

## **THERMAL ANALYSIS AND CHEMISTRY OF INORGANIC BINDERS**

V. ŠATAVA

*Institute of Chemical Technology, Suchbatarova, Prague 6 (Czechoslovakia)*

V. LACH

*Technical University, Brno (Czechoslovakia)*

### **ABSTRACT**

Selected papers from the Conference are reviewed together with some other papers on the thermal analysis of binders.

In 1983 an international conference on the development of science and technology of hydraulic binders until the year 2000 [1] was held in London, and it was stated that progress in this significant field could be expected only through basic research on the processes taking place during the setting of inorganic binders, about which only incomplete information is available at present. This is due to the fact that products that originate during the setting of binders are fixed phases, usually of a colloidal nature, the identification of which is associated with a number of experimental difficulties. Satisfactory information about the mechanism of these processes is also not available.

The methods of thermal analysis are indispensable both for phase analysis and for the investigation of the time course of the binder setting process.

The most significant possibility of the utilization of TA is the continuous investigation of hydration processes, during which an undistorted picture of their behaviour with time is obtained. Quasi-isothermal calorimetry [2–5] is very useful and its refinement can be found in the paper by Hrabě and Světlík [6]. New modifications of this method allow the reaction to be followed from the instant of mixing the reaction components and offer a number of possibilities for application, especially the study of the causes of the existence of the incubation period of tricalcium silicate hydration and the effect of additives on its mechanism.

A method hitherto used only rarely is differential hydrothermal analysis [7–9] (DHA), which is in fact DTA performed under conditions of liquid

water–vapour equilibrium in an autoclave. This device permits the processes taking place in the investigated system during heating to the critical temperature to be followed continuously. It has proved useful in studies of clinker mineral hydration [8], thermal analysis of hydrates [8,10], hydrothermal synthesis, etc. In contrast to the current method of studying such processes that involves stopping the process by sudden cooling, the DHA method provides information undistorted by processes taking place on cooling.

Another possibility of DTA modification is represented by the hydration thermal analysis (HTA) method devised by Lach and Novotný [11]. The curve obtained shows the processes taking place in the initial stage of binder hydration with a continuously increasing temperature. The increase in temperature accelerates the hydration processes, but simultaneously decomposition of unstable hydrates occurs. The interpretation of the curves, which are a superposition of both types of processes, is difficult but the method can certainly be used for modelling technological processes that utilize the heating of mortars and concretes to accelerate their setting.

One of the less used techniques that can be used for the continuous investigation of the processes in binder setting is emanation thermal analysis [12], which provides information on the course of changes in the structure of the setting binder with temperature or time [13].

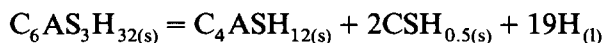
The second field for the application of TA methods is the phase analysis of hydration products [14]. New evidence about the advantages of this technique was provided by Slanička et al. [15] and Škvára et al. [16]. The advantage over XRD is that DTA allows even imperfect crystalline phases to be determined. The combination of DTA and XRD increases the reliability of the identification of individual phases, as demonstrated by Bushnell-Watson and Sharp [17] on the example of the detection of carboaluminate ( $C_4A\bar{C}H_{11}$ ) in hydrated aluminate cements.

This combination permits even more complicated problems to be solved. Nocuń-Wczelik [18] studied the effect of the presence of silica gel on the time course of tricalcium silicate hydration. DTA allowed the differentiation of two forms of  $Ca(OH)_2$  and proved that the presence of  $SiO_2$  stimulates the crystallization of portlandite.

Higher selectivity during the phase analysis of hydrates can be achieved by using the differential hydrothermal analysis (DHA) method [9]. Peaks recorded on the DTA curve correspond to the decomposition of hydrates in a gaseous atmosphere and therefore involve the evaporation of water from the sample over a wide temperature range. In contrast, the peaks on the DHA curve correspond only to enthalpy changes accompanying the hydrate decomposition in liquid water, which takes place over a narrow temperature range, which leads to better resolvability [10].

Up to now the determination of thermodynamic data of hydrates by TA methods has rarely been used, but has been applied to the investigation of equilibrium temperatures of significant reactions and the measurement of

reaction enthalpies. Again, the DHA method can be used to advantage, as the baseline of the curves obtained is generally horizontal, which facilitates the measurement of peak areas. An example of this is the determination of standard enthalpy and the Gibbs energy of formation of ettringite [19] from the measurement of the equilibrium temperature and the reaction enthalpy of processes:



(C = CaO, A = Al<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O, S = SO<sub>3</sub>) which can easily be realized under DHA conditions.

Thermodynamic calculations of chemical equilibria resulting from the data obtained coincide well with experimental results.

## CONCLUSION

TA methods have contributed significantly to the clarification of the mechanism of the processes that cause the setting of inorganic binders. The development of these methods shows new possibilities of application and it is believed that TA methods will maintain a significant position in this field.

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