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Abstract

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DEPENDENCE OF THE METASTABLE SOLUBILITY OF MONOCALCIUM ALUMINATE ON TEMPERATURE

Knowledge of the dependence of the metastable solubility of monocalcium aluminate $CaO \cdot Al_2O_3$(CA) on temperature is necessary for explaining the peculiarities of the hardening of aluminous cement (the principal mineral of which is monocalcium aluminate) at elevated temperatures ([1]–[4]). The metastable solubility of monocalcium aluminate was first determined in ([1]); however, in that work the change in concentration in the liquid phase of a CA suspension was followed by a conductometric method, the use of which for hydrolyzing and incongruently soluble salts is not advisable, since in this case the increase in electrical conductivity is determined mainly by the accumulation in solution of the most mobile ions and does not reflect the kinetics of dissolution of the initial substance. In this connection, in the present work the concentration of the liquid phase of a CA suspension during its dissolution and crystallization of newly formed products was measured analytically, by quantitative determination of Ca^{2+} and Al^{3+} (Al was precipitated as hydroxide, and Ca as oxalate).

The determination of the metastable solubility of a binder is experimentally easy to carry out only when, in its saturated solution, whose concentration is determined by the value of the metastable solubility, the rate of formation of hydrate nuclei is not very high, i.e., the crystallization process proceeds with a noticeable induction period. The higher the solubility of the initial binder in comparison with the solubility of the hydrate, i.e., the greater the supersaturation produced in the course of hydration and the greater the rate of crystallization of the hydrate at this supersaturation, the more difficult is the experimental determination of the solubility value. In this case it is necessary to resort to special procedures that retard crystallization of the newly formed products and make it possible to create in the liquid phase of the suspension a supersaturation corresponding to the metastable solubility of the initial substance ([5], [6]).

During the hydration of monocalcium aluminate in dilute suspensions, crystallization of the newly formed products, even at elevated temperature, proceeds with a noticeable induction period, which makes it possible to determine readily the value of the metastable solubility. In the present work the metastable solubility of CA was determined in the temperature interval 5–70°. Suspensions containing from 0.66 to 6.5% solid phase were studied. The suspension in a special vessel was placed in a thermostat, the temperature in which was main-

Fig. 1. Change in the concentration of CaO and Al_2O_3 in the liquid phase of suspensions of monocalcium aluminate at 45°. Suspension concentration in grams of CA per 1 l: a –15, b –20, c –25

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tained with an accuracy of $±$0.3°. Stirring was carried out with a propeller stirrer at a speed of 400 rpm. This speed, at all temperatures, proved sufficient for the kinetics of dissolution to be independent of the rotational speed of the stirrer. To protect the CA suspensions from carbonation, stirring was carried out

Table 1

Value of the metastable solubility of monocalcium aluminate at various temperatures

Experimental temperature, °C	CaO, g/l	Al_2O_3, g/l	CaO+Al_2O_3, g/l	CaO/Al_2O_3	Experimental temperature, °C	CaO, g/l	Al_2O_3, g/l	CaO+Al_2O_3, g/l	CaO/Al_2O_3
5$±0.3	0	1.32	2.224	1.08	45±0.3	1.626	2.836	4.462	1.04
10±0.3	1.004	1.689	2.693	1.08	50±0.3	1.703	3.040		

in an atmosphere of nitrogen. From the vessel in which the suspension was located, samples were taken at definite time intervals and the liquid phase was analyzed. The suspensions were filtered at the same temperature at which the experiment was carried out.

At each temperature, the kinetics of the change in concentration in the liquid phase of suspensions of different concentrations was studied, which made it possible to find values of the metastable solubility of monocalcium aluminate independent of the suspension concentration. The results of such experiments for a temperature of 45° are presented in Fig. 1. From Fig. 1 it is seen that the content of CaO and Al_2O_3 in the liquid phase of a CA suspension reaches a definite value, which is maintained for a long time and does not depend on the concentration of the suspension. This value, found as the mean for suspensions of different concentrations, determines the magnitude of the metastable solubility of CA at the given temperature (Table 1).

Fig. 1. Change in the concentration of CaO and Al_2O_3 in the liquid phase of suspensions of monocalcium aluminate at 45°. Suspension concentration in grams of CA per 1 l: *a* –15, *b* –20, *c* –25

Fig. 2. Dependence of the metastable solubility of CA on temperature

Figure 2: Fig. 2. Dependence of the metastable solubility of CA on temperature

As is seen from the data of Table 1 and Fig. 2, the solubility of monocalcium aluminate in the temperature interval from 5 to 50° increases with increasing t, and with a further increase in temperature to 70° it decreases somewhat. Monocalcium aluminate dissolves

Fig. 2. Dependence of the metastable solubility of CA on temperature

incongruently: the ratio CaO/Al_2O_3 in the solution saturated with respect to it is always somewhat greater than 1. The excess concentration of CaO corresponding to this ratio is small and practically does not change with increasing temperature. To resolve the question of the change in supersaturation in suspensions of monocalcium aluminate at different temperatures, a detailed investigation of the hydration products of this compound and of their solubility in the same temperature interval is necessary.

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