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APPLICATIONS OF HEDVALL EFFECT IN CEMENT CHEMISTRY

By

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and

P. J. SEREDA

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LES APPLICATIONS DE L'EFFET HEDVALL A LA CHIMIE DU BETON

SOMMAIRE

On a appliqué l'effet Hedvall à des systèmes qui intéressent la chimie du béton, y compris le CaO , le Ca(OH)_2 , le 3CaO.SiO_2 , le $\beta\text{-}2\text{CaO.SiO}_2$ et le 3CaO.SiO_2 hydraté. Les résultats obtenus indiquent que l'effet Hedvall est un nouvel instrument d'évaluation et un moyen d'examiner la réactivité et les mécanismes de réaction.

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Hedvall Effect in Cement Chemistry

THE increased reactivity of a solid during and as a consequence of a crystalline transformation is commonly known as the Hedvall effect¹⁻³. In a wider sense this effect may include increased reactivity near a transition point. The typical data quoted in support of the Hedvall effect refer to reactions in the binary systems containing silver salts with BaO, SrO and CaO yielding the reciprocal pairs⁴⁻⁷.

There are still many unresolved problems in cement chemistry in spite of the use of powerful techniques such as X-ray diffraction, electron microscopy, electron microprobe, NMR and others. One of the problems is concerned with the difference in reactivities of the cement components. It seemed that the reactivity might be studied through the solid state reactions and that the use of the Hedvall effect might resolve the problem.

Fig. 1 Calibration curve for the estimation of AgNO₃ by DTA peak heights.

The two phases, tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) and β dicalcium silicate ($\beta\text{2CaO} \cdot \text{SiO}_2$), which together form 70 to 80% of the cement clinker, play a dominant role in the physical,

chemical and mechanical properties in the hardening of portland cement paste. We have studied reactions between AgNO_3 and $3\text{CaO} \cdot \text{SiO}_2$, $\beta 2\text{CaO} \cdot \text{SiO}_2$, CaO , $\text{Ca}(\text{OH})_2$ and a completely hydrated $3\text{CaO} \cdot \text{SiO}_2$ in order to test the effect in these systems.

Silver nitrate was mixed with different proportions of each of the reactants already mentioned and heated to 250°C in a DTA apparatus. There was a clear indication that some or all of the AgNO_3 was consumed in the reaction. The amount of AgNO_3 reacted in the time involved was determined by estimating the amount of the nitrate remaining in the system after completion of the exothermal reaction. The mixture was heated to a temperature of 250°C which is much greater than the exothermal peak temperature. DTA was then obtained on the cooling mode; an exothermal peak was found, which corresponds to the recrystallization of the unreacted silver nitrate. Calibrations were performed with different proportions of AgNO_3 and SiO_2 . There is a good straight line relationship between the peak height or the peak area and the amount of AgNO_3 in the mixture (Fig. 1). Because it is quick and easy to determine the peak heights, all the estimations were done on this basis.

Table 1 Extent of Reaction of AgNO_3 with Different Reactants

Sample No.	Reactants	Extent of reaction Reactant : AgNO_3 (wt)	Amount of Ca in the reactant (mol)	Amount of Ca reacted (mol)
1	CaO	1 : 5.8	1	0.96
2	$\text{Ca}(\text{OH})_2$	1 : 4.6	1	1.0
3	$3\text{CaO} \cdot \text{SiO}_2$	1 : 1.21	3	0.81
4	$\beta 2\text{CaO} \cdot \text{SiO}_2$	1 : 4.2	2	0.12
5	Hydrated $3\text{CaO} \cdot \text{SiO}_2$	1 : 3.74	6	5.99

The reaction between CaO and AgNO_3 is almost stoichiometric and shows that 96.0% of CaO reacts with AgNO_3 (Table 1). A slightly lower value for the reacted CaO should be attributed to presence of a small quantity of relatively non-reactive CaO formed at a calcination temperature of $1,000^\circ \text{C}$. In other words, this method offers a new tool to study the reactivity of CaO formed in the calcination of limestones. Calcium hydroxide reacts with AgNO_3 stoichiometrically in the weight proportions of 1 : 4.6 which corresponds to the reaction of 1 mol of $\text{Ca}(\text{OH})_2$ with 2 mol of AgNO_3 . This is a quick and elegant method of estimating $\text{Ca}(\text{OH})_2$.

Fig. 2 Differential thermal behaviour of $3\text{CaO} \cdot \text{SiO}_2\text{-AgNO}_3$ system. A, 66.67% AgNO_3 ; B, 60.0% AgNO_3 ; C, 50.0% AgNO_3 .

The reaction of AgNO_3 with $3\text{CaO} \cdot \text{SiO}_2$ may be studied through the thermograms presented in Fig. 2. The curves A, B and C represent, respectively, the mixtures containing 66.6%, 60.0% and 50.0% AgNO_3 . The exothermic peak, due to the reaction between the tricalcium silicate and silver nitrate, is completed within a few minutes. In curves A and B the presence of the exothermal peaks in the cooling mode shows clearly that an excess of AgNO_3 was mixed with the tricalcium silicate initially and, as expected, more nitrate remained unreacted in sample A. In curve C, however, no AgNO_3 remained after the reaction as evidenced by the absence of an exothermal effect in the cooling mode. Curves A and B were used to calculate the amount of AgNO_3 consumed in the reaction and both indicated that 27% of the Ca present in the tricalcium silicate phase had taken part in the reaction. This corresponds to 0.81 mol out of a total of 3 mol of Ca present in the $3\text{CaO} \cdot \text{SiO}_2$ phase (Table 1). These results demonstrate

that about 27% of the tricalcium silicate sample is relatively more reactive than the rest. The conclusion that 27% of $3\text{CaO}.\text{SiO}_2$ had reacted with AgNO_3 in the time involved could also be confirmed by estimating the amount of $3\text{CaO}.\text{SiO}_2$ (73%) which remained unreacted by means of the new DTA method reported elsewhere⁸.

This result confirms the finding obtained with isothermal conduction calorimetry and from the rate of hydration⁹. After an induction period of a few hours the rate of heat development due to hydration reaches a maximum in the region of 7 to 8 h and decreases to a low value at 18 to 24 h. The rate of hydration has been shown to have an analogous behaviour which also suggests that 27% of our $3\text{CaO}.\text{SiO}_2$ is a material with a high reactivity. It seems that all Ca ions in tricalcium silicate are not equivalent and that some of them are more reactive. The Hedvall effect provides a new approach to the study of the relative reactivities of Ca ions in the sample. This does not mean that the remaining calcium silicate does not react with AgNO_3 nor that 27% is a unique proportion. It requires only a few minutes for 27% of the tricalcium silicate to react with AgNO_3 at about 200° C and further heating for about twice this time does not show any difference. Even heating at 250° C for 60 min causes a further reaction of only about 1.5% tricalcium silicate. A similar trend is obvious in the paste hydration but the periods should be reckoned in terms of days and months.

The $\beta 2\text{CaO}.\text{SiO}_2$ phase in portland cement is known to hydrate relatively slowly compared with the $3\text{CaO}.\text{SiO}_2$ phase. One would expect that in the former system the percentage of the reactive part would be lower. This is so, as may be seen from Table 1; the dicalcium silicate phase has reacted about 6 per cent only and this corresponds to 0.12 mol of Ca out of the 2 mol in the sample.

A completely hydrated $3\text{CaO}.\text{SiO}_2$ contains a mixture of $\text{Ca}(\text{OH})_2$ and the C-S-H phase. In this system practically all of the Ca present in the $\text{Ca}(\text{OH})_2$ and in the C-S-H phase reacted with AgNO_3 (Table 1). For calculation purposes the following equation was used:

Our observation has confirmed the validity of this complex equation and also reveals that all the Ca in the C-S-H phase, whether in the interlayer positions or in the layer itself, is equally reactive, by contrast with the observations for the tricalcium silicate phase. The reactivity in the C-S-H phase as defined by the Hedvall effect is in agreement with the fact that CO_2 and even water attacks it; Al and the SO_4 ions can replace the cations and the calcium is extractable with organic

solvents. This may also reflect in the characteristic property for accommodation of its surface with that of the adjacent materials in terms of interfacial bonding.

The Hedvall effect is a useful new tool for the study of various aspects of the physico-chemical phenomena in cement chemistry and probably in other allied fields.

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