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S. I. KONTOROVICH, E. E. SEGALOVA, Academician P. A. REHBINDER

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Abstract

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THE EFFECT OF STRONG ELECTROLYTES ON THE RATE OF HYDRATION OF CALCIUM OXIDE

In the works of many authors (^{1,2}) it was shown that, with the aid of small additions of electrolytes, the rate of hydration of binding materials can be regulated over a wide range. However, the question of the mechanism by which additions of electrolytes act has not yet been definitively clarified. In recent years, detailed studies of the action of electrolytes on the rate of hydration of hemihydrate gypsum were carried out by V. V. Ratinov and co-workers (^{2}), who came to the conclusion that the action of electrolytes is reduced to a change in supersaturation, i.e., to a change in the principal crystallization parameter.

In the present work, the effect of strong electrolytes on the rate of hydration of calcium oxide was studied. The electrolytes were investigated in a concentration range that excludes the formation of any chemical compounds with lime. In the experiments, CaO of two degrees of dispersion was used: 3.0 and 0.14 m^2/g. The more coarsely dispersed CaO (0.14 m^2/g) was used to study the influence of electrolytes that accelerate hydration, since in these cases, when CaO with $S = 3.0\ m^2/g$ is used, the hydration kinetics in water and in electrolyte solutions are practically difficult to distinguish because of their very high rate. The rate of hydration was determined from the heat evolution in an adiabatic calorimeter (^{3}).

The results obtained make it possible to draw the following conclusions. All the electrolytes studied can be divided into two groups according to the character of their influence on the process of CaO hydration. Electrolytes of group I (KCl, KBr, KI, KNO_3, KNO_2, $KMnO_4$, KCNS, NaCl, $CaCl_2$, $CaBr_2$, $Ca(NO_3)_2$, $Ca(C_2H_3O_2)_2$) over the entire range of concentrations studied cause an acceleration of CaO hydration, the greater the larger the electrolyte addition. Electrolytes of group II (K_2SO_4, Na_2SO_4, K_2CrO_4, $K_2Cr_2O_7$, $K_4Fe(CN)_6$, $CaSO_4 \cdot 2H_2O$, $CaCrO_4$, $CaCr_2O_7$), with increasing concentration, cause a continuous slowing of hydration. At the same time, the action of electrolytes on the rate of hydration does not depend on their influence on solubility. Indeed, all electrolytes without common ions in the concentration range studied increase the solubility of $Ca(OH)_2$; however, some of these electrolytes, as is seen from Figs.

Figure 1

Figure 1: Figure 1

1 and 2, increase, while others decrease, the rate of hydration of calcium oxide. Electrolytes with the common ion (Ca^{2+}) at low concentrations decrease, and at high concentrations increase, the solubility of $Ca(OH)_2$; however, these electrolytes at all concentrations change the rate of CaO hydration only in one direction: they either decrease it ($CaSO_4 \cdot 2H_2O$, $CaCrO_4$, $CaCr_2O_7$) or increase it ($CaCl_2$, $CaBr_2$, $Ca(NO_3)_2$, etc.).

Since electrolytes with the common ion (Ca^{2+}) increase the supersaturation (2) arising in the process of CaO hydration as a result of an increase in the ratio $C_a, C_k/C_0$, where C_a and C_k are the concentrations, respectively, of the anion and cation, and C_0 is the solubility of calcium hydroxide, and at the same time affect the rate of CaO hydration differently, it is obvious that the action of these electrolytes on the rate of CaO hydration is not connected with their influence on supersaturation. Electrolytes with large monovalent anions, regardless of the type of cation and of their influence on the solubility of $Ca(OH)_2$, accelerate hydration, while electrolytes with multivalent anions decrease the rate of hydration of calcium oxide.

The peculiarities of the influence of electrolytes on the rate of hydration of CaO are apparently connected with the fact that the hydration of calcium oxide, in contrast to

of the hydration of hemihydrate gypsum, is accompanied by the formation of films of calcium hydroxide hydrate on the surface of the initial particles. Film formation is promoted by the high metastable solubility of CaO (4), the high dissolution rate of calcium oxide, the small value of the diffusion coefficient of $Ca(OH)_2$, considerably smaller than that of gypsum (5), and, finally, the high rate of formation of $Ca(OH)_2$ nuclei at relatively small supersaturations (6). All these factors lead to the fact that the nuclei of crystallization arise in the immediate vicinity of the surface of the dissolving CaO, creating around it a barrier film that hinders further hydration of calcium oxide. Obviously, the greater the rate of dissolution of CaO and the smaller the rate of removal of Ca and OH ions from its surface, which depends on the rate of diffusion, the more favorable are the conditions created for the formation of a newly formed film and the better protective properties the film will possess.

Fig. 1. Kinetics of hydration (by heat evolution) of calcium oxide ($S = 0.14$ m^2/g) in solutions of electrolytes with singly charged anions. $T/B = 0.25$. 1 –water, 2-9 –2.5% solutions: KJ (2), KBr (3), $KMnO_4$ (4), KNO_3 (5), $CaBr_2$ (6), KCNS (7), KCl (8), and $CaCl_2$ (9).

Fig. 2. Kinetics of hydration (by heat evolution) of calcium oxide ($S = 3$ m^2/g) in solutions of electrolytes with multiply charged anions. $T/B = 0.25$. 1 –water, 2-8 –2.5% solutions: $K_4Fe(CN)_6$ (2), $K_2Cr_2O_7$ (3), $CaCr_2O_7$ (4),

Figure 2

Figure 2: Figure 2

Fig. 3. Kinetics of dissolution of CaO ($S = 0.14$ m^2/g) from the change in specific electrical conductivity in 0.01 N electrolyte solutions. 1 —water; 2: a —KCl, b —KNO_3, c —KJ; 3: a —K_2SO_4, b —K_2CrO_4, c —$CaCrO_4$, d —$K_2Cr_2O_7$

Figure 3: Fig. 3. Kinetics of dissolution of CaO ($S = 0.14$ m^2/g) from the change in specific electrical conductivity in 0.01 N electrolyte solutions. 1 —water; 2: a —KCl, b —KNO_3, c —KJ; 3: a —K_2SO_4, b —K_2CrO_4, c —$CaCrO_4$, d —$K_2Cr_2O_7$

$CaCrO_4$ (5), K_2CrO_4 (6), K_2SO_4 (7), and Na_2SO_4 (8).

Therefore, the action of strong electrolytes on the hydration of CaO should apparently be considered from the standpoint of their influence on the conditions for the formation and properties of the protective film of $Ca(OH)_2$. In studying the rate of hydration of hemihydrate gypsum in the presence of electrolytes, an increase was found

of the rate of dissolution of gypsum in potassium chloride solutions (7). In this connection, measurements were made of the effect of the electrolytes listed above on the rate of dissolution of calcium oxide. The rate of dissolution was determined by us from the change in the specific electrical conductivity of the suspension at a stirring rate that removes the limiting effect of diffusion (8).

A correction was introduced for the electrical conductivity of the foreign electrolyte, determined by the following procedure. To $Ca(OH)_2$ solutions (100 ml) of various concentrations, characterized by the corresponding values of specific electrical conductivity (χ_0), 0.1-1.0 ml of concentrated electrolyte solutions was added, and the value χ of the resulting solutions was measured.

Fig. 3. Kinetics of dissolution of CaO ($S = 0.14$ m^2/g) from the change in specific electrical conductivity in 0.01 N electrolyte solutions. 1 —water; 2: a —KCl, b —KNO_3, c —KJ; 3: a —K_2SO_4, b —K_2CrO_4, c —$CaCrO_4$, d —$K_2Cr_2O_7$

solutions. Curves were then plotted for the dependence of χ of $Ca(OH)_2$ solutions with added electrolyte on χ_0 of the initial solution. From these curves the specific electrical conductivity of the calcium hydroxide solution in the presence of particular electrolytes was determined, due only to the ions Ca^{2+} and OH^- that passed into solution during dissolution of CaO.

These experiments showed that, indeed, all the electrolytes investigated increase the rate of dissolution of calcium oxide. Moreover, as is evident from Fig. 3, a sharper acceleration is observed in solutions of those electrolytes that retard the hydration of lime.

On the other hand, it is known (9) that under the action of the field of ions the activation energy of the viscous flow of water molecules forming the immediate environment of the ions changes, i.e., the viscosity of water changes. Moreover, negatively hydrated ions, in the terminology of Samoilov, (Li^+, K^+, Cl^-, Br^-, J^-, ${NO_3}^-$, ${NO_2}^-$, ${MnO_4}^-$, ${C_2H_3O_2}^-$, CNS^-) decrease, while positively hydrated ions (Ca^{2+}, Na^+, ${SO_4}^{2-}$, ${CrO_4}^{2-}$, ${SO_3}^{2-}$, ${PO_4}^{3-}$, ${CO_3}^{2-}$, etc.) increase the viscosity of water.

Consideration from this point of view of the electrolytes listed above showed that, in the concentration range studied by us (0–0.7-2 mol/l), electrolytes that retard hydration should increase, while electrolytes that accelerate hydration should decrease, the viscosity of water. Consequently, electrolytes with polyvalent anions, on the one hand, increase the rate of dissolution of calcium oxide and, on the other, decrease the rate of diffusion of Ca^{2+} and OH^- ions. Both of these factors promote the formation of a denser film of $Ca(OH)_2$ on the surface of the initial particles and, consequently, retard the hydration of CaO.

In solutions of strong electrolytes with large monovalent anions, the rate of dissolution of CaO increases to a significantly lesser extent (Fig. 3), but at the same time the rate of diffusion of $Ca(OH)_2$ increases. The increase in the diffusion rate ensures a more rapid removal of Ca^{2+} and OH^- ions from the surface of the dissolving calcium oxide, which worsens the conditions for formation of the protective film and leads to acceleration of the hydration of calcium oxide.

Department of Colloid Chemistry
Moscow State University
named after M. V. Lomonosov

Institute of Physical Chemistry
Academy of Sciences of the USSR

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