Journal of Thermal Analysis and Calorimetry, Vol. 71 (2003) 821–827

EVALUATING CEMENT HYDRATION BY NON-CONVENTIONAL DTA

An application to waste solidification

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Abstract

This paper presents a method to study cement hydration at ambient temperatures by using a micro processed non-conventional differential thermal analysis (DTA) system, which was used to evaluate the solidification/stabilization process of tannery wastes produced in the leather industry. The DTA curves of pastes composed by slag cement, Wyoming bentonite and waste are obtained in real time and used to analyze the heat effects of the reactions during the first 24 h of hydration. By applying a deconvolution method to separate the overlapped DTA peaks, the energy released in the several hydration stages may be estimated and consequently, the effects of each component on the solidification process. The highest separated DTA peak occurs during the several early stages of cement hydration and is due mainly to tricalcium silicate hydration. Very good correlation shows that the greater is the waste content in the paste composition, the higher is its effect on the rates of reactions occurring during the induction (dormant) period of cement hydration. The presence of bentonite used as a solidification additive in the stabilization process has a similar but less dramatic effect on the dormant period.

Keywords: cement hydration, non-conventional DTA, slag cement, solidification, stabilization, tannery waste

Introduction

The solidification/stabilization (S/S) of hazardous wastes by cement-based binders has the potential for effectively immobilizing hazardous constituents, but may not do so if the cement matrix is altered by the waste. Previous studies on the tanning waste S/S process using thermogravimetry and derivative thermogravimetry [1, 2] after finite hydration times, have shown that the hydration degree of the cement after the first 24 h of the S/S process is highly influenced by the original composition of the paste.

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

During this period of time four stages of cement hydration with exothermal reactions may be identified by isothermal conduction calorimetry [3, 4]. The first one is the pre-induction period, when tricalcium silicate (C_3S) comes in contact with water and begins to react with it within the first 15–20 min. In the second one, known as the dormant or induction period, the C_3S reaction rate slows down and may extend for a few hours and when hydrated calcium sulfate is present, ettringite ($6CaO{\cdot}Al_2O_3{\cdot}3SO_4{\cdot}32H_2O$) begins to form as the main product of hydration of tricalcium aluminate (C_3A). In the third acceleration period setting begins due to the crystallization of the calcium hydroxide ($Ca(OH)_2$) and tobermorite ($3CaO{\cdot}2SiO_2{\cdot}xH_2O$) formed from C_3S hydration, with the rate increasing significantly until a maximum value of heat evolution and paste temperature are reached. Final set of the paste occurs before the end of this period. The fourth stage, called the post-acceleration period, is characterized by a deceleration of the reation rate, and in this period there is a continuous formation of hydration products. After the fourth stage, there is only a slow formation of products, by diffusion controlled reactions.

Isothermal calorimetry, has been used to see the effects of admixtures and operating parameters in cement hydration [5–9] as well as to study plaster mold setting [10], through the continuous measurement of the heat rate evolved from the simultaneous reactions that occur in the respective hydration stages.

The heat effects of cement and plaster hydration reactions may also be monitored by isoperibolic calorimetry [11, 12], which is based on the measurement of the temperature of the paste as a function of hydration time, allowing one to obtain curves with similar shapes to those of isothermal calorimetry. It occurs in semiadiabatic conditions promoted by the thermoinsulating envelope used to prevent great heat exchange between the sample container and the surrounding ambient, whereas isothermal calorimetry is performed measuring the heat exchange between sample and the surrounding ambient, which temperature is always controlled during analysis.

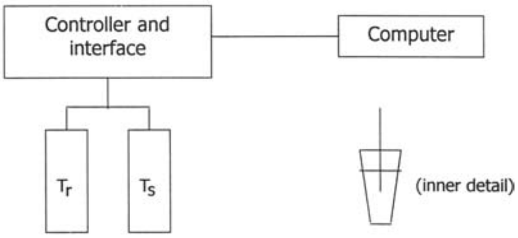
Conventional differential thermal analysis (DTA) is performed by controlling the temperature change rate of the same heating or cooling chamber, where both sample and inert reference are kept [13]. The heat effects associated with physical or chemical changes in the sample are recorded by measuring the difference between its temperature and that of the reference as a function of time or temperature.

In the present paper, a non-conventional DTA system is used to evaluate the effects of the presence of an additive and of a tanning waste on slag cement hydration during the early solidification/stabilization process of the waste. As exothermal hydration reactions occcur, the system, which was previously used by the first author to measure the setting time of plaster molds [14], records the difference between temperature of the sample (T_s) and that of the reference (T_r), which are at independent but same semiadiabatic conditions with respect to the surrounding ambient. This technique, associated with a deconvolution software used to separate the overlapped peaks, is very effective for clarifying and better understanding the main efects of the waste and additive on cement hydration on the first 24 h of the solidification process.

Materials and methods

The slag cement used in this work and designated as AF, is a Type III Portland Cement, code CP III F-32, from Lafarge Company, Brazil. Besides Portland clinker, it contains gypsum, slag from the steel industry and calcium carbonate [15, 16]. The waste, designated as R, is a residual mud containing chromium, dihydrated calcium sulfate and significant amount of organics from a tannery waste treatment station in Franca, SP, Brazil [1]. The Wyoming bentonite, designated as B, is from Sigma Chemical Corporation, St. Louis, MO, USA.

Pastes with AF and a water/cement (W/AF) ratio of 0.5, with and without B and R were analyzed in the non-conventional DTA system, which microprocesses the temperature data in real time. Scheme 1 shows the simplified schematics of the system, which uses Chromel–Alumel thermocouples. The containers are 300 mL (poly)styrene cups inserted in a styrofoam foam vessel. The mixture of solid raw material is prepared and then mixed with the proper amount of water in the sample container. The system records T_s and T_r, the latter from an empty container (T_r), used as reference. The difference (T_s–T_r) as a function of time is calculated by software to obtain the resulting DTA curves.



Scheme 1 Simplified schematics of the non-conventional DTA system. T_r (reference); T_s (sample)

To separate overlapped peaks, PeakFit™ software, SPSS Inc. [17], was applied to the original DTA curve. A set of separated peaks is achieved, and a new DTA curve which represents the sum of the separated peaks is drawn. The software compares the new curve with the original one to evaluate the effectiveness of the peak separation and allows one to choose the mathematical function which best fits with each new peak. In the present case the Gaussian function has given the best results. The area of each peak, which is proportional to the total heat released from the respective reaction within the time limits of the peak, is also calculated by the software.

Results and discussion

Figure 1 shows non-conventional DTA plots of pastes prepared with 20 and 100 g of AF cement with a 0.5 W/AF ratio. The multichannel temperature interface of the system was originally used in TG prototype [18] and its sensitivity, when using Chromel Alumel termocouples, is 0.3°C. These preliminary analyses were done to have a measurement of the effect of cement mass on the order of magnitude of temperature difference signal that could be reached between sample and reference as hydration proceeds. As this difference depends on the instantaneous heat rate generated by the hydration reactions, higher cement masses result in higher DTA signals and consequently, higher resolution. As the 100 g AF case shows a similar curve to those of calorimetric techniques shown in the literature for the early cement hydration stages, this mass of AF was used in all the following paste analyses.

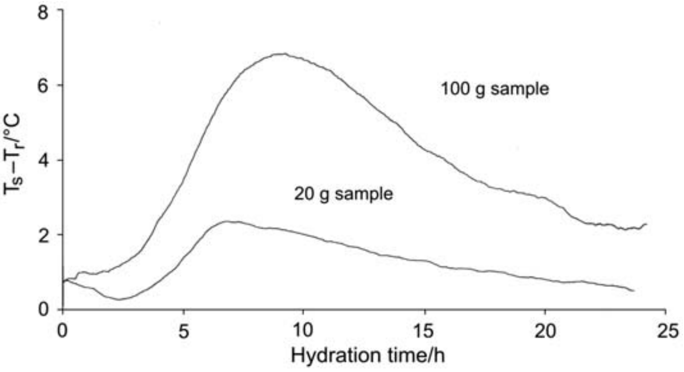


Fig. 1 Non-conventional DTA curves of AF pastes with 0.5 water/cement ratio and different cement masses

Figure 2 shows the DTA curves obtained for pastes containing AF, B and R. Those containing B have a B/AF mass ratio of 0.05, and in those containing R, the R/AF mass ratio is 0.15. It can be seen that the presence of B, even when only 5% of the initial cement mass, shows an accelerating effect on the slag cement hydration, as shown by both the higher exothermal effects noticed during the respective dormant periods, or by the shorter time required to reach the highest DTA peak at the end of the accelerating period of cement hydration. The presence of R accelerates the dormant period much more than B does.

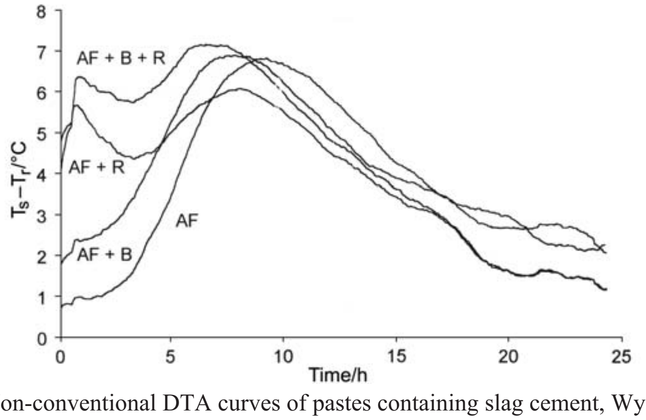


Fig. 2 Non-conventional DTA curves of pastes containing slag cement, Wyoming bentonite and tanning waste

As shown in Fig. 2, when R and B are present there is an accumulative effect of both on AF hydration stages and the maximum DTA peak is attanied in about 7 h. It is important to note when they are not present in the paste the maximum occurs by 10 h. As final set of the paste usually occurs before this maximum is attained [3], the non-conventional DTA curve may also give information about the solidification process of the waste.

Figure 3 shows the DTA curves obtained in pastes containing water, AF and different R/AF mass ratios (0.1, 0.2 and 0.25). From Fig. 3 the influence of the presence of R in the two first hours of the dormant period is clear. As R contains hydrated calcium sulfate [1], the higher is the initial content of R, the higher is the initial calcium sulfate content of the paste. This fact may significantly enhance the ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$) formation from the reaction between that sulfate and tricalcium aluminate in the presence of water, which begins in the pre-induction or dormant period of cement hydration [3, 4] and may explain the higher exothermal effects observed in the first hours of hydration whenever R is present in the initial cement paste.

It is interesting to note in Fig. 3 that the maximum value on the DTA curves decreases as the waste content increases, as well as the area under the DTA curve after the dormant period. As this area is due to the total heat evolved from the several cement hydration reactions that occur in the respective periods and the total cement and water masses are the same, this fact also indicates that some reactions have been significantly accelerated by the presence of the waste in the dormant period.

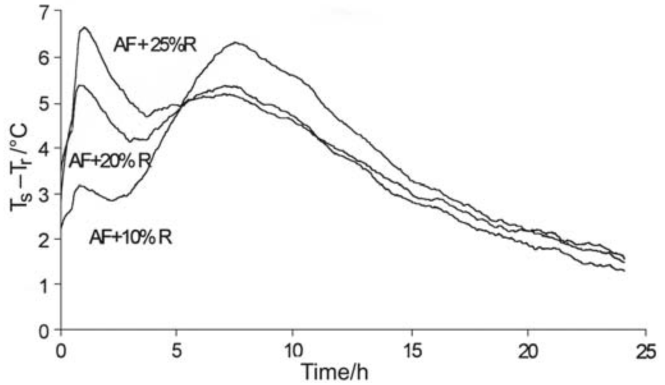


Fig. 3 Non-conventional DTA curves of AF pastes with different waste contents

In order to better analyze the DTA curves, the PeakFit deconvolution method was applied to separate the overlapped peaks due to the simultaneous reactions that occur during the early stages of the AF hydration. Figure 4 shows a typical plot of the method, applied to the DTA curve of the paste containing AF and 0.25 R/AF mass ratio. As occurs in the other pastes containing AF and R, two main peaks are noticed. The first peak (P1) area increases as the waste content increases and is interpreted as being due to the formation of ettringite. It occurs mainly during the dormant period. The second one P2, which is much higher than P1, is due to C_3S hydration and its area decreases as the waste content increases. It begins at the pre-induction period and

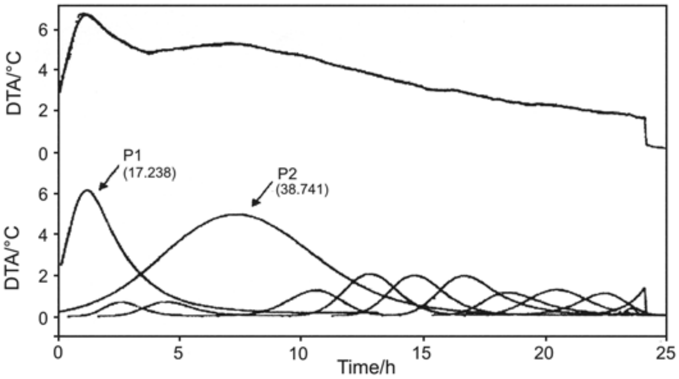


Fig. 4 Typical original DTA curve and deconvoluted peaks of a paste containing AF and 25% of R

continues over all the main periods of early hydration. P2 peak maximum coincides with the corresponding maximum of the DTA curve, which occurs at the end of the acceleration period.

The area of each separated peak is directly proportional to the energy released from the respective exothermal hydration reaction(s). Figure 5 shows P1 and P2 peak area values in arbitrary units a a function of the waste content in the pastes. As can be seen, there is a very good correlation between P1 peak area and the waste content confirming that this reaction is between waste and cement component(s) as discussed before and that it directly accelerates reactions during the dormant period as well as during the subsequent hydration steps. On the other hand it seems that C_3S hydration is somehow affected by the presence of the waste. The fact that there is indeed much more water being consumed by the enhanced hydration reactions during the dormant period may result in less excess water available to promote C_3S hydration as seen by the resulting non-linear correlation of the energy released from this reaction and the waste content.

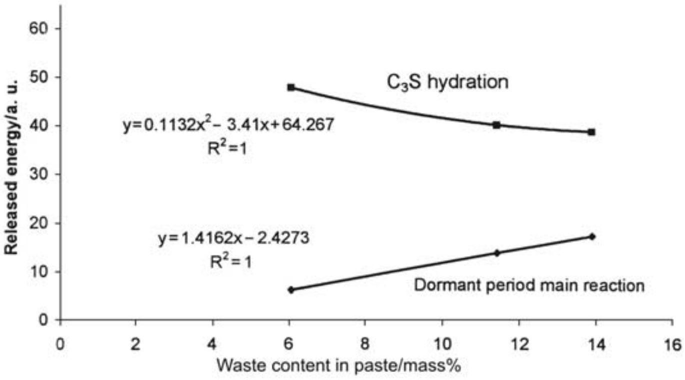


Fig. 5 Effect of the waste content on the energy released from the two main cement hydration reactions in pastes containing AF and R

Conclusions

As in isothermal and isoperibolic calorimetry, non-conventional DTA may be used to study the evolution of cement hydration stages. The technique was applied in this paper to evaluate the early solidification/stabilization process of a tannery waste by slag cement.

The method used to separate the overlapped peaks on the resulting DTA curves allows one to better analyze the several simultaneous reactions and the main effects of the waste and additive on cement hydration during the first 24 h of the solidification process.

Very good correlation obtained from this analysis indicates that the greater is the waste content in the original paste composition, the higher is its accelerating effect on the dormant period of slag cement hydration and the greater is the effect on the subsequent hydration steps.

Dormant period hydration of the slag cement is also enhanced by the presence of the Wyoming bentonite, which was used as a solidification additive in the stabilization process.

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This work is part of a project on Stabilization of Tanning Wastes by Cement sponsored by the Brazilian National Council of Research and Development (CNPq).

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