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# Chemistry

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**Abstract**

**Full Text**

**Chemistry**

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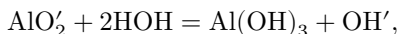
## **ON THE FORMATION OF STABLE AND METASTABLE HYDRATES DURING THE HYDRATION OF ANHYDROUS CALCIUM ALUMINATES ( $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ )**

Much work has been devoted to the physicochemical study of phase equilibria in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ , to which aqueous suspensions of monocalcium  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  (CA) and tricalcium  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  ( $\text{C}_3\text{A}$ ) aluminates also belong (<sup>1-4</sup>). It has been shown that, over a wide temperature interval (from 20 to 215°), the stable compounds in this system are gibbsite  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , cubic hexahydrate tricalcium hydroaluminate  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{C}_3\text{AH}_6$ ), and calcium hydroxide  $\text{Ca}(\text{OH})_2$ . In the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  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  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{aq}$  ( $\text{CA} \cdot \text{aq}$ ) and dicalcium  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{aq}$  ( $\text{C}_2\text{A} \cdot \text{aq}$ ) hydroaluminates (<sup>2,3</sup>), while in the hydration of  $\text{C}_3\text{A}$  there arises metastable hexagonal tricalcium hydroaluminate  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{aq}$  ( $\text{C}_3\text{A} \cdot \text{aq}$ ) (<sup>5</sup>).

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

Analysis of a large body of literature material and the detailed thermographic study carried out by us of the hydration kinetics of CA and  $\text{C}_3\text{A}$  in concentrated aqueous suspensions (<sup>9</sup>) 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  $\text{Ca}(\text{AlO}_2)_2$  and in aqueous solutions undergoes hydrolysis



The hydrolysis constant is

$$K = \frac{[\text{Al}(\text{OH})_3][\text{OH}']}{[\text{AlO}_2']}$$

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  $\text{Al}_2\text{O}_3 \cdot \text{aq}$  decreases—

...is retained. This leads to a gradual increase in the concentration of free  $\text{Ca}(\text{OH})_2$  in the solution<sup>(3)</sup>. The aging of  $\text{Al}_2\text{O}_3 \cdot \text{aq}$ , 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  $\text{Ca}(\text{OH})_2$  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  $\text{Al}_2\text{O}_3 \cdot \text{aq}$  is low, and a low concentration of free  $\text{Ca}(\text{OH})_2$  persists for a long time in the aqueous phase. Under these conditions, from the supersaturated solution formed upon dissolution of CA, the hydrate  $\text{Ca}(\text{AlO}_2)_2 \cdot \text{aq}$  ( $\text{CA} \cdot \text{aq}$ ) crystallizes; it is stable at low concentrations of  $\text{Ca}(\text{OH})_2$  in solution.

The aging of  $\text{Al}_2\text{O}_3 \cdot \text{aq}$  and the continuous increase in the concentration of free  $\text{Ca}(\text{OH})_2$  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<sup>(4,10)</sup>, the double salt  $\text{Ca}(\text{AlO}_2)_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{aq}$ , or  $\text{C}_2\text{A} \cdot \text{aq}$ , is formed.

However, the concentration of  $\text{Ca}(\text{OH})_2$  corresponding to the stability of  $\text{C}_2\text{A} \cdot \text{aq}$  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  $\text{Ca}(\text{OH})_2$  in the liquid phase of the suspension until, finally, a concentration of  $\text{Ca}(\text{OH})_2$  is reached that corresponds to the formation of a new double salt,  $\text{Ca}(\text{AlO}_2)_2 \cdot 2\text{Ca}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ —cubic tricalcium hydroaluminate ( $\text{C}_3\text{AH}_6$ ).

As is known<sup>(1,3)</sup>, when stable equilibrium is reached, the concentration in solution is, calculated as CaO, 0.33 g/l, and, calculated as  $\text{Al}_2\text{O}_3$ , 0.02 g/l. This is the concentration of the solution at the invariant point, where two stable solid phases coexist—gibbsite and  $\text{C}_3\text{AH}_6$ . In the hydration of calcium aluminates at room temperature this point is practically never reached, since the solubility of the  $\text{Al}_2\text{O}_3 \cdot \text{aq}$  formed remains for a very long time (for months) higher than the equilibrium solubility of gibbsite. For the same reason, most investigators<sup>(1,5,6)</sup> have noted that  $\text{C}_3\text{AH}_6$  dissolves congruently.

Fig. 1. Thermographic study of the products of interaction of cubic tricalcium hydroaluminate and  $\text{Ca}(\text{OH})_2$ ; molar ratio  $\text{Ca}(\text{OH})_2 : \text{C}_3\text{AH}_6 = 2$ .  $\text{C}_3\text{AH}_6$  gives endothermic effects on thermograms at 310–340° and at 480° <sup>(12)</sup>,  $\text{Ca}(\text{OH})_2$ —at 500°,  $\text{C}_4\text{A} \cdot \text{aq}$ —at 200° <sup>(12)</sup>.

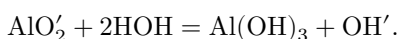
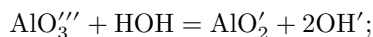
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The gradual sequential transition of hydroaluminates from  $\text{CA} \cdot \text{aq}$ ...

into  $\text{C}_2\text{A} \cdot \text{aq}$  and then into  $\text{C}_3\text{AH}_6$  is possible only at low temperature in sufficiently concentrated suspensions, when the aging of  $\text{Al}_2\text{O}_3 \cdot \text{aq}$  proceeds very slowly and, from the supersaturated solution formed upon dissolution of  $\text{CA}$ , only one hydroaluminate,  $\text{CA} \cdot \text{aq}$ , crystallizes. With increasing temperature or increasing W/S, the aging of  $\text{Al}_2\text{O}_3 \cdot \text{aq}$  is accelerated, and the concentration of  $\text{Ca}(\text{OH})_2$  corresponding to the formation of the double salts  $\text{C}_2\text{A} \cdot \text{aq}$  and  $\text{C}_3\text{AH}_6$  may be reached before all of the initial  $\text{CA}$  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  $\text{C}_3\text{A}$  is apparently a salt of orthoaluminic acid,  $\text{Ca}_3(\text{AlO}_3)_2$ , and its hydrolysis in aqueous solutions proceeds in two stages



The first stage of this hydrolysis is not associated with the separation of aluminum hydroxide; therefore it occurs instantaneously, and a high concentration of  $\text{Ca}(\text{OH})_2$  is immediately created in the solution, sufficient for the formation of the highly basic double salt  $\text{Ca}(\text{AlO}_2)_2 \cdot 2\text{Ca}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ . Therefore, when anhydrous  $\text{C}_3\text{A}$  dissolves in water,  $\text{CA} \cdot \text{aq}$  and  $\text{C}_2\text{A} \cdot \text{aq}$  can never be formed as hydration products. However, the cubic hydroaluminate crystallizes very slowly <sup>(11)</sup>, 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  $\text{Ca}(\text{AlO}_2)_2 \cdot 2\text{Ca}(\text{OH})_2 \cdot \text{aq}$  ( $\text{C}_3\text{A} \cdot \text{aq}$ ), whose metastability is due to its higher solubility compared with stable  $\text{C}_3\text{AH}_6$ . With time this compound completely recrystallizes into the less soluble stable  $\text{C}_3\text{AH}_6$ . Hexagonal  $\text{C}_3\text{A} \cdot \text{aq}$  cannot form during hydration of CA, since by the time the concentration of  $\text{Ca}(\text{OH})_2$  necessary for this is reached in the aqueous phase of the CA suspension, the initial CA will already have hydrated with the formation of  $\text{CA} \cdot \text{aq}$  and  $\text{C}_2\text{A} \cdot \text{aq}$ , which are not capable of producing supersaturation with respect to  $\text{C}_3\text{A} \cdot \text{aq}$ ; therefore in this case the less soluble  $\text{C}_3\text{AH}_6$  crystallizes immediately.

From solutions of calcium aluminates saturated with lime, the tetracalcium hydroaluminate crystallizes; it is also a double salt,  $\text{Ca}(\text{AlO}_2)_2 \cdot 3\text{Ca}(\text{OH})_2 \cdot \text{aq}$  ( $\text{C}_4\text{A} \cdot \text{aq}$ ). In the literature dealing with the study of phase equilibria in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  (<sup>1</sup>),  $\text{C}_4\text{A} \cdot \text{aq}$  is regarded as a metastable compound. However, in contrast to other metastable calcium hydroaluminates, for  $\text{C}_4\text{A} \cdot \text{aq}$  the concentration of CaO corresponding to its saturated solution has been firmly established (1.08 g CaO/L (<sup>10</sup>)). The unambiguous nature of this value is connected with the fact that dissolution of  $\text{C}_4\text{A} \cdot \text{aq}$  is not accompanied by the separation of aluminum hydroxide, and therefore a concentration of  $\text{Ca}(\text{OH})_2$  is established in its solutions that does not depend on the experimental conditions. As our experiments have shown, the notion that  $\text{C}_4\text{A} \cdot \text{aq}$  is metastable is erroneous, evidence for which is the formation of  $\text{C}_4\text{A} \cdot \text{aq}$  from stable  $\text{C}_3\text{AH}_6$  and  $\text{Ca}(\text{OH})_2$ . As can be seen from Fig. 1, which presents the results of one such experiment,  $\text{C}_3\text{AH}_6$  transforms into  $\text{C}_4\text{A} \cdot \text{aq}$ , and this transition occurs rather rapidly. This shows that in a saturated lime solution the stable compound is  $\text{C}_4\text{A} \cdot \text{aq}$ , not  $\text{C}_3\text{AH}_6$ . The region of stable existence of  $\text{C}_4\text{A} \cdot \text{aq}$  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  $\text{Ca}(\text{OH})_2$  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  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  were carried out.

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

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