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Abstract

Full Text

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FEATURES OF THE KINETICS OF SUPERSATURATION IN AQUEOUS SUSPENSIONS OF CALCIUM OXIDE

The study of the hardening of various mineral binders has shown (1–3) that the kinetics of structure formation is determined mainly by the kinetics of the supersaturation that arises in the suspension during dissolution of the initial binder. Although the literature gives measurements of the magnitude of supersaturation in suspensions of certain mineral binders (4), only for hemihydrate gypsum (5) and tricalcium (2,6) and monocalcium (7) aluminates has a maximum stable supersaturation been established, which may be regarded as the conditional solubility of the corresponding compounds.

The aim of the present work was to investigate the kinetics of supersaturation in aqueous suspensions of calcium oxide in order to explain the features of its hydration hardening and to clarify the nature of the supersaturations in these suspensions.

Fig. 1. Effect of stirring rate on the kinetics of electrical conductivity in aqueous suspensions of CaO; $T/V = 0.34\%$.
1 –120 rpm; 2 –400 rpm; 3 –800 rpm; 4 –1600 rpm; 5 –2000 rpm.

Reference literature contains no data on the solubility of CaO. However, it is known (8,9) that calcium oxide, when dissolved in water, gives solutions supersaturated with respect to $Ca(OH)_2$, and that the magnitude of these supersaturations is not constant.

The kinetics of supersaturation in aqueous suspensions of calcium oxide was determined conductometrically in a special vessel with platinized platinum electrodes, a stirrer, and a thermometer. The experiments were carried out in a nitrogen atmosphere at a temperature of $21.6 \pm 0.05^{\circ}$.

Figure 1 shows the change in electrical conductivity (concentration) of an aqueous CaO suspension as a function of the stirring rate of the suspension. Analysis of the curves in Fig. 1 shows that the stirring rate affects not only the rate at which the maximum electrical conductivity is reached, but also its absolute value. This is explained by the fact that, as the stirring rate increases, the quantity of ions that has time to pass into the bulk increases before the supersaturation in them falls owing to crystallization. Independence of the kinetics of electrical conductivity from the stirring rate is achieved only at 1600 rpm, after elimination of the limiting influence of diffusion. However, even at this stirring rate it is not possible to detect a stable supersaturation,

not depending on the size of the CaO charge, which is explained by the enormous rate of growth of nuclei that arise already at relatively small supersaturations ([9]).

The only way to detect a stable level of supersaturation is to introduce into an aqueous suspension of CaO such additives of surface-active substances ([3]) which, practically without changing the solubility, can stabilize the nuclei being formed, preventing their growth ([10], [11]) and thereby slowing the decrease of supersaturations in the liquid phase of the suspension.

Table 1

Initial concentration of SSB solution, %	Electrical conductivity of the initial SSB solution, χ, 10^8 ohm^{-1} cm^{-1}	Concentration of SSB remaining after 2 min after introduction of CaO, %	Electrical conductivity of SSB solution after 2 min after introduction of CaO, χ, 10^8 ohm^{-1} cm^{-1}
0.08	0.17	0.0125	0.05
1.6	2.3	0.175	0.17
3.2	3.7	0.23	0.45

For this purpose we used additions of sulfite-alcohol stillage (SSB) and glucose. Preliminary experiments showed that both these additions only slightly decrease the solubility of $Ca(OH)_2$. In addition, it was shown that, upon introduction of CaO, adsorption of SSB from the solution proceeds so rapidly and in such large amounts that the increase in electrical conductivity due to the residual concentration of SSB may be neglected (Table 1).

Fig. 2. Kinetics of the electrical conductivity of an aqueous CaO suspension with various additions of surface-active substances; S/L = 1.2%. 1 –without addition; 2-4 –glucose solutions: 2 –0.016%, 3 –0.08%, 4 –0.12%; 5-7 –SSB solutions: 5 –0.15%, 6 –0.3%, 7 –0.6%.

Figure 2: Fig. 2. Kinetics of the electrical conductivity of an aqueous CaO suspension with various additions of surface-active substances; S/L = 1.2%. 1 –without addition; 2-4 –glucose solutions: 2 –0.016%, 3 –0.08%, 4 –0.12%; 5-7 –SSB solutions: 5 –0.15%, 6 –0.3%, 7 –0.6%.

It is seen from Fig. 2 that the introduction of surface-active additives into aqueous CaO suspensions leads to a sharp increase in their electrical conductivity, and, when sufficiently large additions are introduced, a stable level of supersaturation is reached, remaining constant for 3-5 min and then slowly decreasing.

The constancy of this level for several minutes indicates the existence of a temporary equilibrium between the dissolution of CaO and the formation of $Ca(OH)_2$ nuclei. The dissolution process, at the optimum stirring rate (1600 rpm), proceeds at an enormous rate, since the maximum supersaturation is reached practically instantaneously.

Fig. 2. Kinetics of the electrical conductivity of an aqueous CaO suspension with various additions of surface-active substances; S/L = 1.2%. 1 –without addition; 2-4 –glucose solutions: 2 –0.016%, 3 –0.08%, 4 –0.12%; 5-7 –SSB solutions: 5 –0.15%, 6 –0.3%, 7 –0.6%.

Thus, additions of surface-active substances, by preventing the growth of nuclei, create conditions for the occurrence in the solution of a high supersaturation constant in time, despite the fact that in the presence of surface-active additives the rate of formation of calcium hydroxide nuclei even increases (12).

It was then necessary to investigate the dependence of the maximum supersaturations obtained on the size of the CaO charge. To clarify this question, equal charges of calcium oxide were successively introduced into a solution of the surface-active substance (0.5 g CaO per 250 ml of solution). This method of introducing calcium oxide prevents strong heating of the suspension, which occurs when a large charge of CaO is introduced into the solution at once, and makes it possible to carry out conductometric measurements under practically isothermal conditions. The greatest temperature rise (0.5°) is observed only upon introduction of the first CaO charge. The temperature rise upon

with the introduction of subsequent portions, decreased each time and, upon introduction of the 3rd and 4th portions, was practically equal to zero.

In Fig. 3 the moment of introduction of each portion of CaO is indicated by an arrow. From Fig. 3 it is seen that introduction of CaO into a solution of a surface-active substance leads to a sharp increase in electrical conductivity, which remains constant for several minutes. The rise in electrical conductivity

Fig. 3. Dependence of the electrical conductivity of an aqueous CaO suspension in the presence of surface-active substances on the size of the CaO portion. 1 –electrical conductivity of a saturated $Ca(OH)_2$ solution; 2 –0.8% SSB solution; 3 –0.08% glucose solution

Figure 3: Fig. 3. Dependence of the electrical conductivity of an aqueous CaO suspension in the presence of surface-active substances on the size of the CaO portion. 1 –electrical conductivity of a saturated $Ca(OH)_2$ solution; 2 –0.8% SSB solution; 3 –0.08% glucose solution

upon introduction of each subsequent portion of CaO, just like the rise in temperature, becomes ever smaller and, finally, with further introduction of calcium oxide the electrical conductivity ceases to depend on the amount of CaO in the solid phase.

The independence of the maximum electrical conductivity from the size of the CaO portion indicates the existence of a constant supersaturation level, which may be regarded as the conditional solubility of calcium oxide.

Fig. 3. Dependence of the electrical conductivity of an aqueous CaO suspension in the presence of surface-active substances on the size of the CaO portion. 1 –electrical conductivity of a saturated $Ca(OH)_2$ solution; 2 –0.8% SSB solution; 3 –0.08% glucose solution

Dissolution of CaO proceeds until the maximum supersaturation is reached, which conditionally determines the equilibrium concentration of ions in the solution in the presence of solid calcium oxide. Further dissolution occurs only as calcium oxide hydrate crystallizes out from the solution in the form of nuclei, the growth of which is inhibited by the surface-active additive. Such a temporary equilibrium is maintained as long as, on the one hand, solid calcium oxide is still preserved in the suspension and passes into solution, and, on the other hand, there is enough surface-active substance to stabilize the nuclei being formed.

After a stable level of electrical conductivity, independent of the CaO portion, had been established, attempts were made to determine the conditional solubility of calcium oxide corresponding to this level by the direct analytical method of determining hydroxyl ions in the solution. However, it turned out that the usual procedure, consisting in filtering samples of the suspension through a filter with a pore diameter of 2 μ, does not give reproducible results even when the electrical conductivity is constant, i.e., when the concentration in the solution is constant, because colloidal nuclei-particles of $Ca(OH)_2$ stabilized by the surface-active substance pass into the filtrate.

It is possible to determine the concentration of solutions containing colloidal particles potentiometrically with the aid of a hydrogen electrode after it has been shown that the surface-active substances–SSB and glucose–do not poison the hydrogen electrode.

The determined pH values were 12.98 for a CaO suspension in an SSB solution and 13.01 in a glucose solution. The smaller pH value in the first case is apparently explained by a decrease in the solubility of CaO in the presence of ...

in the absence of the calcium ion of the same name in calcium lignosulfonates. Recalculation of $p_\mathrm{a}H$ into concentration without taking into account the activity coefficient gives the value of the greatest supersaturation (conditional solubility of CaO) of the order of 2.70 g/l in the SSB solution and 2.85 g/l in the glucose solution. The actual conditional solubility of CaO is greater, since in such concentrated solutions the activity coefficient is considerably less than unity.

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CITED LITERATURE

1. E. E. Segalova, V. N. Izmailova, P. A. Rebinder, DAN, **110**, No. 5 (1956); E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, DAN, **114**, No. 1 (1957); E. E. Segalova, P. A. Rebinder, Abstracts of Reports, 4th All-Union Conference on Colloid Chemistry, 1958, p. 130.
2. E. S. Solov' eva, E. E. Segalova, ibid., p. 136.
3. E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, DAN, **113**, No. 1 (1957).
4. R. H. Bogue, *The Chemistry of Portland Cement*, N.-Y., 1947.
5. P. P. Budnikov, Gypsum, Its Study and Application, 1943; P. F. Konovalov, E. I. Morozov, Cement, **5** (1956); Ya. L. Zabezhinskii, V. B. Ratinov, T. I. Rozenberg, DAN, **108**, No. 6 (1956); V. B. Ratinov, Ya. L. Zabezhinskii, T. I. Rozenberg, DAN, **109**, No. 5 (1956).
6. E. E. Segalova, E. S. Solov' eva, P. A. Rebinder, DAN, **117**, No. 5 (1957).
7. E. E. Segalova, Z. D. Tulovskaya, E. A. Amelina, Abstracts of Reports, 4th All-Union Conference on Colloid Chemistry, 1958, p. 140.
8. P. Mecke, *Zement*, **48** (1935).

9. R. Hedin, *Chemical Processes in the Hardening of Portland Cement*, 1945.

10. A. M. Smirnova, V. P. Sukhova, Abstracts of Reports, 4th All-Union Conference on Colloid Chemistry, 1958, p. 144.

11. R. Marc. G. Jung, Physical Chemistry and Its Application to Problems of Mineralogy, Petrography, and Geology, 1933; M. Tovbin, S. Krasnova, ZhFKh, **23**, issue 7 (1949).

12. D. S. Kamenetskaya, Crystal Growth, 1957.

Note: Figure translations are in progress. See original paper for figures.