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Travaux Pratiques de Matériaux de Construction

Section Matériaux 6^{e} semestre

Groupe n° :

Calorimétrie

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Soumis deux semaines après la TP, avec la date, le nom de groupe spécifié

TRAVAUX PRACTIQUES DE MATERIAUX DE CONSTRUCTION

ISOTHERMAL CALORIMETRY

Spring semester 2023

1. INTRODUCTION

Objectif du TP

The main objective of this TP is to demonstrate how hydration kinetics of cement samples can be studied using isothermal calorimetry. This method measures heat, and the exercise aims to show how this measurement can be used to analyzed the hydration kinetics.

Elements de theorie (types of calorimetry, how isothermal calorimetry works, the basics of hydration)

Calorimetry is a scientific method used to measure the amount of heat released or absorbed during a physical or chemical process. It involves using specialized instruments called calorimeters to take precise measurements of heat energy. Calorimetry is used in many fields of science, to gain a better understanding of how different materials react under different conditions.

In the cement industry, calorimetry is used to measure the heat generated during the process of cement hydration, which is when cement is mixed with water and undergoes a chemical reaction. The heat generated during hydration is crucial in determining the setting and hardening of concrete, which is essential for construction applications. By using calorimetry, scientists and engineers can determine the amount of heat released during cement hydration and evaluate how it changes over time. This information helps to optimize cement formulations and develop cement-based materials with improved performance characteristics, such as increased strength and durability.

There are several types of calorimeters that are utilized in the cement field. Among them, isothermal calorimetry is the most widely used technique, in which the heat production rate or thermal power of a sample is continuously measured over time at a constant temperature (refer to figure 1, a). On the other hand, semi-adiabatic calorimeters measure the heat generated during cement hydration in a partially insulated container, and the resulting temperature increase is recorded to determine the rate of hydration (refer to figure 1, b).

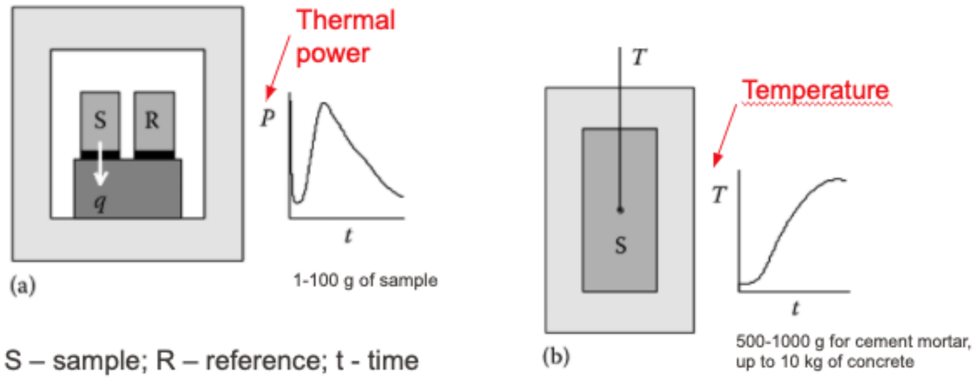

Figure 1. a) isothermal calorimeter. b) semi-adiabatic calorimeter.

2. ANALYSE

Here the idea is to show why we use calo in cement field and based on that, what different possibilities can we find (curve shape, peaks, position, heat flow)

TAM AIR is mostly used in the cement field. It has the advantages of high sensitivity, multi-sample channels, lowest baseline drift, and long-term temperature stability.

The cement hydration process is exothermic, so we can use isothermal calorimetry to measure the total heat of cement hydration. The reaction rate can be also monitored in the different phases. For an individual cement type, the heat flow curve can be totally different and it can be separated into several phases. So, the usual purpose of doing isothermal calorimetry is to identify the hydration kinetics by obtaining the heat flow curve.

1) Heat flow curve

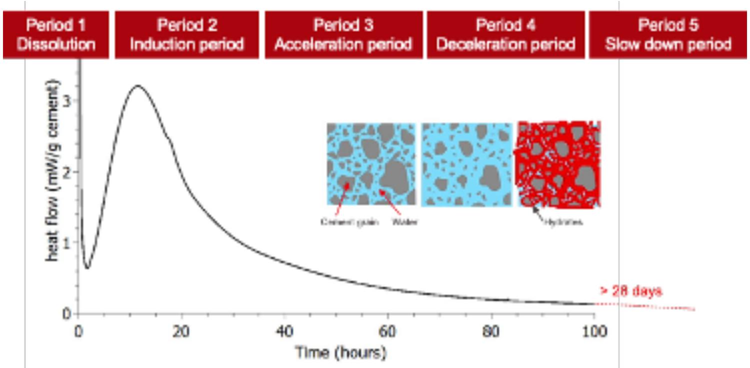

Fig. 2 the heat flow of a typical Portland cement with a 5-hydration period.

For example, we can use the heat flow curve to differentiate the cement types, the hydration speed, the optimal sulfate dosage, retardation, and acceleration, understand the impact of other factors (T, w/c, finesse, admixture), etc.

The influence of SCMs on hydration kinetics can be also analysed as shown in Fig. 3. The addition of different mineral admixtures accelerates the hydration of clinker. Especially, limestone can act as the C-S-H nucleation sites which show a better condition compared with other SCMs. Acceleration of hydration in blended systems means more hydration products form than only clinker hydrates.

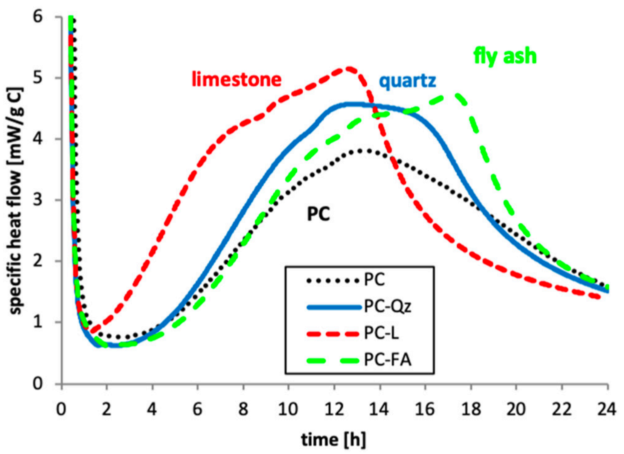

Fig. 3 Heat flow measured for Portland cement (PC) compared with blended systems with 50% replacement of limestone (L), quartz (Qz) and fly ash (FA).

2) The accumulative heat releases

The cement hydration process needs water to proceed, so the impact of water content in the mix can make a difference in the total heat release as shown in Fig. 4.

As supplementary cementitious materials (SCMs) are also widely used to replace cement, the Iso Cal can be used to identify the reactivity of the pozzolans, such as fly ash, ground blast furnace slag, calcined clay, silica fume, etc. The more total heat released from the cement hydration, the pozzolan is more reactive to form more hydrates. The example is shown in Fig. 5. by the influence of the kaolinite content in calcined clay.

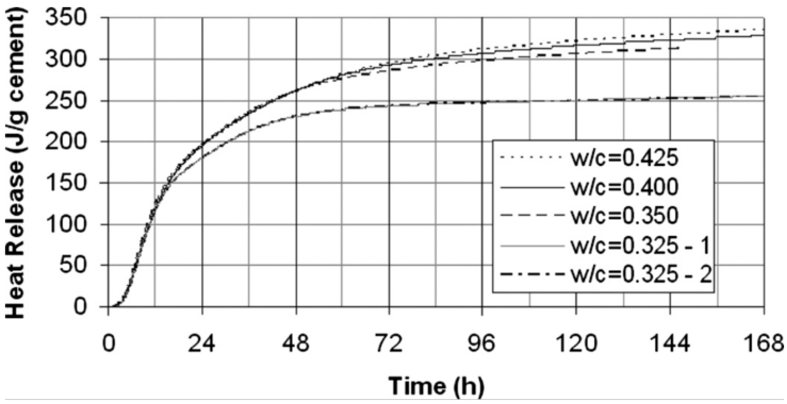

Fig. 4 The heat release in the cement hydration with different w/c ratios.

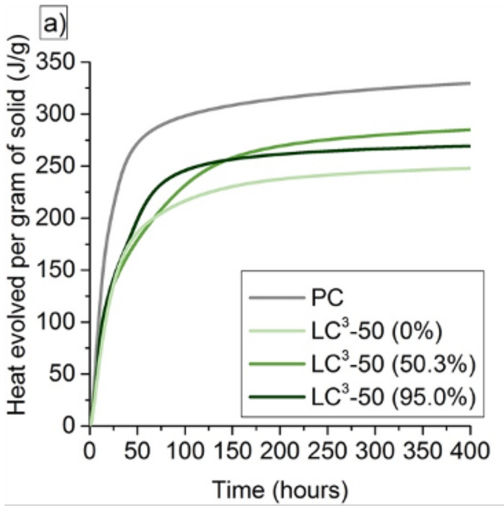

Fig. 5 The heat release from cement with different kaolinite content clays.

Fig. 6 is another example to know the total amount of the SCMs that we can replace cement with and compromise the degree of hydration.

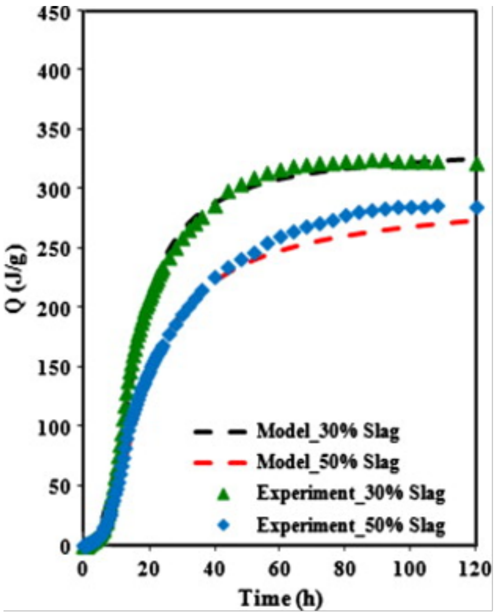

Fig. 6 The heat release from slag blended cement.

Preparation des echantillons (for cement paste and why we need references, why water? etc…)

To prepare the sample for isothermal calorimetry, several tools and materials are required, including a balance, plastic containers, a stirrer, anhydrous materials, glass ampoules, and a chronometer. The following steps are typically followed:

- Weigh the anhydrous components using a balance, following a predetermined mix design. The components are then mixed with a blender or by hand to ensure homogeneity.
- The powder is then mixed with distilled water with a fixed water-to-cement (or binder) ratio, for two meaning in a stirrer for two minutes.
- Transfer the resulting paste into a glass ampoule. The amount of paste used may vary, but it is generally around 10 g.
- Close the ampoule with a lid and place it into the calorimeter.

The calorimeters work also with references. In this case, it has to be a substance that should have a similar heat capacity as the samples an no heat production, as water. The amount of water in the reference ampoule is calculated to have the same specific heat capacity as the relative cement paste sample in the corresponding channel.

3. ETUDE DE CAS

In this section they will have to treat the raw data, plot the curves and identify the type of sample/cement. We can give them a cement sample, LC3, alite, undersulfated sample…. Ideas?

Two different samples were characterized through isothermal calorimetry. The pastes were prepared using a w/b ratio of 0.4 and around 10g of paste.

The heat flow (mW) was measured over 7 days and the heat (J) was automatically calculated by the software as the integration of the heat flow over time.

The raw data acquired after 7 days are reported in the attached excel file as provided by the software TAM Air.

Prepare an excel file in which you can correct the raw data of each sample. The data should be corrected according to the paste mass (poured in the ampoule) and the time needed to prepared the sample (from the addition of water to the mix until the insertion of the ampoule into the calorimeter). Both values are included in the attached file.

Normalize the heat flow and heat per (i) paste content and (ii) cement content.

Plot two graphs using the corrected and normalized data: one for the heat flow and one for the heat. For each graph, overlap the curves of the two samples to compare them.

Identify the main steps of cement hydration (Dissolution, Induction, Acceleration, Deceleration periods) and hydration peaks.

Highlight the differences between the two samples and identify which type of sample they are. Provide a detailed justification for your assumption.