Evaluation of isothermal calorimetry for characterization of very early and early cement reactions : a critical literature review

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EVALUATION OF ISOTHERMAL CALORIMETRY FOR CHARACTERIZATION OF VERY EARLY AND EARLY CEMENT REACTIONS - a critical literature review

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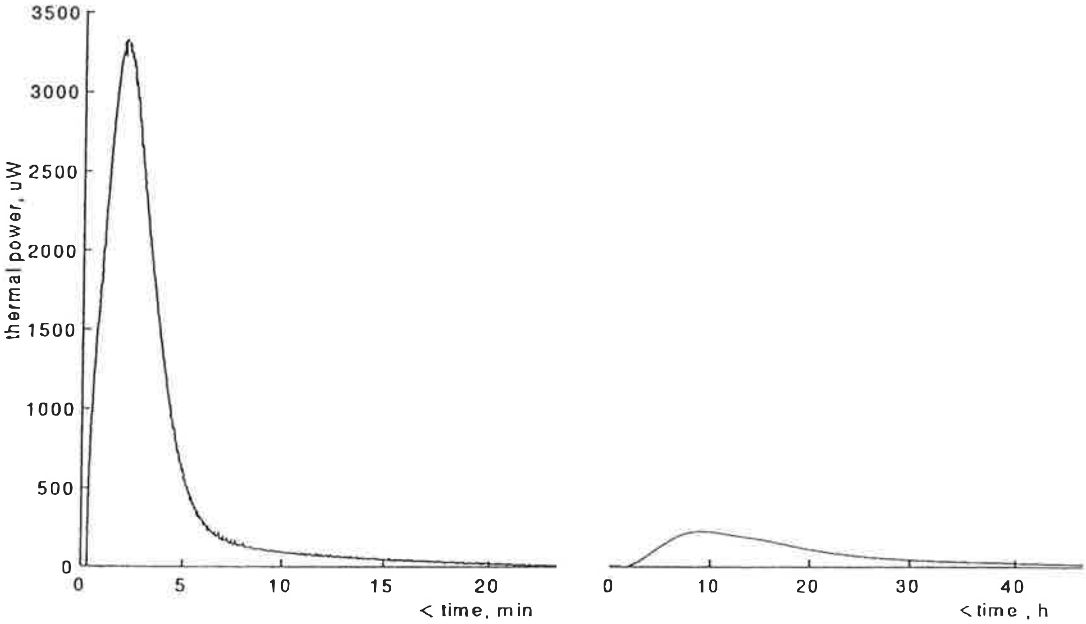

Results from an isothermal microcalorimetric measurement of the reaction between 80 mg cement (Cementa SRPC) and 40 mg water [1]. Note the different time scales of the two diagrams - the heat evolved in the second main peak is much larger than the heat of the early peak.

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1 Introduction

This is the result of a literature review made in conjunction with a a preliminary study of very early and early cement and clinker reactions by isothermal microcalorimetry.

2 The review

Concrete - one of the most important technical materials used in our society - is made by mixing Portland cement, water and aggregates. When cement is mixed with water, its constituent compounds undergo a series of chemical reactions which are responsible for the hardening of concrete. These reactions are all exothermic and the rate of heat evolution is an important parameter because (1) the resulting temperature gradients in massive concrete constructions may result in cracking, and (2) the heat production rate (the thermal power) reflects the rate of the different phases of the cement reaction.

The reaction between cement and water can be divided into four main stages: 1: Very early reactions during 0–10 minutes involving wetting processes and rapid reactions of some clinker components, 2: The dormancy period, lasting approx. 3 hours, which is characterized by very low thermal power, 3: The main reaction, about 3–24 hours after mixing, 4: Later reactions at low thermal power continuing for long periods of time (years).

The thermal power can be directly monitored by calorimetry giving results of analytical as well as thermodynamic importance. Most measurements on cement hydration are made on stage 3. This proposal is focused on the needs and possibilities for accurate calorimetric measurements of the very early and early part of cement reactions (stages 1 and 2).

The very early cement reactions start immediately after addition of water to the dry cement. With many cements at least 50% of the hydration during the first 3 hours can occur within the first 10 minutes [2–5]. These reactions are related to the rapid hydration of the aluminate and ferrite phases and have a major influence on the properties of fresh concrete. Their rates are much influenced by the calcium sulphate added the cement in order to retard the setting of the concrete. It is also known that the most common superplasticizers used today have a high influence on the rate of these early reactions. It is therefore essential that reliable methods are available by which the first stages of the cement reactions can be monitored.

Three types of calorimeters are currently used for the *direct monitoring* of cement reactions: adiabatic calorimeters, semiadiabatic (isoperibol) calorimeters, and isothermal calorimeters. Further, *solution calorimetry* is used to determine the heat of hydration after 7 days and later, and *differential scanning calorimeters (DSC)* are used to estimate the amounts of different compounds at different times.

Thermal power data for cement reactions determined under adiabatic or semiadiabatic conditions often refer to a temperature range which is sufficiently large to significantly affect the reaction rate. Thermal power data determined under essentially isothermal conditions, *at different temperatures*, are more useful, from practical as well as fundamental point of view. Isothermal calorimetry is the most accurate technique available to study the rate of heat release in hydrating cement [6–11].

The most widely used isothermal cement calorimeters are the English JAF calorimeter (also called the BCA calorimeter [12]) and a Dutch calorimeter designed at Dept. of Applied Physics in Delft, Netherlands [13]. The heat flow sensors in these calorimeters are thermopiles in contact with a heat sink. Several other heat conduction calorimeters have been used in cement measurements (e.g. [14–16]). Recommended measurement procedures for the use of heat conduction calorimeters for cement reactions have been issued [17].

After about 7 days of hydration *microcalorimeters* are required to monitor the process, e.g. of the types produced by Thermometric (Sweden) and Setaram (France). Only a few studies using such instruments for the studies of early [11, 18–20] or late [21] cement reactions have been reported.

Some very simple calorimeters used for measurements of cement reactions at near isothermal conditions have been described [22–24]. These calorimeters are difficult to calibrate and it is questionable if measurements reported from work with such instruments are reliable.

Isothermal calorimetric measurements during the first phase is far from trivial, in particular due to problems of arranging the mixing process in the calorimetric vessel and due to the thermal inertia of the calorimeters. Values reported for the thermal power during the first reaction phase are few [15, 23, 25–26] and are judged to be unreliable.

When publications on calorimetric studies of cement reactions are compared with corresponding reports from more fundamental areas such as physical chemistry and biochemistry it is apparent that cement calorimetry is conducted on a very low scientific level - which is not due to the complex nature of cement chemistry. A few observations: Many papers show diagrams from calorimetric measurements, but give no or very little information on how the measurements were performed (e.g. [25–29]; some papers do not even state which type of calorimeter that was used, e.g. [26–28, 30]. When early reactions are measured it is not stated if a dynamic data correction procedure was applied, e.g. [16, 23, 30–31]. Hardly ever statements are made on the accuracy or even the precision of the measurements.

3 Discussion

It is felt that precision and accuracy of isothermal calorimetric techniques should be evaluated, in particular when applied to the earliest cement reactions. The following objectives are proposed:

- to assess the performance of different types of calorimeters for isothermal studies of very early and early cement reactions.

- to study if the water-binder ratio is an important parameter for the early reactions (it probably is).
- to compare the results of isothermal calorimetric measurements with measurements by other techniques (DSC, conductivity) on a range of cements and clinker components.
- to present guidelines for isothermal calorimetric techniques applied to very early cement reactions, including evaluation and reporting of results.

Measurements should be made on different materials: commercial cements with admixtures, pure cement phases with added calcium sulphates etc.

4 References

1. Wadsö, L., Early cement and clinker reactions studied by isothermal calorimetry; a preliminary investigation. Div. Building Materials, Lund University, Sweden, ISSN 0348-7911 TVBM U95-02
2. Uschikawa, H., Ogawa, K. and Uchiada, S., Influence of character of clinker on the early hydration process and rheological property of cement paste. Cement Concr. Res. 15 561–572 1985
3. Uchikawa, H., Hanehara, S., Shirasaka, T. and Sawaki, D., Effect of admixture on hydration of cement, adsorptive behavior of admixture and fluidity and setting of fresh cement paste. Cement Concr. Res. 22 1115–1129 1992
4. Tang, F.J. and Gartner, E.M., Influence of sulphate source on Portland cement hydration, Adv. Cement Res. 1(2) 67 1988
5. Stürmer, S., Müller, A and Stark, J., Hydration of C_3A and $C_2(A,F)$ - separated from sulphate-resisting and white Portland cement - under conditions of normal hardening and heat treatment. Cement Concr. Res. 24(3) 503–513 1994
6. Milestone, N.B. and Rogers, D.E., The use of an isothermal calorimeter for determining heats of hydration at early ages. World Cement Technol. 12(8) 374–380 1981
7. Bensted, J., Some applications of conduction calorimetry to cement hydration. Adv. Cement Res. 1(1) 35–44 1987
8. Killoh, D.C., A comparison of conduction calorimeter and heat of solution methods for measurement of the heat of hydration of cement. Adv. Cement Res. 1(3) 180–186 1988
9. Livesey, P., Donnelly, A. and Tomlinson, C., Measurement of the heat of hydration of cement. Cement Concr. Compos. 13 177-185 1991
10. Sorrentino, F. and Castanet, R., Application of thermal analysis to the cement industry, J. Therm. Anal. 38 2137–2146 1992
11. Bronswijk, J.P., de Loo, M. and van Loo, W., Heat measurement with the Thermal Activity Monitor. World Cement August 23–26 1993
12. Forrester, J.A., A conduction calorimeter for the study of cement hydration. Cement Technol. 1(3) 95-99 1970

13. Stein, H.N., Influence of some additives on the hydration reactions of Portland cement. I. Non-ionic organic additives. J. Appl. Chem. 11 474–482 1962

14. Pöllmann, H., Kuzel, H.-J. and Mayer, H.W., Heat-flow calorimetry in cement chemistry. Construction and application of a low cost high-sensitive calorimeter. Proc. 13th Int. Conf. Cement Microsc. Eds. Gouda, G.R., Nisperos, A. and Bayles, J., Int. Cement Microsc. Ass. 254–272 1991

15. Adams, L.D., The measurement of very early hydration reactions of Portland cement clinker by a thermoelectric conduction calorimeter. Cement Concr. Res. 6 293–308 1976

16. Wilding, C.R. and Double, D.D., A study of inorganic and organic admixtures using combined calorimetric and ultrasonic pulse velocity techniques. Br. Ceram. Proc. 35 349–357 1984

17. Cembureau, Recommended procedure for the measurement of the heat of hydration of cement by the conduction method, Cembureau January Paris 1977

18. Prosen, E.J., Brown, P.W., Frohnsdorff, G. and Davies, F., A multichambered microcalorimeter for the investigation of cement hydration, Cement Concr. Res. 15 703–710 1985

19. Damidot, D., Nonat, A. and Barret, P., Kinetics of tricalcium silicate hydration in diluted suspensions by microcalorimetric measurements. J. Am. Ceram. Soc. 73(11) 3319–3322 1990

20. Hu, S., Yang, H., Liu, S. and Chen, D., Kinetic analysis of the hydration of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ and the effect of adding $NaNO_3$. Thermochim. Acta246 129–140 1994

21. Bäckström, E. and Sandberg, P, in Microcalorimetric investigations of building materials. Div. Building Materials, ed. Wadsö, L., Lund University, Sweden, ISSN 0348-7911 TVBM-3063 1994

22. Gragg, F.M. and Skalny, J., A simple calorimeter for hydration studies, Cement Concr. Res. 2 745–748 1972

23. Zgambo, T.P., Cohen, M.D. and Daugherty, K.E., Construction of a multicell microcalorimeter. Thermochim. Acta 108 79–90 1986

24. Currell, B.R., Grzeskowlak, R., Midgley, H.G. and Parsonage,J.R., The acceleration and retardation of set high alumina cement by additives. Cement Concr. Res. 7 420–432 1987

25. Breval, E., C_3A-hydration - experimental studies. Proc. Cembureau Sem. Koge, Denmark, May 25–26 1975

26. Ramachandran, V.S. and Lowery, M.S., Effect of a phosphonate-based compound on the hydration of cement and cement components. Am. Concr. Inst. SP 148-8 131-151 1994

27. Bensted, J., A conduction calorimetric investigation of Portland cements containing natural gypsum, borogypsum and citrogypsum. Il Cemento 2 93–100 1982

28. Arligue, G. and Grandet, J., Etude par calorimetrie de l'hydratation du ciment Portland en presence de zinc. Cement Concr. Res. 15 825–832 1985

29. Winslow, D.N., Bukowski, J.M. and Young, J.F., The early evolution of the surface of hydrating cement. Cement Concr. Res. 24(6) 1025–1932 1994

30. Yun, W.X., Kang, H.Y. and Ning, W.C., Method for correcting the time lag of a conduction calorimeter and its application. Thermochim. Acta 123 177–182 1988

31. Yilmas, V.T. and Glasser, F.P., Early hydration of tricalcium aluminate-gypsum mixtures in the presence of sulphonated melamine formaldehyde superplasticizer. Cement Concr. Res. 21 765–776 1991