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INITIAL HYDRATION OF CEMENTITIOUS SYSTEMS USING A SIMPLE ISOTHERMAL CALORIMETER AND DYNAMIC CORRECTION

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Abstract

A simple isothermal calorimeter ideal to study hydration of cementitious systems is described together with an ampoule design to allow addition of water and mixing with the ampoule inside the calorimeter. An overview of dynamic corrections is given, and the utilisation of the different dynamic corrections on the calorimeter output is discussed. Correction of data on β-hemihydrate hydration to form gypsum has shown good kinetic agreement with data from synchrotron X-ray diffraction.

Keywords: cement hydration, dynamic correction, initial reactions, isothermal calorimetry

Introduction

Isothermal calorimetry has been shown to be a useful technique to study the hydration of cementitious systems [1, 2]. In addition to giving the total heat of hydration, the method also offers the possibility to follow the variation in thermal power with time, e.g. the hydration kinetics. This makes isothermal calorimetry a versatile tool when studying the effects of additives such as accelerators and retarders on the hydration reactions. During the last decade, the method have been used to study a variety of systems, i.e. mixes of Portland cement and high alumina cement [2], the effect of lithium salts on these cement mixes [3, 4], $CaCl_2$ addition to lead-retarded cement [5] and the effect of sodium salts on alkali-slag cements [6, 7].

In most studies isothermal calorimetry is utilised to investigate the influence on the major thermal power peak in Portland cement hydration, appearing typically at around 10 h in a pure cement paste [1, 8]. The initial reactions are usually not in focus, consequently the cement and water is mixed outside the calorimeter in order to obtain a homogeneous paste [2–5]. The major drawback of this technique is the inaccuracy in the first hour of measurement and the resulting loss of information about the very early hydration. The reactions taking place during the first minutes of hydration may be of interest when studying for example the addition of gypsum to Portland ce-

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ment and the consequent ettringite formation, or cements or cemetitious materials with very fast setting. Some solutions to overcome this problem have been suggested, Shi and Day [6, 7] weighs the water in a syringe and injects it into the cement after thermostating it to the same temperature as the calorimeter and thus enables the mixing of cement and water inside the calorimetric cell. Zielenkiewicz and Kamiński [9] have developed the method further and mix the cement and water under vacuum to ensure good wetting of the cement particles. To make it possible to thermostate the water above the sample inside the calorimeter, the designs of these calorimetric cells are rather complicated.

Most calorimeters in use do not measure the thermal power developed in the calorimetric cell directly, but rather the temperature difference between the cell and the surroundings. In thermocouple heat conduction calorimeters, the thermal power is conducted through a heat flow sensor before being absorbed by the surrounding environment. As a consequence, the heat accumulation in the calorimetric cell has to be taken into account when studying reactions taking place over a short period of time. For simple systems with good heat conduction, the accumulated heat can be expressed as $C_c[dT_c(t)/dt]$, where C_c [J K^{-1}] is the heat capacity of the entire calorimetric cell including the sample and $T_c(t)$ is the temperature of the cell. To avoid disturbances from changes in the surroundings, a reference cell containing a material with the same heat capacity as the studied system is usually introduced in the calorimetric design. Assuming the same disturbances on the measurement and reference cell, the relationship between the thermal power produced in the calorimetric cell, P [W], and the output voltage from the heat flow sensor, U [V], can be described by the Tian equation

$$P(t)=\varepsilon_1\left[U(t)+\tau\frac{\mathrm{d}U(t)}{\mathrm{d}t}\right] \tag{1}$$

where ε_1 [W V^{-1}] is the calibration coefficient of the thermopile and $\tau=C_c/K_1$ [s] is the time constant of the instrument. K_1 [W K^{-1}] is the thermal conductivity of the thermopile.

This is the most common dynamic correction and in most commercial isothermal calorimeters this correction is embedded in the data collection software [10]. Equation (1) is applicable to construction of the calorimetric cell where the temperature within the cell is uniform at all times during the process [11]. When the reactions are too fast or the studied system or the calorimeter contains thermal transfer barriers, the system will have non-uniform temperature during the process and a more complex correction is necessary [11]. Instead of assuming uniform temperature in the entire calorimetric cell, we assume two temperature zones, each with uniform temperature. Setting up heat balances for the sample and reference cells, Eq. (2) can be obtained with or without making assumptions on where the transfer barriers are located.

$$P(t)=\varepsilon\left[U(t)+(\tau_1+\tau_2)\frac{\mathrm{d}U(t)}{\mathrm{d}t}+\tau_1\tau_2\frac{\mathrm{d}^2U(t)}{\mathrm{d}t^2}\right] \tag{2}$$

The easiest way to refer to τ_1 and τ_2 is as the first and second time constants of the calorimeter without reference to the sample or the calorimeter [11]. No special transfer barriers are specified and the elements that make the system may interact with each other as they would in a real system. It is important to note that the time constants do not have any physical interpretation in this case.

An alternative to describing the dynamic properties of the calorimeter by differential equations is to describe them using the frequency characteristics of the calorimeter [11]. This can be obtained by deconvolution of the experimental data, i.e. by the Fourier transform, and is readily done by a computer [12]. In order to do this correction, the frequency transfer function of the calorimeter must be known. The frequency transfer function, $G(s)$, can be found by taking the Fourier transform of the impulse response. The easiest way to determine the impulse response, $g(t)$, is by applying a constant power, W_0, and differentiate the response, $U(t)$ (Eq. (3)).

$$g(t)=\frac{1}{W_0}\frac{\mathrm{d}U(t)}{\mathrm{d}t} \quad [\mathrm{s}^{-1}] \tag{3}$$

When the frequency transfer function is known, the original thermogram, $P_{\mathrm{corr}}(t)$, can be reconstructed from the calorimeter output, $P_{\mathrm{e}}(t)$, using the algorithm in Fig. 1 [12].

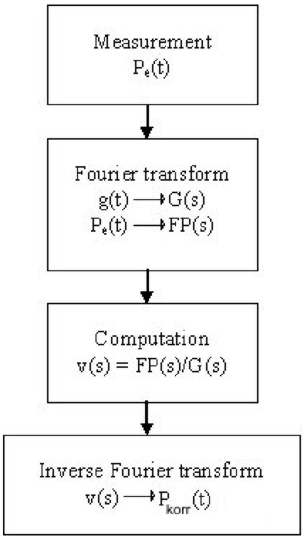

Fig. 1 The algorithm for correcting measurement data with deconvolution using the frequency transfer function, $G(s)$ [12]

This paper describes the opportunity to obtain accurate data on the first minutes of hydration of cementitious systems both with respect to thermal power and to real time. This is done by introducing a method for addition of water and the mixing of cement and water in the calorimetric cell in a simple isothermal calorimeter in combination with dynamic correction of the calorimeter output. It evaluates the important parameters when doing calibration to obtain parameters for dynamic corrections and analyses the practical use of the different models for dynamic correction.

Calorimeter design

The utilised calorimeter is designed for systems such as cement hydration, with a relatively high thermal power. The design of a calorimeter unit is shown in Fig. 2. The heat sink, a large aluminium block, contains two cavities where the calorimeter unit is placed, one for the measurement cell (S) and one for the reference (R). The thermocouple plate (TCP) is placed underneath the ampoule holder and has a sensitivity of approximately 0.7 V W^{-1}. Temperature stability is achieved by a 50 mm thermal insulation [14]. A similar calorimeter is now commercially available (TAM Air, Thermometric AB, Järfalla, Sweden). The ampoules are made of glass and are closed by rubber stoppers (Fig. 3). In order to mix cement and water with the ampoule placed in the calorimeter, two steel tubes were fitted in the rubber stopper. A mixer made from a thin steel tube was placed in the tube in the centre of the stopper. Water was added through the second tube using a syringe with a steel capillary glued inside the needle. When performing experiments, the cement was weighed in the ampoule and placed in the calorimeter. When thermal equilibrium was achieved, temperated water was added. Data were collected using a TC-08 thermocouple logger (Pico Technology Ltd., UK).

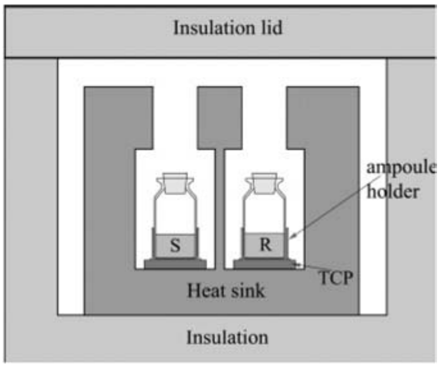

Fig. 2 The design of a calorimeter unit with sample (S) and reference (R)

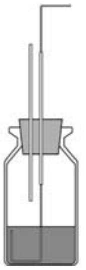

Fig. 3 The ampoule in which the experiments were performed. The rubber stopper was fitted with steel tubes to make mixing of cement and water inside the ampoule possible

Calibration

In order to determine the calibration coefficient, ε, a current, I, is sent through an electrical resistance, R, in an aluminium container during a given time, Δt. The energy produced can be calculated according to

$$Q = RI^2\Delta t \tag{4}$$

The output from the calorimeter is registered, $U(t)$, and ε can be calculated by Eq. (5).

$$\varepsilon = \frac{Q}{\int U(t)\mathrm{d}t} \tag{5}$$

To study the dynamic properties of different cement pastes, resistances were embedded in the cement pastes. The calibrations were performed one day after casting. Different cementitious systems were studied; Portland cement, gypsum and a blend of calcium aluminate cement, Portland cement and β-calcium sulphate hemihydrate. Calibrations were also performed on different amounts of cement paste. All resistances were placed in the center of the cement paste. As a consequence the distance from the resistance to the thermocouple plate will be proportional to the amount of cement paste in the ampoule. A current was sent through the resistance as described above. The output voltage can be fitted to the input thermal power using Eq. (1) or (2) to calculate τ or τ_1 and τ_2 respectively. The fit was done using a least squares routine in Matlab that minimises the residual between the thermal power input and the thermal power calculated from Eq. (1) or (2) by finding the best fit values of the time constants. Fittings were performed on both the whole input pulse and on various parts of the output decay in order to investigate the influence on the time constants. In order to find the frequency transfer function, the current were left on for approximately one hour, and the impulse response was calculated according to Eq. (3). The calibration results were tested on actual measurements to see the practical use of the dynamic corrections.

Results and discussion

The ultimate goal with dynamic corrections is to recreate the thermal power produced in the sample from the calorimeter output. A summary of the corrections with the different methods on a calibration pulse is given in Fig 4. For correction according to Eq. (2), results from least square fitting of both the whole calibration pulse and a part of the calorimeter output decline are presented. All the corrections fail to reproduce the calibration pulse completely. Primarily, the problem is to reconstruct the rapid changes of the pulse where the current was turned on and off.

The corrections done with deconvolution and with Eq. (2), when the whole pulse was used for fitting, give the faster responses. They reach the thermal power of the calibration pulse approximately 30 s after the current is turned on. On the other hand they

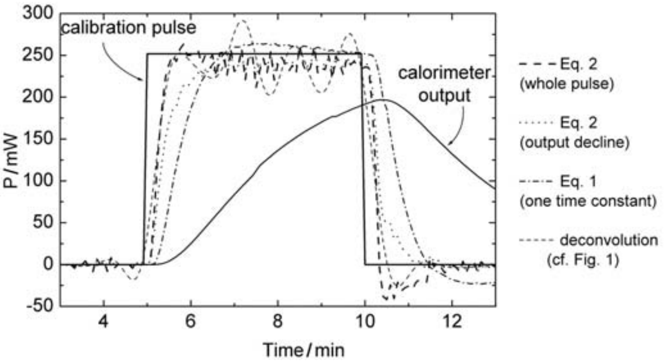

Fig. 4 The different dynamic corrections and their ability to reproduce the calibration pulse

both seem to correct too much, especially the correction with Eq. (2). This is visible directly after the current is turned off, where the corrected curves get negative values for approximately one minute. The negative peak is a mirror image of the second derivative, an evidence for the exaggerated use of the second derivative. The reason for the over-correction lies in the least square fitting. The fitting procedure wants to minimize the sum of the squares of the residuals between the calibration pulse and the corrected output curve. The largest residuals will be found where the current is turned on and off, because the corrections are not fast enough to reproduce these sudden changes. As a consequence the least squares method tries to make the response from the correction as fast as possible at these rapid changes and uses the second derivative to obtain the wanted response as it is the component containing the steeper changes.

When using only a part of the output decline for calculating time constants, the corrected curve uses somewhat longer time to reach the thermal power of the calibration pulse, but the early response to change is approximately the same as the correction done with parameters obtained from fitting to the whole pulse (Fig. 4). The great difference lies in the slower decline down to zero after the current is turned off. Hence it does not overcorrect because the area around the rapid change of the pulse, where the fitting is most difficult, has not been utilised in the fitting. When using only one time constant (Eq. (1)) the response from the correction is much slower than the one with two time constants. The curve corrected with deconvolution has a very high noise level which had to be reduced by filtering in order to see the signal. This noise reduction creates the large amplitudes and long periodicity of the fluctuations in the corrected curve. As a result of the high noise level, the method was not found applicable on actual experiments in this study as it was impossible to filter out the signal from the noise in the fast processes. The results from this method are dependent on how the filtering is done. To use the method, a good understanding of noise reduction with filters is necessary as well as a smooth transfer function.

The utilisation of the remaining three corrections on experimental results is shown in Fig. 5. The system is the cement blend (calcium aluminate cement, Portland cement and β-calcium sulphate hemihydrate). Reactions start immediately after addition of water due to gypsum formation from hemihydrate and AFt formation [13]. Correction with

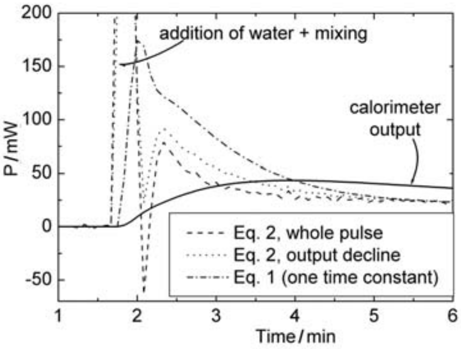

Fig. 5 The different dynamic corrections applied on an experimental curve. The cement is a blend of calcium aluminate cement, Portland cement and β-calcium sulphate hemihydrate and the water to cement ratio is unity

Eq. (1) (one time constant) fails to separate the heat generated by addition of water and mixing from the chemical reactions because the reactions are faster than the time constant. With Eq. (2) it is possible to completely separate the two and thus possible to remove the contribution to the thermal power from water addition and mixing.

When using the calibration result from fitting to the entire calibration pulse, we get over-correction as we did on the calibration pulse, e.g. the corrected curve has a peak below zero, which is unrealistic because the initial reactions and wetting of the cement should produce heat. Correcting with the results from fitting only to the a part of the decline of the calorimeter output, a good separation is obtained between the thermal power produced upon adding water and mixing and the initial reaction, without over-correction. As seen in Fig. 5, the thermal power contribution form mixing can readily be removed and the corrected curve does not go below zero. Figure 5 underlines the importance of using the calibration results with great consideration on experimental data, as the parameters obtained on calibration are obtained by a mathematical procedure which does not consider the physical interpretation of the results. It does also show that it is possible to do good dynamic correction on a system with an immediate reaction while mixing the cement and water in the calorimeter.

The difficulty in reproduction of abrupt changes in the input thermal power, as turning on and off the calibration current is illustrated in Fig. 4. By only using the decline in the calorimeter output in the calculation of the time constants in Eq. (2), Fig. 5 shows that it is possible to obtain parameters which work better on correction of real experiments. The time constants obtained on fitting depend on what part of the decline that is used in the fitting. Figure 6 shows the sum and product of the time constant, as used in calculation in Eq. (2), from fitting different parts of the decline. The part of the decline used in fitting is defined in percentages of the maximum of the calorimeter output. The sum of the time constants is somewhat influenced by the upper limit while the product is strongly dependent on the upper limit and to some extent influenced by the lower limit. This dependency can be explained by looking at the large difference in thermal power input and output as when discussing the over-correction when using the whole pulse for fitting. The

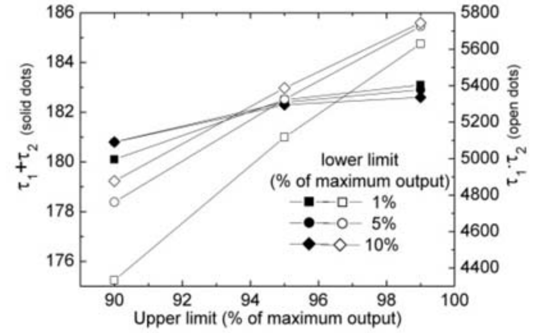

Fig. 6 The parameters in Eq. (2) as used in calculations as a function of the size of the output decline used in the fitting. The parameters obtained by using the whole pulse are $\tau_1+\tau_2=185$, $\tau_1 q \tau_2=7325$. The sample is 4 g of the blended cement

closer to the experimental maximum, i.e. the higher the upper limit used, the harder it is to correct the experimental curve to P=0, and thus the least square fitting routine uses the second derivative to quickly push the corrected thermal power down. As a consequence, the product of the time constants increases with the upper limit. The slight increase in the sum of the time constants shows that the first derivative helps in pushing the corrected curve down. The upper limit is the far most important parameter when performing fits on the calorimeter output decline. When the upper limit is high, i.e. close to the output maximum, the lower limit is no longer important for the product of the time constants. When the upper limit is low the product of the time constants decreases as the tail of decline increases, i.e. small lower limit. When the tail gets long, the difference between the calorimeter output and the line P=0 is small and so it is not necessary to do such a strong correction as it is close to the maximum of the output. As the decline is exponential, the number of data points between 5 and 1% at the lower limit is large, and therefore the influence of the tail is increased in the least square fitting. To avoid the problems with reconstructions of the abrupt changes in thermal power while the calibration current is turned on and off, it would be better to use a current that can be changed continuously and add an input thermal power which is more similar to that of a chemical reaction. A data logger which can log both the input current and the calorimeter output would be necessary and fitting can be done with Eq. (2).

Table 1 Time constant according to Eqs (1) and (2) for three cementitious systems. The sample size is 4 g (2 g of cement and 2 g of water)

Cement type	τ (Eq. (1))	τ_1 (Eq. (2))	τ_2 (Eq. (2))
Portland cement	194	57	143
Gypsum	166	40	129
Blended cement*	192	55	137

* Blend of calcium aluminate cement, Portland cement and β-calcium sulphate hemihydrate

Table 1 gives an overview of the three different cementitious systems and their time constants obtained according to Eqs (1) and (2), when the conditions during calibration were similar. Portland cement shows the larger inertia of the three while gypsum is the faster. The difference in the materials thermal qualities underlines the importance of performing calibration on the specific material of interest.

Figure 7 shows the influence of the sample size on the time constants for the blended cement. Using one time constant (Eq. (1)), the time constant increases with increasing sample size. When using two time constants (Eq. (2)), but both the sum and the product of the two time constants, which are the important parameters in Eq. (2), increase with increased sample size (Fig. 7). This means that the larger the sample, the greater inertia. As the resistance is placed in the middle of the sample, the result can be explained by the increasing distance from the resistance producing the heat to the thermocouple plate as the sample gets larger. At the same time will the heat capacity of the calorimetric cell in Eq. (1), C_c, and the heat capacity of the sample in Eq. (2), increase when the sample gets larger as they are not specific heat capacities and thus dependent on the mass of the different substances they include. It is therefore important to interpret these results whit great consideration, because in a real sample with chemical reactions taking place, the heat is uniformly distributed throughout the sample and the influence of the sample size might not be as significant as it is when the heat is produced in a resistance. To better simulate the real experimental conditions it might be suitable to use a resistance wire which can be distributed better in the sample and consequently represent the heat distribution in the sample more realistically.

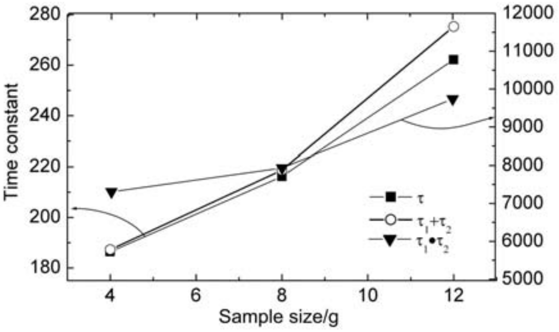

Fig. 7 The variation in time constants in with the sample size (total mass) of the blended cement, the time constant in Eq. (1) and the sum and product of the time constants as in calculations with Eq. (2)

Several variations in calibration current and time were tested during calibration to see the influence on the time constants. The calibration current did not have any noticeable effect on the resulting time constants achieved upon least squares fitting. On the other hand did the time the calibration current was applied show to give variations in the resulting time constants (Fig. 8). When looking at the important parameters in Eqs (1) and (2), it is clear that τ in Eq. (1) and $\tau_1+\tau_2$ in Eq. (2) increase with the calibration time while $\tau_1 q \tau_2$ is fairly constant (Fig. 8). From a mathematical point of

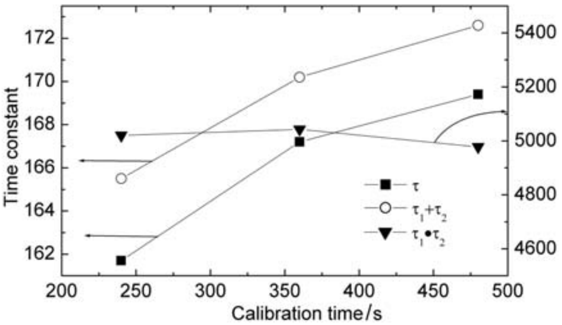

Fig. 8 The variation in time constants with calibration time, the time constant in Eq. (1) and the sum and product of the time constants as in calculations with Eq. (2). The sample is 4 g of the blended cement

view, this means that the first derivative becomes more important in the fitting as the calibration time increases. The absolute size of the first and the second derivates are the same when the current is constant, while the maximum output from the calorimeter increases when the time the current is applied becomes longer. The maximum of the calorimeter output will always be the value measured just after the current is turned off. When the least square fitting uses Eqs (1) and (2) to try and correct the thermal power to zero, a larger calorimetric output needs a larger correction, e.g. when the current has been applied for a longer time. Because the size of the first derivative is independent on the calibration time, the larger correction reflects in a larger time constant (Eq. (1)) or larger sum of the time constants (Eq. (2)). The reason only the first derivative is influenced is because it has a larger absolute value and it has a value different from zero for a longer period of time than the second derivative and hence it is a stronger tool for pushing a large part of the corrected curve down.

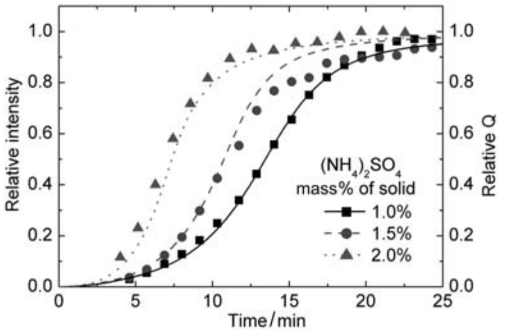

Fig. 9 The relative intensity of gypsum from synchrotron X-ray diffraction (dots, left axis) and the normalised accumulated heat measured with calorimeter and corrected according to Eq. (2) (lines, right axis) as functions of time for formation of gypsum from β-hemihydrate accelerated with 0.5% gypsum and different amounts of ammonium sulphate. The water to solid ratio was unity

The ability to get good kinetic measurements with correction according to Eq. (2) is illustrated in Fig. 9. It shows three systems with gypsum formation from β-calcium sulphate hemihydrate accelerated by addition 0.5% gypsum and different amounts of ammonium sulphate. Measurements have been done both with synchrotron X-ray diffraction (dots) and with the described calorimeter (lines). The X-ray diffraction measurements were done in-situ as previously described [13], and each spectrum was collected for a total of 30 s. The calorimeter output was corrected according to Eq. (2), the heat from addition of water and mixing removed and the thermal power integrated to get the total heat of hydration. The difference increases some as the reaction is slower. The X-ray data are collected over 30 s, consequently they represent an average of the gypsum content during this time interval. The two methods have very different sample sizes and sample geometries and crystallisation is a sensitive phenomenon that might be influenced by these factors. Reproduction of similar X-ray experiments has shown variations at about 5% of the hydration time [15]. Considering the influencing factors, the measurements with X-ray diffraction and calorimetry coincide well and show that it is possible to obtain good kinetic information with isothermal calorimetry using dynamic corrections. The measured heat of hydration for the reactions is -16 kJ mol^{-1} which coincides well with thermodynamic data for dissolution of β-hemihydrate and crystallization of gypsum at 20°C [15].

Concluding remarks

It is possible to obtain kinetically correct data and good thermodynamic data by dynamic correction of the output from a simple calorimeter, as the one described here, when the correction is done with great consideration. A further step to get a better thermal model of the calorimeter and sample might be to simulate the output by modeling the heat transfer of the calorimeter and sample or do calibrations using a resistance wire and a power source that can be continuously changed and monitored.

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