FROM THE CONCRETE TO THE PASTE: A SCALING OF THE CHEMISTRY

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ABSTRACT

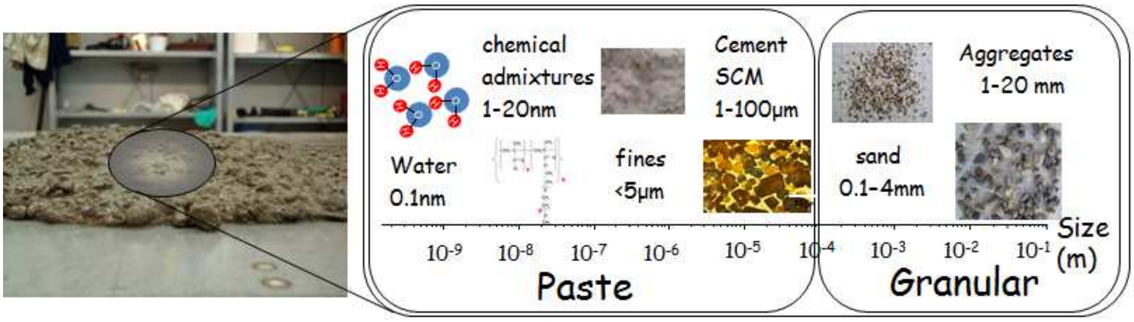
The design of a concrete is a time consuming process which need large amounts of materials and generates huge costs. A reduction of this work is however possible if the characterization is only made with the equivalent or constituting paste of the mortar or concrete. In order to make the scaling between concrete and cement paste, isothermal and semi-adiabatic calorimetric techniques are used to follow the evolution of the heat rate and cumulative heat. The paper demonstrates that the results obtained with the isothermal calorimetry can be also generated with the semi-adiabatic calorimetry which is a more suitable tool to follow the chemistry evolution during the hydration of cementitious material in the conditions met in the reality. We demonstrate the ability of the semi-adiabatic calorimeter to study the effects of the mixing protocol, admixture additions and curing conditions on the hydration kinetics of the concrete and its equivalent paste.

Keywords: calorimetry; semi-adiabatic; mix; hydration;

INTRODUCTION

Mortar and concrete are prepared with complex formulations containing a broad range of materials, which are chemically reactive, or not. Their usage has to be in contrary extremely simple and robust for the users. for the users who desire to mix a powder and aggregates with water to obtain a viscous fluid which is further applied to form a solid material with the desired mechanical properties. The desired quality of mortar and concrete depends on the application which imposes the mixing condition, workability, flowability and also curing conditions - time, robustness against temperature and humidity, strength evolution - as well as its final performances including mechanical properties, appearance or durability which affects the temporal chemical resistance. Most of these performances can be tuned with the used of admixtures, which control mainly the physico-chemistry of the constitutive paste composed with the elements smaller than 0.1mm. A description of the different elements of a concrete classified by their size, schematically presented in Fig. 1, differentiates the constitutive paste responsible for the chemistry of the concrete from the sands and aggregates.

Figure 1. Schematic description of the different concretes constituents by sizes



Product quality with its cost and time to market can be improved (i) with a reduction of the consumed material and energy needed to design the optimal formulation, (ii) with more quantitative characterizations and (iii) deeper investigation of the impact of the raw materials nature on the early age properties of the cementitious materials. The binders, water and admixtures present in the constituting paste, are responsible for the chemistry occurring in the early age of cementitious materials as sands and aggregates can be considered as inert fillers. However, the inert constituents have an influence on the physical properties, as they affect mix, flow and strength properties. The comprehension of their influences on the physical properties, but also indirectly, on the chemistry, is therefore primordial to able the scaling and usage of smaller quantities of pastes to study concretes and mortars. The reactivity of cementitious materials can be followed by standardized calorimetric measurements, which are performed either under isothermal or semi-adiabatic condition [1, 2]; in the first case, the energy needed to maintain a constant temperature of the cementitious sample is recorded as a function of the time, while in the semi-adiabatic technique, the evolution of the temperature developed during the hydration is followed.

The compatibilities between the nature of binders, plasticizers and other admixtures as well as their effect on the hydration kinetics at different proportions, the effects of the external parameters such as the mixing condition in terms of mixing time and sequence of the components addition, and the influence of the curing temperature on the rate of hydration are primordial parameters for the application of cementitious materials. All these phenomena can be observed and quantified with the semi-adiabatic calorimetry as exposed in this paper.

MATERIALS AND METHODS

Isothermal measurements have been performed with a commercial calorimeter (Calmetrix), which maintains the isothermal condition by a Peltier element; the energy needed to maintain the sample temperature is directly proportional to the energy released during the hydration. The semi-adiabatic calorimeter has been customized by using highly accurate temperature sensors (PT100, type B) in a series of 4 calibrated semi-adiabatic containers of different volume: 75, 200, 1500 and 25000ml. As a part of the heat generated by the hydrating cement is dissipated over time due to the thermal lost, the total heat induced by cement hydration can be approximated with the Eq. 1:

$$Q(t) = \frac{\rho V c_p \left(T(t) - T_e\right) + kA\int_0^t \left(T(t) - T\right)dt}{m_b} \tag{1}$$

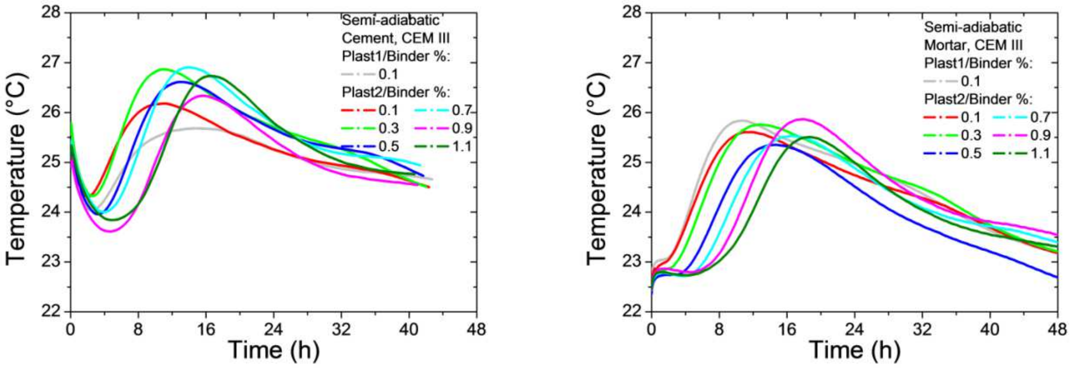
Where T_e is the exterior temperature (K), $T(t)$ the sample temperature (K), A the contact surface between sample and cell, V the sample volume, c_p the specific heat capacity of the sample, ρ its density, k the thermal transfer constant of the box and m_b the total mass of binder. In order to allow a rapid comparison between the different formulations; three characteristics points with the corresponding times and temperatures are extracted from the evolution of the heat rate: (i) minimal Hydration, (ii) maximal Hydration and (iii) maximal Temperature. The measurements of the energy needed during the mix have been recorded with an Anton Paar rheometer, Physica 301, equipped with a knitter cell.

FROM THE ISOTHERMAL TO THE SEMI-ADIABATIC CALORIMETRY

Both semi-adiabatic and isothermal calorimeters give the temporal evolution of the heat rate; however in the semi-adiabatic condition due to the chemical activity of the cementitious material, the sample temperature evolves naturally while in the isothermal, the temperature is kept constant. As temperature has a remarkable impact on the hydration kinetics [3], isothermal and semi adiabatic conditions generally lead to different evolutions of the heat rate. In the field, the temperature of a fresh mortar or concrete is not constant and can increase of up to 60 °C above the ambient temperature. This self-heating plays an important role of auto-catalization of the hydration reactions and therefore has to be taken into account to reproduce the field conditions in the laboratory.

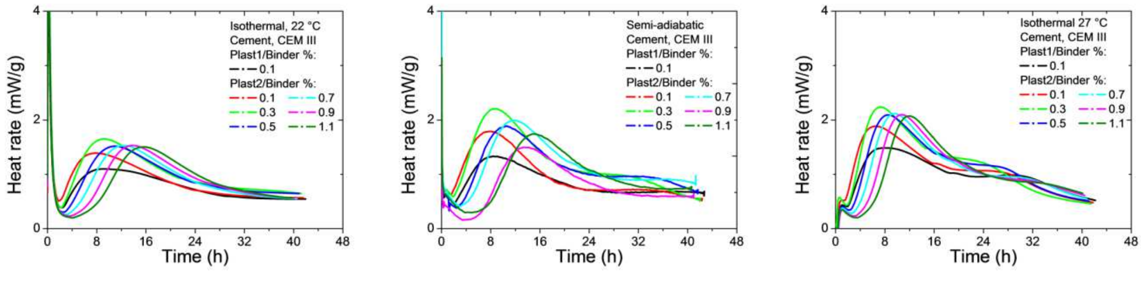
In order to allow a good comparison of the temporal heat rate and cumulative heat evolutions obtained with both techniques, a cement paste and a mortar have been prepared with a CEM-III 32.5 N. The CEM-III has the advantage to be less reactive than CEM-I and CEM-II, and as a consequence, the temperature evolutions recorded with the semi-adiabatic calorimeter for both cement and mortar are limited to a narrow range between 22 and 27 °C as it can be seen in the two graphics of Fig. 2.

Figure 2. Temperature evolutions over time for CEM-III samples measured in semi-adiabatic calorimeter; 75 mL samples for cement paste (left) and 200 mL samples for mortar (right). The evolution of the temperature as a function of the time are ordered for the Plasticizer 2, from the left to the right respectively with the concentrations ranging from 0.1 to 1.1%.



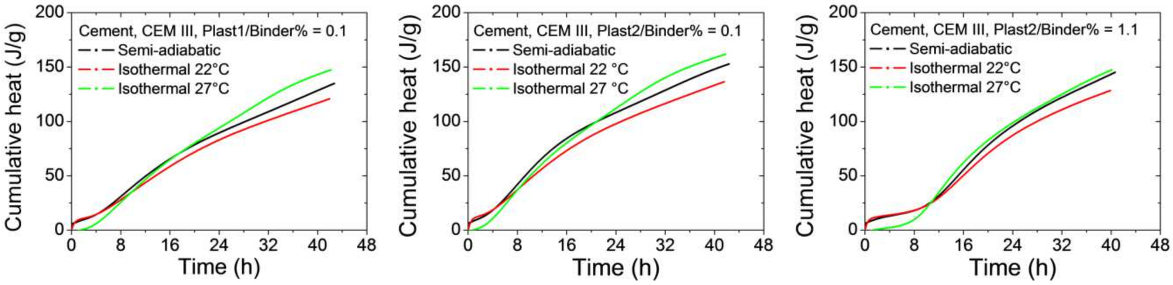
In order to investigate the effect of the temperature on the hydration kinetics, the isothermal measurements have been made at 22 and 27°C; representing the lower and upper limit of the temperature recorded in semi-adiabatic conditions. The resulting heat rates of the cement paste samples differing in the dosages of a plasticizer are represented in the three graphics of Fig. 3.

Figure 3. Heat rate of a cement paste (CEM III, W/B=0.4): semi-adiabatic (middle), isothermal at 22 °C (left) and at 27 °C (right). The evolution of the heat rate as a function of the time are ordered for the Plasticizer 2, from the left to the right respectively with the concentrations ranging from 0.1 to 1.1%.



A general good correlation between the two techniques is obtained with similar evolution of the heat rate profile. The semi-adiabatic heat rate lies between both isothermal evolutions due to the natural temperatures which are between both extremes. The evolution of the cumulative heat represented in the three graphics of Fig. 4 confirms the effect of the temperature on the cement hydration and also demonstrate the excellent quantitative correlation between the two techniques. In all cases, the evolution of the cumulative heat obtained in semi-adiabatic conditions is between the two curves measured at 22 and 27 °C. However, the evolution of the cumulative heat obtained at 27 °C is in the first hours negative due to the temperature difference between the initial sample at approximately 25 °C and the instrument temperature imposed at 27 °C. Tests performed with the two different calorimeters types demonstrate that the semi-adiabatic-calorimetry is the suitable tool to follow quantitatively the chemistry evolution during the hydration of cementitious material in the condition met in the reality.

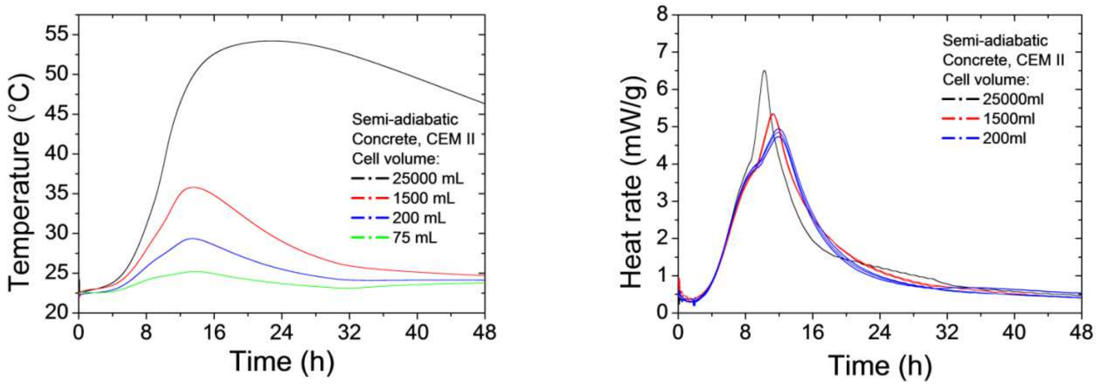
Figure 4. Cumulative heat obtained in semi-adiabatic conditions (black, middle), isothermal 22 °C (red, down) and 27 °C (green, up). From left to right: CEM-III0.1% of Plast1, 0.1% and 1.1% of Plast2.



THE IMPACT OF THE SAMPLE VOLUME

One of the main advantages of the semi-adiabatic over the isothermal measurements is the ability to scale or even to reproduce the behaviour of the mortar and concrete in the laboratory. As the temperature has a significant impact on the hydration rate of the cementitious material, the volume of the measuring sample has to be adjusted for the application: a larger volume of concrete accumulates more heat than a smaller one, therefore its temperature increases faster and reaches higher maximal values. The effect of the sample's self-acceleration, and thus the scaling of the measurement, is made with different cell volumes of 75, 200, 1500 and 25000ml placed in different insulation boxes. The surface to volume ratio of the different cells is then not kept constant, so that the heat exchanges with the outside is not the same for the 4 different cells, leading to different temperature evolution as shown with in the left graphic of Fig. 5. The temperature increase of the concrete in the 75mL cell is rather low with a maximum of approximately 2 °C. However, the maximum temperature difference reached is 6 °C with the 200mL cell, 12 °C with 1500mL, while over 30°C with 25000mL. The cumulative heat obtained with all the cells is about the same after 24 hours within an error of +/-5%. However, the evolution of the heat rate demonstrates the effect of the increased auto acceleration with the cell's size due to the higher temperature. A quantitative measurement of a concrete cannot be done with the smallest cell due to the size of the larger aggregates. As it can be seen from the evolution of the heat rate represented in the right graphic of Fig. 5, the position of the second hydration peak is shifted towards lower times due to the higher curing temperature. Therefore even though the minimum hydration time is constant, the strength evolution should be faster for the larger volumes. The profile of the heat rate depends on the curing temperature and confirms that the calorimetric measurements have to be done with the same conditions as met in the field.

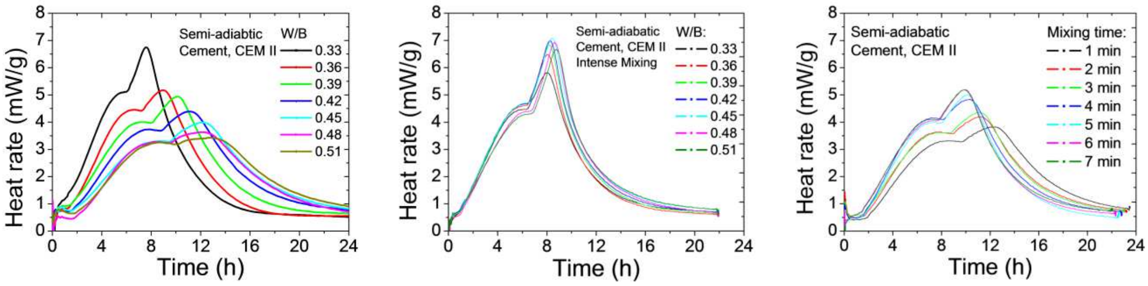
Figure 5. Cell size effect on the evolution of the temperature (left) and heat rate (right), for a concrete prepared with a CEM II. The lower temperature correspond to the smaller volume, and the faster evolution of the heat rate to the higher volume of cell.



THE IMPACT OF THE MIXING ENERGY ON THE CEMENT HYDRATION

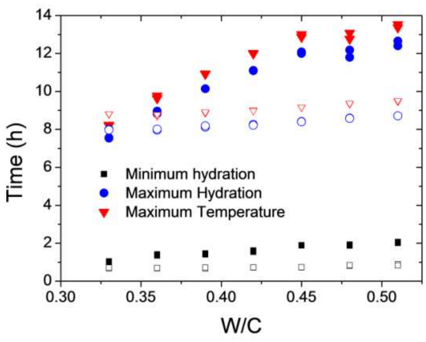
The preparation of a fresh cement paste, mortar or concrete follows a standard mixing protocol which defines the type of mixer, mixing time and speed and the addition sequence of the different components, as the admixtures can be added in a second step of the mix. In order to study the impact of mixing on the cement viscosity and hydration kinetics, rheological and calorimetric measurements have been performed on cementitious materials prepared with different mixing designs. One of the most accepted argumentations of the acceleration of the reactivity with the increasing mixing time is the generation of surfaces or finer particles which are acting as nuclei for the precipitation of the hydrates [4, 5]. During mixing the friction between the particles increases the temperature of the material [6] which impacts also the hydration. A longer and more intense mix therefore tends to accelerate the hydration kinetics. In order to study the impact of the mixing intensity on the kinetics, three series of samples prepared by varying mix design and mixing protocol have been measured with semi-adiabatic calorimetry: (i) first the W/B ratio has been varied from 0.33 to 0.51 using identical mixing protocol; 80 % of water is added in the first step of the mix and 20 % + plasticizer in the second, (ii) secondly the mixing protocol changes ; all samples are in the first step prepared with the same quantity of water which corresponds to the W/B of 0.33 and in the second gently step the rest of water and plasticizer is added to reach the final W/B from 0.33 to 0.51, avoiding to introduce additional mixing energy, (iii) in the last series the time of mixing has been increased from 2 to 8 min while the W/B is kept constant. The evolution of the heat rate for different W/B ratios prepared with the first mix protocol is shown in the left graphic of Fig. 6. The effect of the W/B ratio on the curing kinetics is clearly showed with an evolution of the heat rate peaks from approximately 8h for the W/B of 0.33 to approximately 12h for 0.51. This behaviour is not caused by the water content but rather by the viscosity of the paste. Since lower W/B leads to a higher viscosity and as the samples are mixed with identical speed and time, a higher energy is consumed for the lower W/B. A higher mixing energy leads to the creation of more surfaces favourable for the precipitation of the hydrate and increases the temperature of the sample.

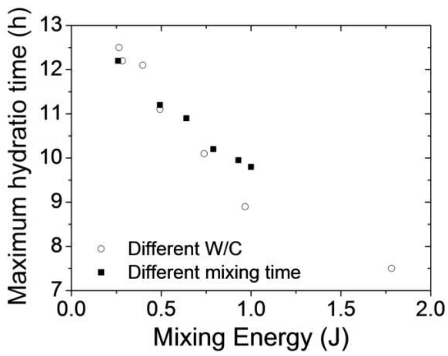
Figure 6. Effect of the water to cement ratio and mixing protocol on the semi-adiabatic heat rate evolution of the cement paste prepared with CEM-II: W/B with constant mixing protocol (left), W/B with constant mixing energy (center) and mixing time with constant W/B (right). The evolution of the heat rate is evolving from left to right respectively with the increase of the W/C (left and middle) and the increase of the mixing time (right).



This simple effect is confirmed with the second mixing protocol where all the samples are prepared with the constant mixing energy and thus equal amount of surface is formed. Equalized heat rate evolutions are obtained and only minor delays in the hydration peaks can be still observed due to the higher heat capacity of water [6] as it can be seen in the central graphic of Fig. 6. Last series are prepared by changing the mixing time at constant W/B. A shift of the heat rate peak from approximately 12h to 10h is observed when the mixing time is increased from 1 to 7 minutes (right graphic of Fig. 6). The mixing time has therefore an impact on the hydration kinetics as a longer mixing time leads to higher energy consumption [8]. However, mixing times longer than 6 minutes does not significantly accelerate the kinetics anymore as the mixing energy is much lower at high W/B and mixing time has to be extremely long for the to obtain the same total energy than those obtained at low W/B.

Figure 7. Left: effect of the W/B ratio and mixing protocol on the hydration kinetics of a cement paste prepared with a CEM-II. Full points: equal mixing protocol, hollow points: equal mixing energy. Right: relation between the mixing energy and the time to maximum hydration.





CONCLUSION

This paper demonstrates that the results obtained with the semi-adiabatic calorimetry are quantitatively comparable to those obtained with isothermal. Furthermore we show that the measurements of different sample's volumes allow the creation of a better, scalable correlation between the conditions obtained in the field during the application and the laboratory. We prove that the modifications of the rheological properties resulting by the sequence of the addition of components and mixing procedure have an additional effect on the retardation of the hydration kinetics. A direct link between mixing energy and hydration kinetic of a cement paste constitutive in a SCC has been made. The delayed addition of a part of the water or of the plasticizer increases the viscosity: the retardation of the hydration kinetic, which may appears with the plasticizer, is not then not only chemical but also physical, as the plasticizer involves a reduction of the viscosity and then a reduction the mixing energy which create a retardation of the hydration rate and therefore of the setting properties.

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