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Abstract

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ON THE FORMATION OF STABLE AND METASTABLE HYDRATES DURING THE HYDRATION OF ANHYDROUS CALCIUM ALUMINATES ($CaO \cdot Al_2O_3$ and $3CaO \cdot Al_2O_3$)

Much work has been devoted to the physicochemical study of phase equilibria in the system $CaO—Al_2O_3—H_2O$, to which aqueous suspensions of monocalcium $CaO \cdot Al_2O_3$ (CA) and tricalcium $3CaO \cdot Al_2O_3$ (C_3A) aluminates also belong ([1–4]). It has been shown that, over a wide temperature interval (from 20 to 215°), the stable compounds in this system are gibbsite $Al_2O_3 \cdot 3H_2O$, cubic hexahydrate tricalcium hydroaluminate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (C_3AH_6), and calcium hydroxide $Ca(OH)_2$. In the system $CaO—Al_2O_3—H_2O$ metastable equilibria are of very great importance, since the metastable hydrates formed under these conditions pass rather slowly into stable compounds. Thus, in the hydration of CA there arise metastable monocalcium $CaO \cdot Al_2O_3 \cdot aq$ ($CA \cdot aq$) and dicalcium $2CaO \cdot Al_2O_3 \cdot aq$ ($C_2A \cdot aq$) hydroaluminates ([2,3]), while in the hydration of C_3A there arises metastable hexagonal tricalcium hydroaluminate $3CaO \cdot Al_2O_3 \cdot aq$ ($C_3A \cdot aq$) ([5]).

Studies devoted to the ionic composition of aluminate solutions ([6,7]) have shown that, despite the existence of a whole series of different calcium hydroaluminates in aqueous solutions, regardless of their $Ca(OH)_2$ content, practically only the monovalent ion of aluminic acid AlO_2' is always present (Heyrovský ([8]) assigns this ion the composition $Al(OH)_4'$).

Analysis of a large body of literature material and the detailed thermographic study carried out by us of the hydration kinetics of CA and C_3A in concentrated aqueous suspensions ([9]) make it possible to present in the following way the general regularities of the formation of particular metastable compounds in the process of hydration of calcium aluminates, the causes and sequence of their mutual transformations, and also the dependence of the composition of metastable hydroaluminates on the experimental conditions—temperature, concentration of suspensions, and composition of the initial anhydrous aluminate.

Monocalcium aluminate is a salt of metaaluminic acid $Ca(AlO_2)_2$ and in aqueous solutions undergoes hydrolysis

$$AlO_2' + 2HOH = Al(OH)_3 + OH',$$

The hydrolysis constant is

$$K = \frac{[Al(OH)_3][OH']}{[AlO_2']}.$$

As a result of hydrolysis, colloidal aluminum hydroxide is precipitated, having a solubility many times greater than that of gibbsite. Gradually, with aging, i.e., recrystallization leading to coarsening of the crystallites, the solubility of $Al_2O_3 \cdot aq$ decreases—

···is retained. This leads to a gradual increase in the concentration of free $Ca(OH)_2$ in the solution ([3]). The aging of $Al_2O_3 \cdot aq$, like any recrystallization process, proceeds the faster the higher the temperature and the lower the concentration of the suspension, i.e., the larger the volume of water in which the recrystallizing substance dissolves. Therefore the concentration of free $Ca(OH)_2$ in the aqueous phase of a CA suspension depends strongly on the temperature and on the concentration of the suspension.

At low temperature, even in dilute CA suspensions, the rate of aging of $Al_2O_3 \cdot aq$ is low, and a low concentration of free $Ca(OH)_2$ persists for a long time in the aqueous phase. Under these conditions, from the supersaturated solution formed upon dissolution of CA, the hydrate $Ca(AlO_2)_2 \cdot aq$ ($CA \cdot aq$) crystallizes; it is stable at low concentrations of $Ca(OH)_2$ in solution.

The aging of $Al_2O_3 \cdot aq$ and the continuous increase in the concentration of free $Ca(OH)_2$ in the aqueous phase lead to the fact that, beginning at a certain concentration amounting, calculated as CaO, to approximately 0.12–0.16 g/l ([4,10]), the double salt $Ca(AlO_2)_2 \cdot Ca(OH)_2 \cdot aq$, or $C_2A \cdot aq$, is formed.

However, the concentration of $Ca(OH)_2$ corresponding to the stability of $C_2A \cdot aq$ is lower than that which corresponds to equilibrium with gibbsite. Therefore the continuing aging of aluminum hydroxide causes a further increase in the concentration of $Ca(OH)_2$ in the liquid phase of the suspension until, finally, a concentration of $Ca(OH)_2$ is reached that corresponds to the formation of a new double salt, $Ca(AlO_2)_2 \cdot 2Ca(OH)_2 \cdot 4H_2O$—cubic tricalcium hydroaluminate (C_3AH_6).

As is known ([1,3]), when stable equilibrium is reached, the concentration in solution is, calculated as CaO, 0.33 g/l, and, calculated as Al_2O_3, 0.02 g/l. This is the concentration of the solution at the invariant point, where two stable solid phases coexist—gibbsite and C_3AH_6. In the hydration of calcium aluminates at room temperature this point is practically never reached, since the solubility of the $Al_2O_3 \cdot aq$ formed remains for a very long time (for months) higher than the equilibrium solubility of gibbsite. For the same reason, most investigators ([1,5,6]) have noted that C_3AH_6 dissolves congruently.

Fig. 1. Thermographic study of the products of interaction of cubic tricalcium hydroaluminate and $Ca(OH)_2$; molar ratio $Ca(OH)_2 : C_3AH_6 = 2$. C_3AH_6 gives endothermic effects on thermograms at 310–340° and at 480° ([12]), $Ca(OH)_2$—at 500°, $C_4A \cdot aq$—at 200° ([12]).

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The gradual sequential transition of hydroaluminates from $CA \cdot aq \cdots$

into $C_2A \cdot aq$ and then into C_3AH_6 is possible only at low temperature in sufficiently concentrated suspensions, when the aging of $Al_2O_3 \cdot aq$ proceeds very slowly and, from the supersaturated solution formed upon dissolution of CA, only one hydroaluminate, $CA \cdot aq$, crystallizes. With increasing temperature or increasing W/S, the aging of $Al_2O_3 \cdot aq$ is accelerated, and the concentration of $Ca(OH)_2$ corresponding to the formation of the double salts $C_2A \cdot aq$ and C_3AH_6 may be reached before all of the initial CA has been consumed. In this case these salts will begin to crystallize during the hydration of the initial aluminate, and the composition of the hydration products will depend on the experimental conditions that determine the rate of aging of aluminum hydroxide and the rate of dissolution of the initial aluminate (temperature, W/S, fineness of the aluminate).

Anhydrous C_3A is apparently a salt of orthoaluminic acid, $Ca_3(AlO_3)_2$, and its hydrolysis in aqueous solutions proceeds in two stages

$$AlO_3''' + HOH = AlO_2' + 2OH';$$

$$AlO_2' + 2HOH = Al(OH)_3 + OH'.$$

The first stage of this hydrolysis is not associated with the separation of aluminum hydroxide; therefore it occurs instantaneously, and a high concentration of $Ca(OH)_2$ is immediately created in the solution, sufficient for the formation of the highly basic double salt $Ca(AlO_2)_2 \cdot 2Ca(OH)_2 \cdot 4H_2O$. Therefore, when anhydrous C_3A dissolves in water, $CA \cdot aq$ and $C_2A \cdot aq$ can never be formed as hydration products. However, the cubic hydroaluminate crystallizes very slowly ([11]), and therefore a more hydrated salt of the same basicity, which crystallizes more readily, has time to precipitate from the solution—the hexagonal tricalcium hydroaluminate $Ca(AlO_2)_2 \cdot 2Ca(OH)_2 \cdot aq$ ($C_3A \cdot aq$), whose metastability is due to its higher solubility compared with stable C_3AH_6. With time this compound completely recrystallizes into the less soluble stable C_3AH_6. Hexagonal $C_3A \cdot aq$ cannot form during hydration of CA, since by the time the concentration of $Ca(OH)_2$ necessary for this is reached in the aqueous phase of the CA suspension, the initial CA will already have hydrated with the formation of $CA \cdot aq$ and $C_2A \cdot aq$, which are not capable of producing supersaturation with respect to $C_3A \cdot aq$; therefore in this case the less soluble C_3AH_6 crystallizes immediately.

From solutions of calcium aluminates saturated with lime, the tetracalcium hydroaluminate crystallizes; it is also a double salt, $Ca(AlO_2)_2 \cdot 3Ca(OH)_2 \cdot aq$ ($C_4A \cdot aq$). In the literature dealing with the study of phase equilibria in the system $CaO—Al_2O_3—H_2O$ ([1]), $C_4A \cdot aq$ is regarded as a metastable compound. However, in contrast to other metastable calcium hydroaluminates, for $C_4A \cdot aq$ the concentration of CaO corresponding to its saturated solution has been firmly established (1.08 g CaO/L ([10])). The unambiguous nature of this value is connected with the fact that dissolution of $C_4A \cdot aq$ is not accompanied by the separation of aluminum hydroxide, and therefore a concentration of $Ca(OH)_2$ is established in its solutions that does not depend on the experimental conditions. As our experiments have shown, the notion that $C_4A \cdot aq$ is metastable is erroneous, evidence for which is the formation of $C_4A \cdot aq$ from stable C_3AH_6 and $Ca(OH)_2$. As can be seen from Fig. 1, which presents the results of one such experiment, C_3AH_6 transforms into $C_4A \cdot aq$, and this transition occurs rather rapidly. This shows that in a saturated lime solution the stable compound is $C_4A \cdot aq$, not C_3AH_6. The region of stable existence of $C_4A \cdot aq$ is very small and corresponds to CaO concentrations in solution exceeding 1.08 g CaO per 1 L. The notion of the metastability of this compound is connected with the fact that maintaining such a high concentration of $Ca(OH)_2$ constant is difficult even in concentrated suspensions of aluminates, all the more so ···

is difficult in dilute suspensions, with which all studies of phase equilibria in the system $CaO—Al_2O_3—H_2O$ were carried out.

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REFERENCES

1. R. H. **Bogue**, *The Chemistry of Portland Cement*, N. Y., 1947, ch. 24; H. H. **Steinour**, Research and Develop. Labs. Portland Cement Assoc., Bull. 34, Chicago, 1951; H. F. W. **Taylor**, *Progress in Ceramic Science*, Oxford–London–N. Y.–Paris, 1961; E. T. **Carlson**, J. Res. Nat. Bur. Stand., **61**, No. 1, 1 (1958); F. G. **Buttler**, H. F. W. **Taylor**, J. Chem. Soc., **1958**, 2103; N. A. **Toropov**, O. I. **Sokolova**, Tr. Leningr. tekhnol.

inst. im. Lensoveta, issue 56, 1960.

2. I. V. **Kravchenko**, *Alumina Cement*, M., 1961; S. I. **Schneider**, J. Am. Ceram. Soc., **42**, No. 4, 184 (1959).

3. L. S. **Wells**, E. T. **Carlson**, J. Res. Nat. Bur. Stand., **57**, No. 6, 335 (1956).

4. T. V. **Rubetskaya**, in: *Concretes and Binders*, M., 1955, p. 95.

5. T. **Thorvaldson**, N. S. **Grace**, Canad. J. Res., **1**, 36 (1929); T. **Thorvaldson**, N. S. **Grace**, V. A. **Vigfusson**, Canad. J. Res., **1**, 201 (1929).

6. G. **Assarsson**, Sver. geol. undersökn. Årsbok, **30**, Ser. C, No. 399 (1936).

7. L. S. **Wells**, J. Res. Nat. Bur. Stand., **1**, No. 6, 951 (1928).

8. J. **Heyrovsky**, J. Chem. Soc., **117**, 1013 (1920).

9. Z. D. **Tulovskaya**, E. E. **Segalova**, ZhPKh, **37**, No. 2 (1964).

10. H. **Lafuma**, Ciment, **30**, 174 (1925).

11. F. E. **Jones**, J. Phys. Chem., **48**, No. 6, 311 (1944); W. **Eitel**, J. Am. Concr. Inst., **28**, No. 7, 679 (1957); J. **D' Ans**, H. **Eick**, Zement–Kalk–Gips, **6**, No. 9, 302 (1953).

12. G. L. **Kalousek**, C. W. **Davis**, W. E. **Schmertz**, J. Am. Concr. Inst., **20**, No. 10, 693 (1949).

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