil., mho	Uncombined CaO in soln. at equil. m. e. per liter	Ratio of comb. CaO to SiO_2 at equil.
1.0	20.0	0.05	0.000053	0.21	0.040
1.0	10.0	.10	.000086	.35	.065
2.0	20.0	.10	.000110	.44	.078
3.0	30.0	.10	.000115	.46	.085
3.0	20.0	.15	.000160	.64	.118
4.0	20.0	.20	.000215	.86	.157
6.0	30.0	.20	.000237	.95	.168
5.0	20.0	.25	.000278	1.12	.194
6.0	20.0	.30	.000327	1.32	.234
9.0	30.0	.30	.000348	1.39	.254
7.0	20.0	.35	.000362	1.46	.277
8.0	20.0	.40	.000374	1.50	.325
12.0	30.0	.40	.000374	1.50	.350
9.0	20.0	.45	.000375	1.50	.375
10.0	20.0	.50	.000370	1.49	.426
15.0	30.0	.50	.000370	1.49	.450
12.0	20.0	.60	.000368	1.48	.526
14.0	20.0	.70	.000445	1.79	.611
16.0	20.0	.80	.000548	2.20	.690
18.0	20.0	.90	.000647	2.60	.770
20.0	20.0	1.00	.001056	4.27	.782
22.0	20.0	1.10	.001525	6.24	.788
24.0	20.0	1.20	.002001	8.42	.779
26.0	20.0	1.30	.002350	10.06	.797
28.0	20.0	1.40	.002576	11.10	.845
30.0	20.0	1.50	.002763	11.95	.903
32.0	20.0	1.60	.003068	13.37	.932
34.0	20.0	1.70	.003206	14.05	.998
37.0	20.0	1.85	.003453	15.23	1.089
40.0	20.0	2.00	.003792	16.83	1.159
48.0	20.0	2.40	.004834	21.93	1.304
56.0	20.0	2.80	.005497	25.32	1.534
70.0	20.0	3.50	.006908	32.52	1.874
75.0	20.0	3.75	.007610	36.09	1.946

Figure 1 shows the results of the experiments entered on log–log paper. The concentrations of the calcium oxide solution at equilibrium in milliequivalents ($C \times 10^3$) are plotted as abscissas and the ratios of combined CaO/SiO_2 (X) as ordinates (Columns 5 and 6, Table I). A graph consisting of several straight lines is obtained by connecting the points. The numerals accompanying these points give the molecular ratios of CaO/SiO_2 at the start of the experiments (Column 3, Table I).

The portion A–B represents equilibria attained with suspensions having initial ratios of CaO/SiO_2 from 0.05 to 0.30. The fact that all points fall upon or very close to a straight line indicates that the Freundlich equation is applicable in that range and that the calcium oxide is adsorbed by the silica in suspension. Evaluating the constants $1/n$ and a yielded the equation

$$X = 159.6\ C^{0.98} \qquad (2)$$

which enables the calculation of the adsorption of calcium oxide in the range A–B, that is, from 0.05 to 0.30 initial CaO/SiO₂ ratios.

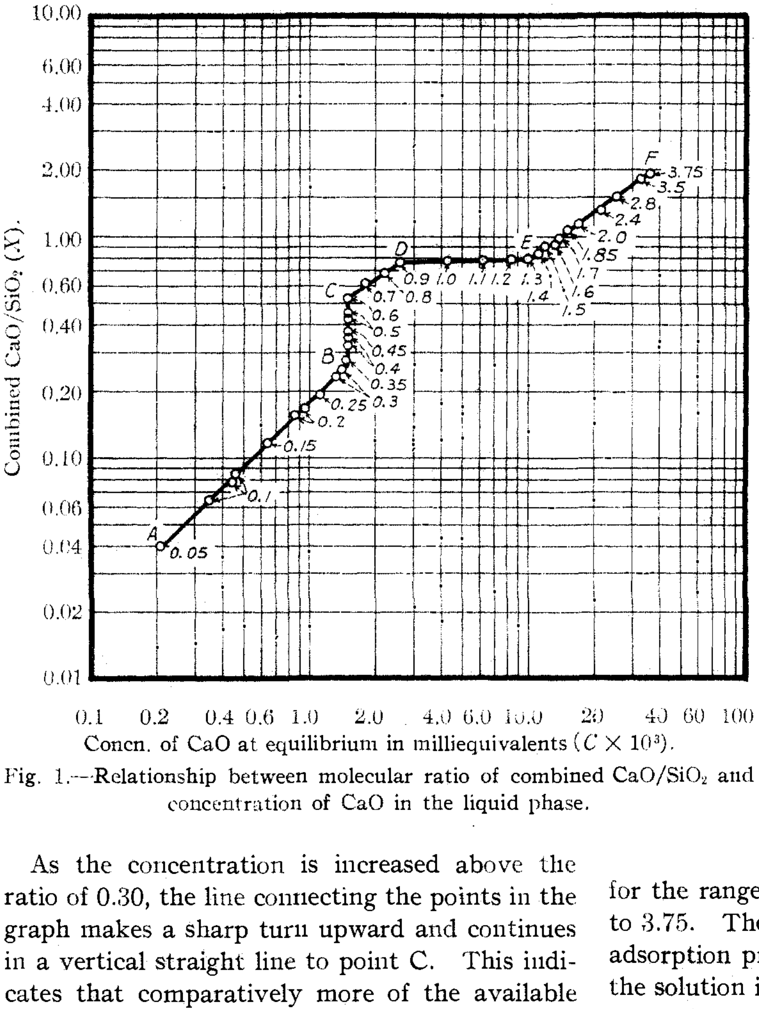

Fig. 1.—Relationship between molecular ratio of combined CaO/SiO₂ and concentration of CaO in the liquid phase.

As the concentration is increased above the ratio of 0.30, the line connecting the points in the graph makes a sharp turn upward and continues in a vertical straight line to point C. This indicates that comparatively more of the available calcium oxide is combined with silica than in the range A–B, and equilibria are being attained when the concentrations of the calcium oxide solutions have been reduced to one containing approximately 1.5 m. e. of calcium oxide per liter. C, which is at the end of this range, is located near a point where the ratio of combined CaO/SiO₂ is 1 to 2. Therefore, it seems justified to assume that, after the first phase of adsorption reactions has been completed and an equilibrium concentration of 1.5 m. e. of calcium oxide per liter has been reached, a further increase in calcium oxide concentration leads to chemical combination of calcium oxide and silica to form a hydrated CaO·2SiO₂. This combination is completed when the initial ratio of CaO/SiO₂ has been raised to 0.60.

From point C to point D the straight connecting line proceeds upward at an angle, and Freundlich's adsorption isotherm is again applicable for that range. It appears that further increases of the calcium oxide concentration lead to an adsorption of calcium oxide onto the newly formed CaO·2SiO₂ hydrate. The adsorption equation for this range is

$$X = 44.95\ C^{0.68} \qquad (3)$$

Point D on the graph is reached with a sample having an initial CaO/SiO₂ ratio of 0.9, and the ratio of combined CaO/SiO₂ becomes 4 to 5. On increasing the initial CaO/SiO₂ ratio from 0.9 to 1.3, no more adsorption is taking place. The line leads horizontally to point E. In this range, D–E, the combination of calcium oxide and silica proceeds to a state in which the ratio of 4CaO to 5SiO₂ is maintained, and only after increasing the initial CaO/SiO₂ ratio above 1.3 is more calcium oxide being combined.

Beyond point E, the line proceeds upward again, indicating a third range of adsorption reactions. The calculation of the constants gives the adsorption equation

$$X = 23.38\ C^{0.74} \qquad (4)$$

for the range of initial CaO/SiO₂ ratios from 1.3 to 3.75. The ratio of combined CaO/SiO₂ in the adsorption product at point F is 1.946 to 1, and the solution in which it is stable at equilibrium is very close to the saturation point of calcium oxide at that temperature. This suggests that a hydrated 2CaO·SiO₂ exists in a saturated solution of calcium oxide. The exploration of the field with still higher concentrations of calcium oxide is not possible with the conductivity method used in this investigation, since its usefulness ends when the solution at equilibrium is saturated.

Discussion

The study of the reactions of calcium oxide and silica in the presence of water revealed that, under the conditions of the experiment, definitely identified adsorption reactions take place. It also showed that chemical compounds are formed in which the ratios of calcium oxide to silicon dioxide are very close to 1:2, 4:5, and 2:1, corresponding to $CaO \cdot 2SiO_2 \cdot xH_2O$, $4CaO \cdot 5SiO_2 \cdot xH_2O$, and $2CaO \cdot SiO_2 \cdot xH_2O$.

The adsorptive capacity of hydrated silica for calcium oxide has been studied by Shaw and MacIntire[2] in connection with a research on the components of soils. These investigators found that "the adsorption of $Ca(OH)_2$ by hydrated silica occurs in accordance with the Freundlich adsorption isotherm, when the final concentrations of $Ca(OH)_2$ are above 0.005 *N*. When the final concentrations are less than 0.005 *N*, several inflections appear in the adsorption curve and these point to a series of chemical combinations between the $Ca(OH)_2$ and the SiO_2." No information is given in their paper about the causes of these inflections and the nature of the chemical combinations. The adsorption isotherm calculated by Shaw and MacIntire does not agree with the equation established in this paper for the same range of concentrations. This discrepancy can be explained easily by the fact that the former equation expresses the adsorption phenomena for a contact period of only five days, while the latter was established after equilibrium had been attained. The chemical combinations in concentrations below 0.005 *N* strength, or less than 5 m. e. calcium oxide per liter, the existence of which was held possible by Shaw and MacIntire, have been established in the present paper, together with the two additional ranges of adsorption reactions in the lower field of concentrations.

The possibility that adsorption reactions can take place in the system CaO–SiO_2–H_2O has been advanced also by Baylis,[3] who stated that there may be a definite chemical reaction between calcium hydroxide and hydrous oxides of silica forming a compound closely approaching $CaO \cdot SiO_2$. In addition to this, considerable calcium hydroxide appears to be adsorbed by this compound when the concentration of calcium hydroxide in the surrounding solution is increased over that necessary to form the definite compound. Although the present investigation proves the existence of adsorption phenomena, a definite hydrated calcium silicate in which the ratio of calcium oxide to silicon dioxide is unity, was not found.

Flint and Wells[4] carried out an extensive study of the reactions of calcium oxide and silica in the presence of water and state that the solid phase in equilibrium with solutions which contain only a few hundredths of a mole of calcium oxide per mole of silicon dioxide may consist of hydrated silica with a small amount of adsorbed calcium oxide. Determinations of the OH ion concentration showed that calcium oxide and silica in solution are combined in a ratio of less than 1CaO to $1SiO_2$ at low calcium oxide concentrations and at a ratio greater than 1 to 1 at high calcium oxide concentrations. It appeared that the molar ratio $2CaO:1SiO_2$ is approached when the solid phase is in equilibrium with a saturated calcium oxide solution.

The findings of the present study support the assumption of Flint and Wells that calcium oxide is adsorbed by silica at low concentrations and that a hydrated $2CaO \cdot SiO_2$ is stable in saturated calcium oxide solution. There are, however, some differences in the findings about the formation of chemical compounds in the intermediate range. While Flint and Wells obtained data which they assume to represent compositions of the ratio $1CaO:2SiO_2$ and $1CaO:1SiO_2$, the conductivity determinations revealed the formation of two hydrated silicates in which the ratios of calcium oxide to silicon dioxide are 1:2 and 4:5. No hydrated monocalcium silicate was found.

By agitating an excess of diatomaceous earth in calcium oxide solutions, Cummins and Miller[5] obtained in the solid phase a compound having a molecular ratio of CaO to SiO_2 of 5:6, corresponding to the formula $5CaO \cdot 6SiO_2$.

The question concerning the types of hydrated calcium silicates which may exist in aqueous solutions was attacked in the opposite direction by Kühl and Mann[6] by preparing anhydrous melts of calcium oxide and silica of various predetermined compositions and agitating them in calcium oxide solutions of varying concentrations. These investigators found that a hydrated calcium silicate which is less basic than $CaO \cdot SiO_2 \cdot xH_2O$ does not exist. A gel of the composition $CaO \cdot SiO_2 \cdot aq.$ is stable in a solution containing 0.131 g. calcium oxide per liter, and a series of hydrated calcium silicates exists having ratios of calcium

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[2] W. M. Shaw and W. H. MacIntire, *Soil Sci.*, **29**, 429–56 (1930).

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[6] H. Kühl and A. Mann, *Tonind. Ztg.*, **58**, 862–5, 896–7, 918–19, 930–2, 944–5, 955–7, 990–1, 1003, 1014–16 (1934).

oxide to silicon dioxide ranging from 1:1 to 2:1. Since the materials used by Kühl and Mann were synthetic melts and the products at equilibrium not formed by the combination of the basic constituents calcium oxide and silica but by hydrolysis or hydration of the silicates, the results do not lend themselves to a direct comparison with the observations reported here.

Summary

On the basis of the results secured by means of the conductivity method and under the conditions of the experiment, the reactions between calcium oxide and silica proceed in the following manner:

With dilute solutions the silica adsorbs calcium oxide in accordance with the Freundlich adsorption isotherm. Above an initial ratio of CaO/SiO_2 of 0.30 and up to 0.60, chemical combination takes place, and a reaction product is formed in which the ratio of CaO/SiO_2 is 1 to 2. This product is stable in a solution containing 1.5 m. e. of calcium oxide per liter.

On increasing the calcium oxide concentration further above an initial ratio of 0.60, adsorption takes place again, which proceeds until the initial ratio of CaO/SiO_2 is 0.90 and the ratio of combined CaO/SiO_2 is 4 to 5.

The reaction product with the ratio of 4CaO to $5SiO_2$ is stable up to an equilibrium concentration of 10 m. e. of calcium oxide per liter. With higher concentrations of calcium oxide and initial ratios from 1.3 to 3.75, a third range of adsorption reactions takes place. As the point of saturation of the calcium oxide solution at equilibrium is reached, the ratio of CaO/SiO_2 in the reaction product approaches 2:1, indicating the probable existence of a hydrated $2CaO{\cdot}SiO_2$ in saturated calcium oxide solution.

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The Electron Diffraction Investigation of the Molecular Structures of (1) Phosphorus Oxytrichloride, Oxydichlorofluoride, Oxychlorodifluoride, Oxytrifluoride, Fluorodichloride, Pentafluoride, and Trifluorodichloride, and of (2) Disilane, Trichlorosilane, and Hexachlorodisilane

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The molecular structures of the halogen derivatives of the non-metals are of special interest because of the systematic deviations from additivity of bond radii which are observed in many of these substances.[3,4] With the exception of those of the first row elements, the observed distances in the halogen derivatives are all smaller than the sum of the corresponding radii for single covalent bonds. This decrease is apparently greatest in the silicon compounds and is less marked in the elements toward the right and in the lower rows of the periodic table. The effect, moreover, is greatest in the fluorides and decreases in order with the other halogens. While the regular way in which the effect varies from one element to another suggests that the same causes are operating in all of them, the nature of the causes is not entirely certain. It seemed desirable to extend the investigation of phosphorus and silicon compounds, where the effect is greatest, and we have determined the structures of a number of mixed fluorine and chlorine derivatives of phosphorus, including some oxygen compounds, as well as those of three silicon compounds.

The diffraction patterns were obtained in the usual way,[5] whereby a beam of electrons traverses a sample of the vapor and the diffracted electrons are recorded on a photographic emulsion. The apparent maxima as well as some of the minima were measured visually on a comparator, and the observed diameters were converted to the s_0 values [equal to 4π $(\sin \theta/2)/\lambda$] listed in the tables below. The s_0 values for the maxima were used with the visually estimated intensities, I_k, in the calculation of the functions shown in Figs. 1 and 8 representing the observed radial

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[2] At present National Research Fellow at Princeton University.

[3] L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934); L. O. Brockway and H. O. Jenkins, *ibid.*, **58**, 2036 (1936).

[4] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

[5] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).