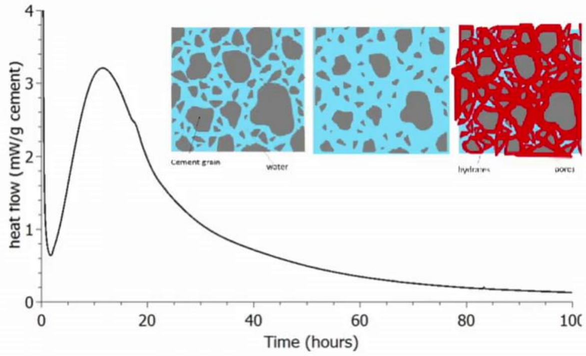
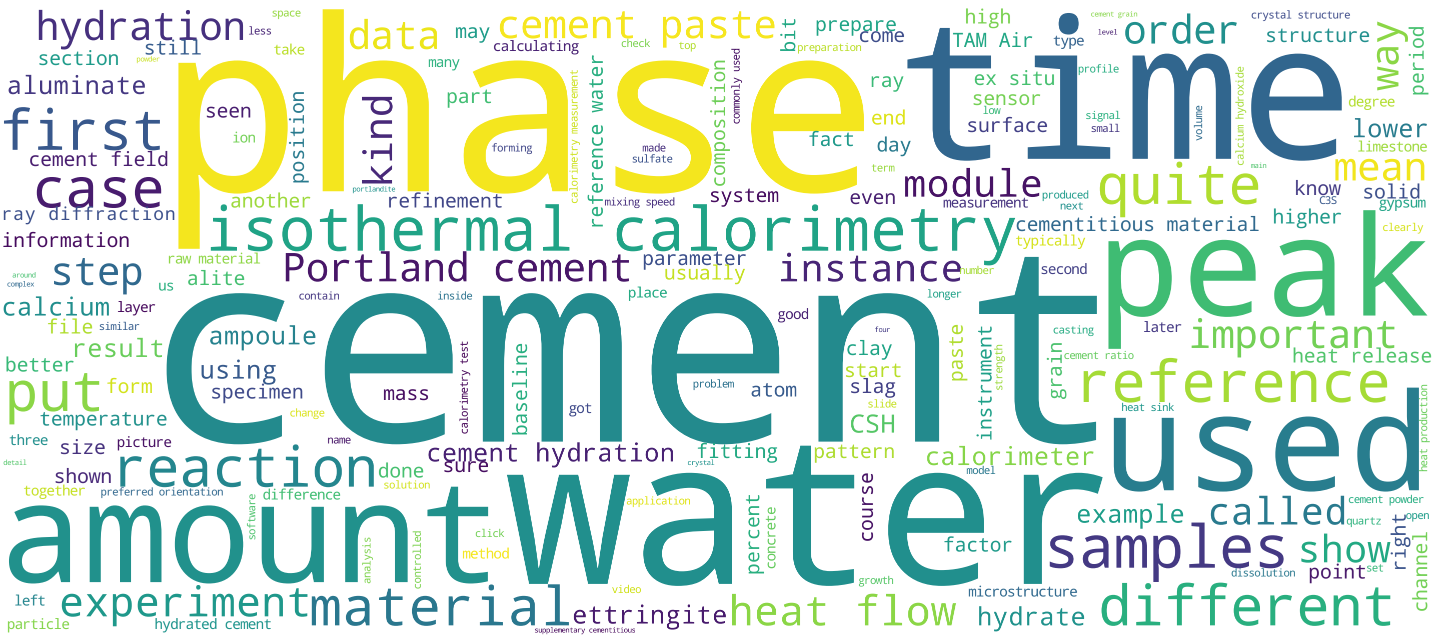


Isothermal Calorimetry

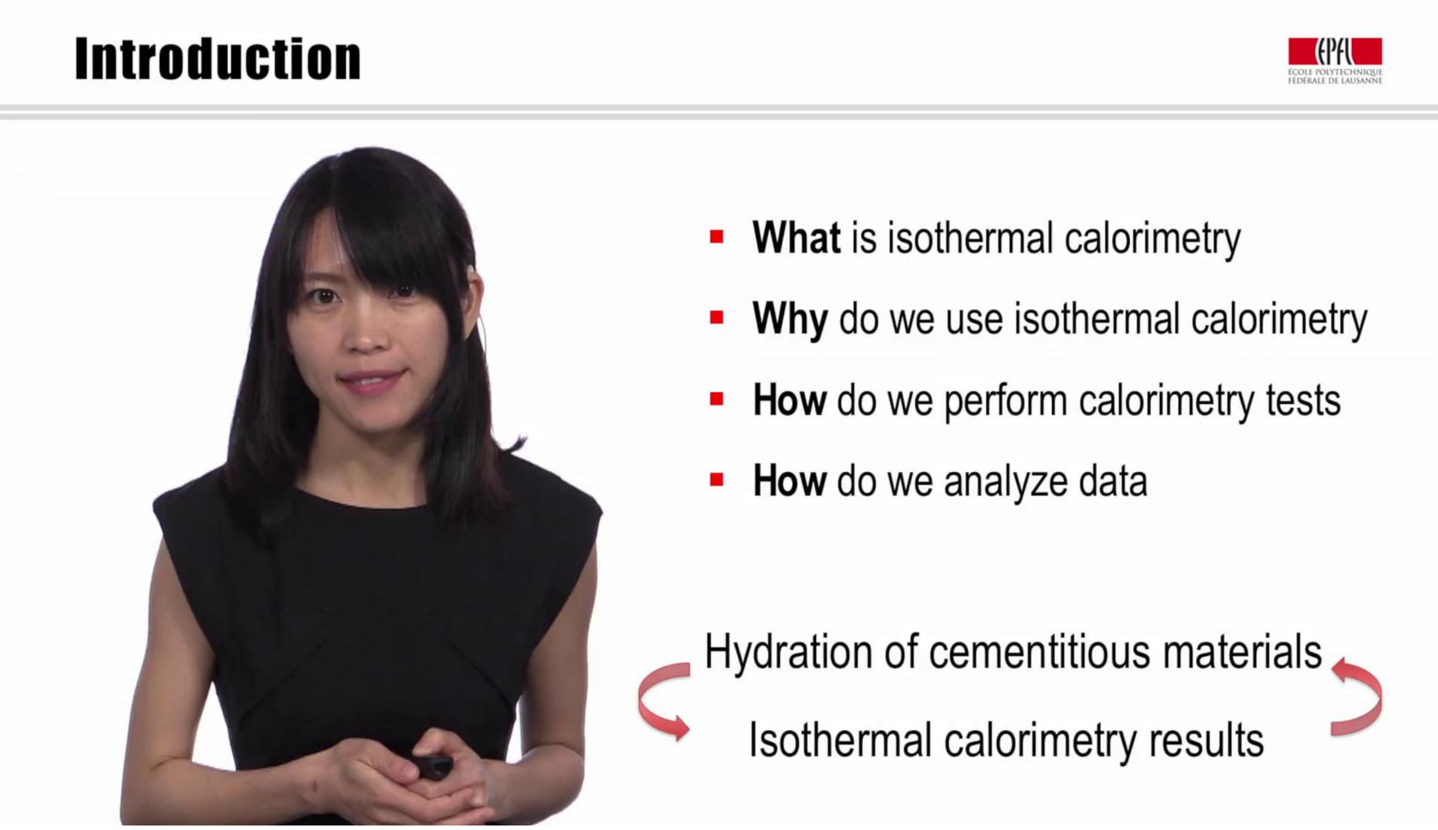
Laboratory of Construction Materials

Zhangli Hu



Search MOOC

Video



Hi. My name is Zhangli Hu. In previous sessions, you have learnt about cement hydration including phases assemblage and the microstructure evolution. In this section, I will give you a bit more detailed information about the heat release of cement hydration. Most specifically in a practical point of view, we will have a closer look at the application of isothermal calorimetry in cement field. The main goal of this module is to introduce 2 Ws and 2 Hs focusing on bridging the isothermal calorimetry results with the hydration characteristics of cement. The 2 Ws are : what is isothermal calorimetry and why do we use it in cement field? The 2 Hs represent : how do we perform a calorimetry test and how should we treat the data in order to get the information we want?

Notes

Summary

0m 04s

What is isothermal calorimetry?

Calorimetry

A measurement of **heat** and **heat production rate**

- Isothermal (heat conduction) calorimetry
- Semiadiabatic (adiabatic) calorimeters
- Solution calorimeters
- Differential scanning calorimetry

Calorimetry is the measurement of heat and heat production rate. There are several different kinds of calorimetry commonly used in cement field, isothermal calorimetry is one of them. Besides this one, which we will mainly focus on today, techniques such as semiadiabatic or adiabatic calorimetry, solution calorimeters and differential scanning calorimetry. All of them can be seen in the applications in cement field.

Notes

Summary

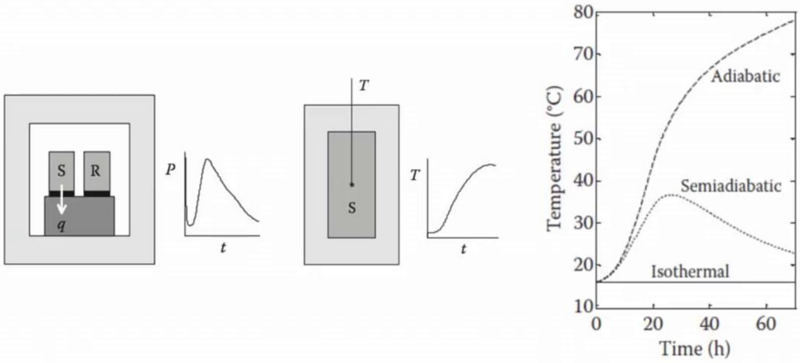
1m 02s

What is isothermal calorimetry?

Calorimetry

A measurement of **heat** and **heat production rate**

- Isothermal (heat conduction) calorimetry
- Semiadiabatic (adiabatic) calorimeters
- Solution calorimeters
- Differential scanning calorimetry



A practical guide to microstructural analysis of cementitious materials, 2016

The first of two types or three kinds of calorimeters are the most frequently used calorimetric methods. Both of them are quantifying the hydration kinetics but the way for realizing it is different. In isothermal calorimeter, the heat production rate is directly measured. That is why it is also called heat conduction calorimetry. While in semiadiabatic calorimetry the sample is isolated and temperature is the signal which is being recorded and later transformed to the rate of heat release. In adiabatic calorimetry, besides the isolation being the same as in semiadiabatic, the calorimeter is also surrounded by an adiabatic shield and the flow of heat from the specimen is prevented. The easiest way to distinguish them are the different time, temperature, trajectories and sample sizes. As indicated in the figure shown here, temperature is controlled to be constant in isothermal calorimetry while in the other two kinds of calorimeters, the temperature is evolving. Small samples such as cement pastes are commonly used in isothermal calorimetry, while in others, big samples like mortars and concrete are often used.

Notes

Summary

1m 33s

What is isothermal calorimetry?

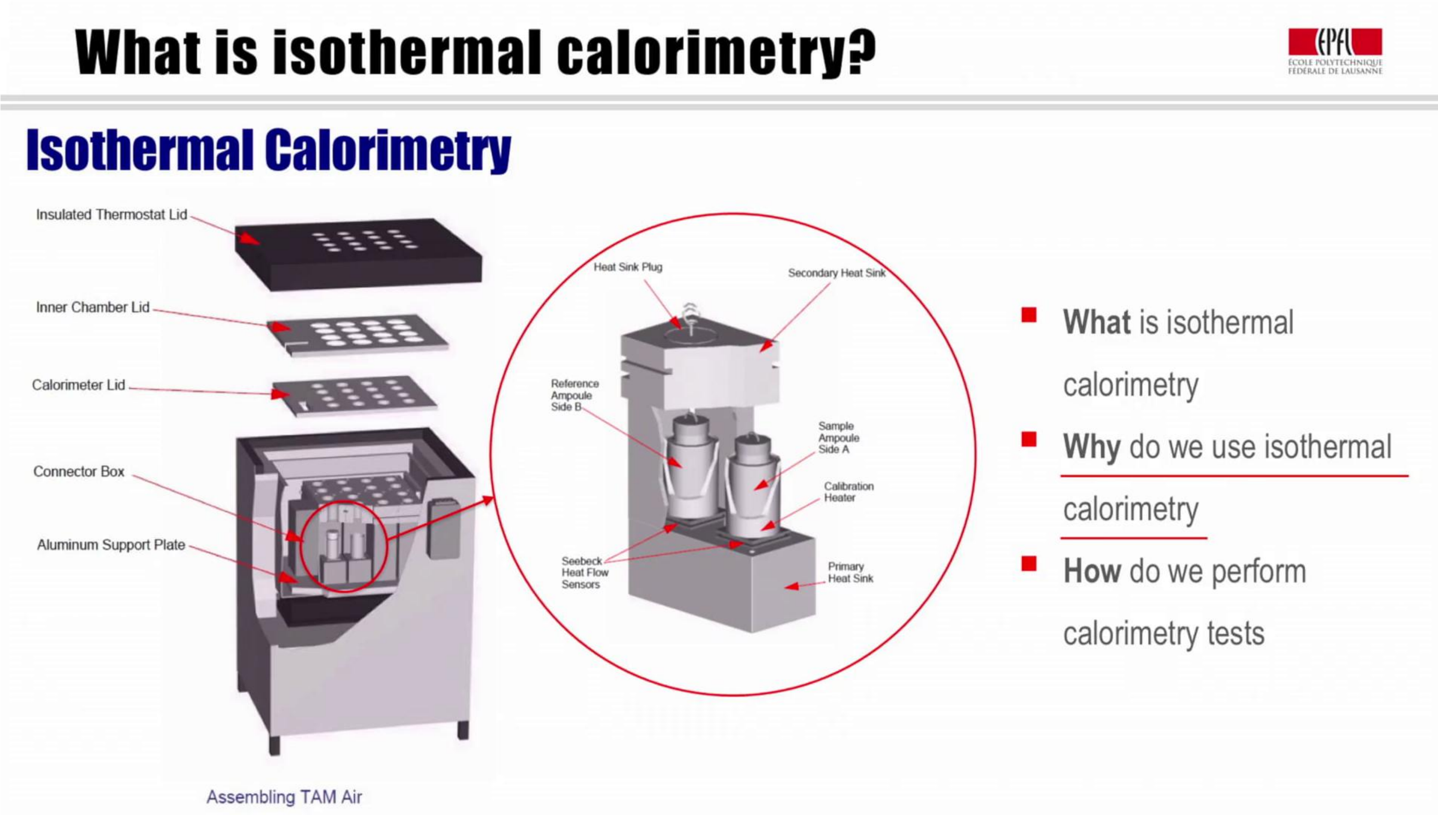
Isothermal Calorimetry

Let's have a look at the instruments for isothermal calorimetry. There are several commercial instrument brands. We will use TAM Air, produced by TA instruments company in the US as an example. If you order an isothermal calorimetry, it basically looks like a sealed box. It is composed of a body of channels for samples and operating temperature control panel. If you look inside, then we can see different parts of the instruments. These three lids are more used for getting a thermostated environment. Principally the most important part of the calorimeter is the heat collecting place which you see in the red circle.

Notes

Summary

3m 04s



If we zoom in on this part, we can see samples and references are placed on a heat flow sensor and both are on top of a heat sink. The heat that is produced by the sample will be collected by the sensor as heat is conducted to the heat sink placed in a thermostated environment. At this moment we can start to ask ourselves why do we want to use this instrument?

Notes

Summary

Why do we need calorimetry measurements?

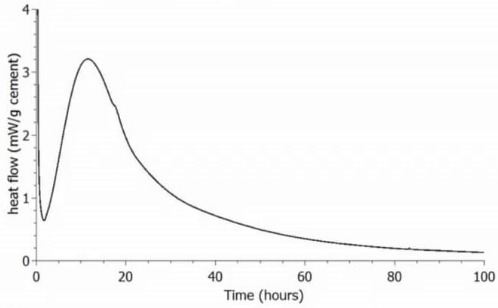
- Physical, chemical and biological are related to enthalpy changes
- Hydration of cement is exothermic

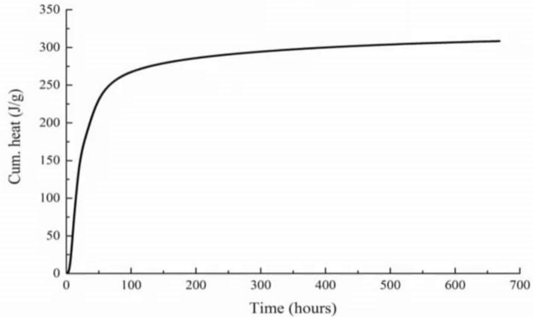
$$yC_3S + H_2O \rightarrow (3y-x)CH + C_x - S_y - H$$

$$yC_2S + H_2O \rightarrow (2y-x)CH + C_x - S_y - H$$

$$C_3A + C\$H_2 + H_2O \rightarrow C_6A\$_3H_{32}$$

$$C_3A + C_6A\$H_{32} + 4H_2O \rightarrow 3C_4A\$H_{12}$$



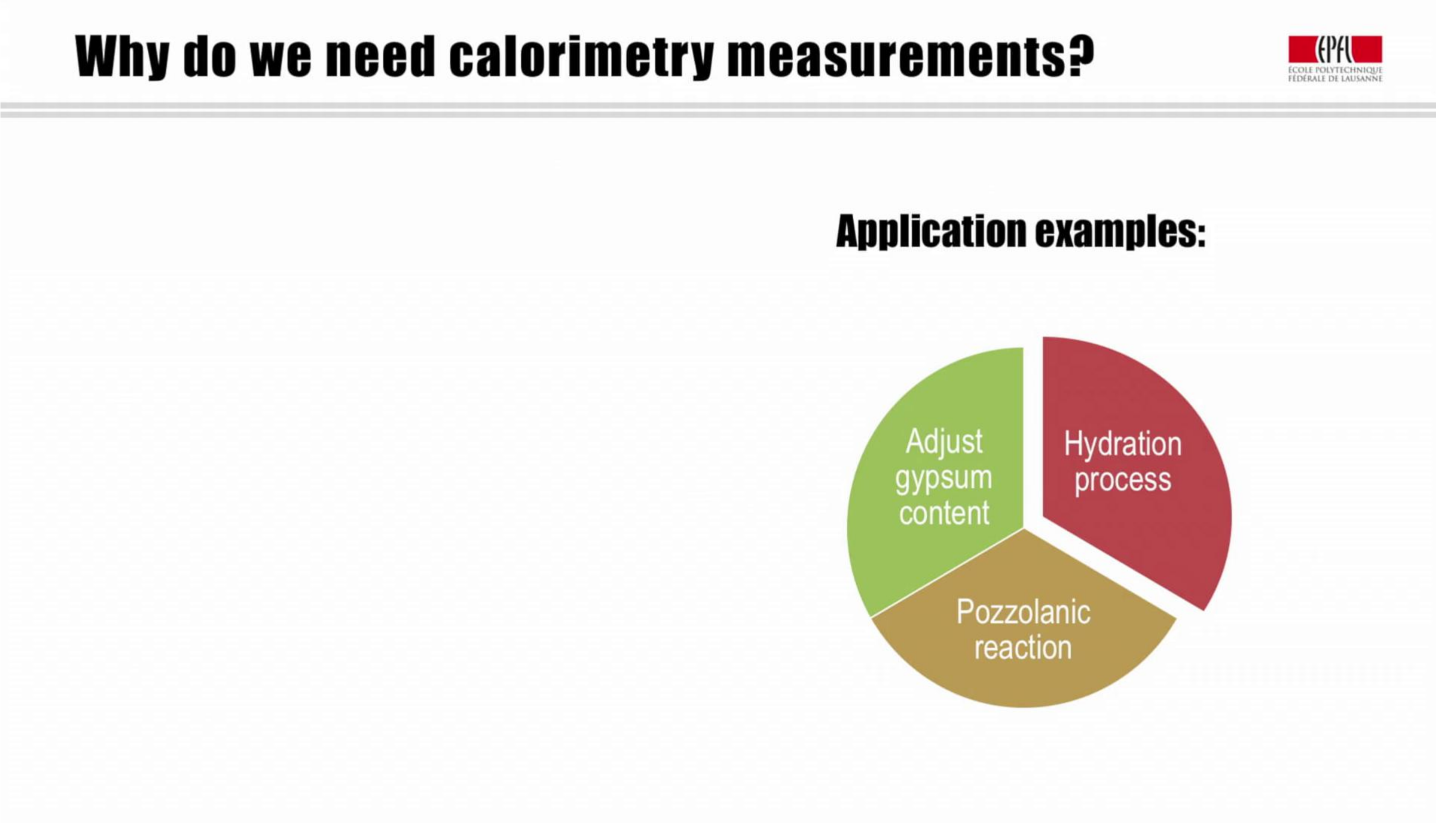


Calorimetry is a heat measuring machine. It is actually a generic way of studying processes, as all processes, physical, chemical and biological are generally related to enthalpy changes. In addition, cement hydration is an exothermic reaction which is associated with the hydration of different main clinker phases with water. The pictures on the right side are typical curves we can obtain from calorimetry measurements.

Notes

Summary

4m 22s

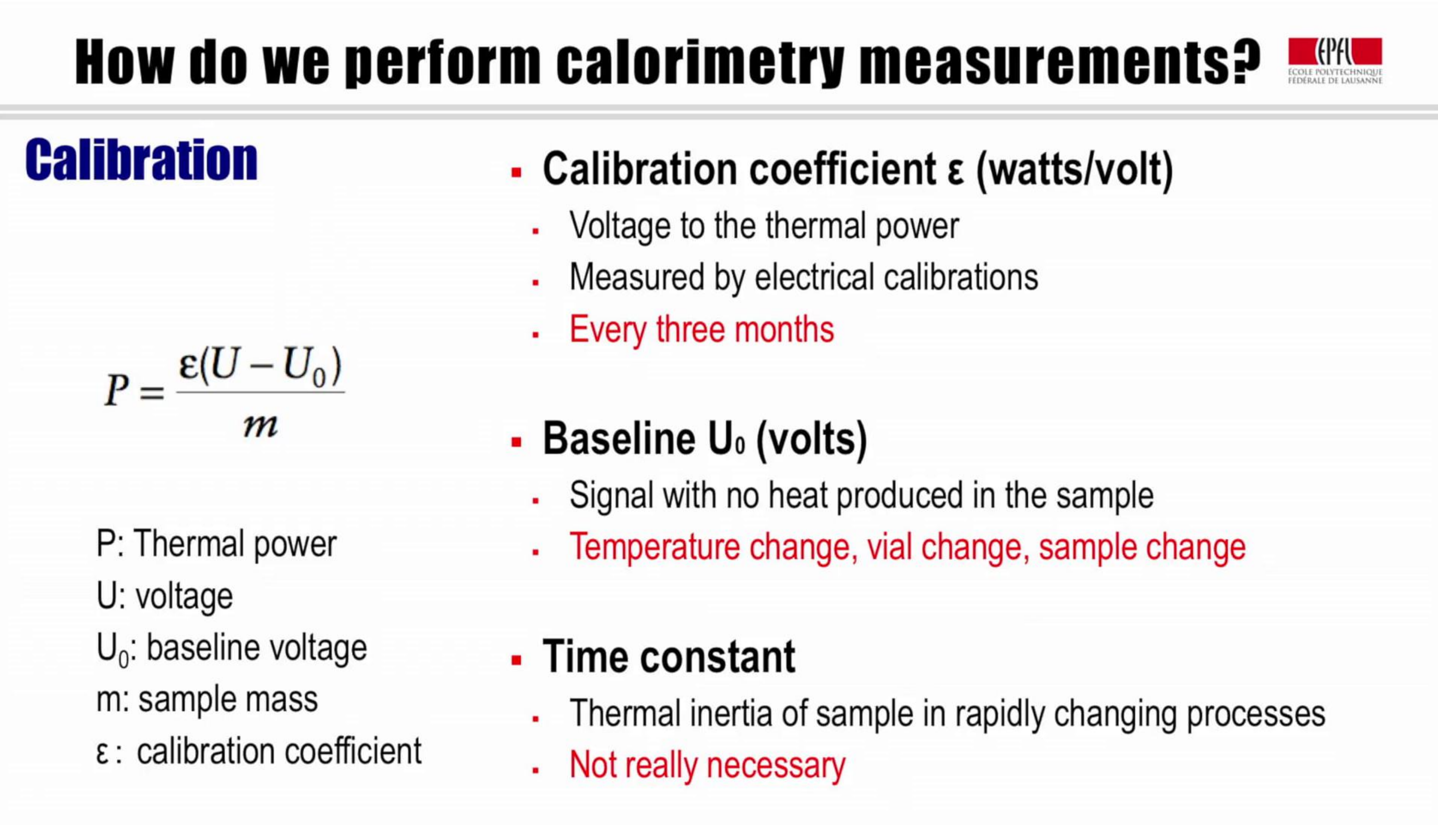


In cement field, isothermal calorimetry is often used on these purposes such as following the hydration processes, adjusting the gypsum content or checking the pozzolanic reaction of the supplementary cementitious materials. From now on we will go through all the steps for performing a calorimetry test. In order to give a vivid explanation, some videos have been inserted in the module.

Notes

Summary

4m 56s

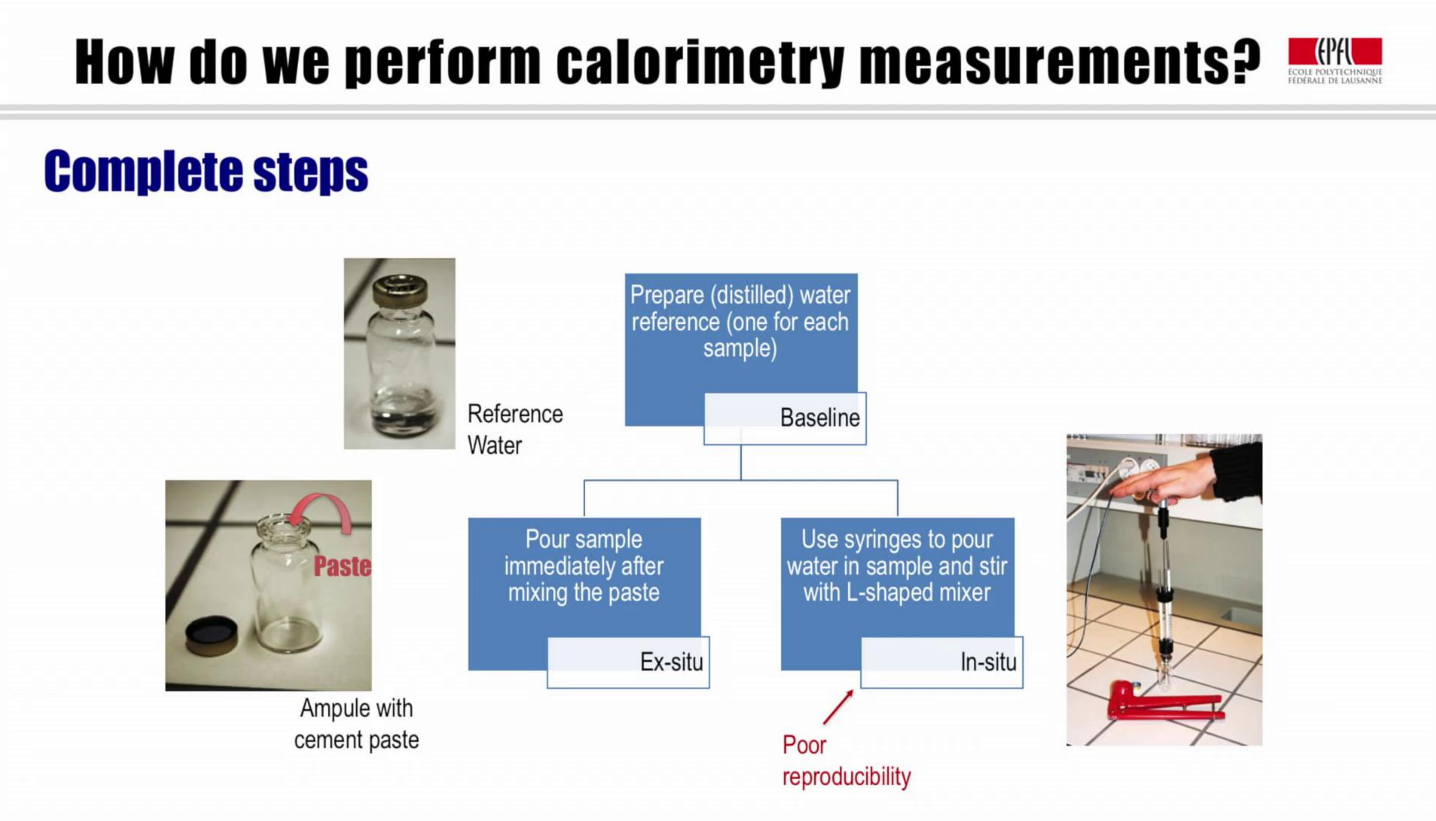


Before we can perform a test, making sure that the instrument is in a good condition is very important. This can be done by calibration. Isothermal calorimetry is actually a very stable instrument but proper calibration will help to significantly reduce noise. Based on heat flow measurement principle, the thermal power P is proportional to the voltage signal from the sensor U, as indicated in the equation. To establish the relationship, two parameters need to be determined : the calibration coefficient ε and baseline for the U0. ε is measured by electrical calibration. Usually we do these every three months with the software. U0 is a signal with no heat produced in the sample but a reference inside. The calibration should be done when we change the temperature, the file or samples. There is another calibration called time constant, which is typically 100 to 1000 seconds. This calibration is not necessary for cement hydration since the timescale of cement hydration is much longer than this time constant.

Notes

Summary

5m 24s



A complete isothermal calorimetry measurement is composed of two main steps. First step is preparing the reference and performing a baseline. The second step is casting the specimens and starting the experiments. There are basically two ways to prepare the specimen : the so-called ex-situ and in-situ. As the name implies, in the case of ex-situ, specimens are cast externally and being poured inside the glass ampule. In the case of the in-situ, the specimens are mixed with the L-shaped mixer inside of the ampoule placed in the channel holes. In order to get good reproducibility, an ex-situ preparation will be shown in this section.

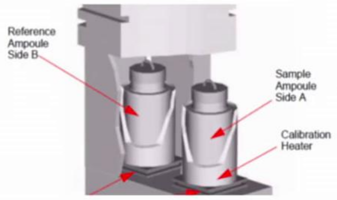
Notes

Summary

6m 49s

How do we perform calorimetry measurements?

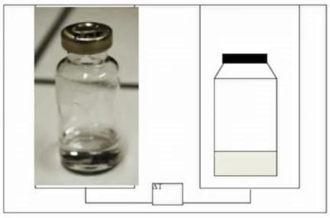
Reference and Baseline



Substance used as reference should have <u>similar heat capacity</u> as the sample and no heat production

e.g. water, quartz

! NO old hydrated cement samples



$$Cp = 4.18 \cdot Mf_{water} + 0.75 \cdot Mf_{cement}$$

$$m_{ref} = \frac{Cp \cdot m_{paste}}{Cp_{water}}$$

$$Cp = 4.18 \cdot \frac{0.4}{1.4} + 0.75 \cdot \frac{1}{1.4} = 1.73 \frac{J}{gK}$$

$$m_{ref} = \frac{1.73 \cdot 10}{4.18} = 4.14g$$

First thing we need to do now is to select a reference and prepare it. The principle for choosing a reference is that the reference should have no heat production during temperature change. Commonly used references are water and quartz sand. Please remember to not use old hydrated cement samples, since the hydration of cement, even when it is mature, will not be ended completely. To ensure a stable baseline and reduce background noise, the sample and reference ampoule should have the same thermal response. This is the draw for calculating the mass of the reference. Here is an example of calculating a reference for ten grams of cement paste with water cement ratio of 0.4. By knowing the specific heat capacity of water and cement powder, the mass of the reference can be calculated.

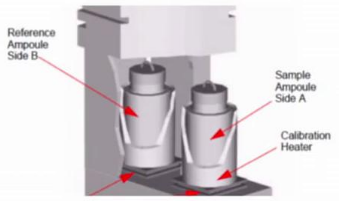
Notes

Summary

7m 41s

How do we perform calorimetry measurements?

Reference and Baseline

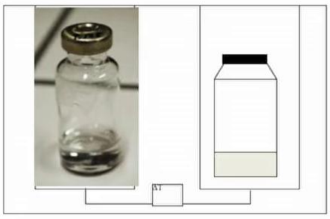


Substance used as reference should

as the sample and no heat productio

e.g. water, quartz

! NO old hydrated cement samples



$$Cp = 4.18 \cdot Mf_{water} + 0.75 \cdot Mf_{cement}$$

$$m_{ref} = \frac{Cp \cdot m_{paste}}{Cp_{water}}$$

$$Cp = 4.18 \cdot \frac{0.4}{1.4} + 0.75 \cdot \frac{1}{1.4} = 1.73 \frac{J}{gK}$$

$$m_{ref} = \frac{1.73 \cdot 10}{4.18} = 4.14g$$

References for different studied systems should be calculated based on the components and mass of the whole samples. So you should use different reference water for different systems.

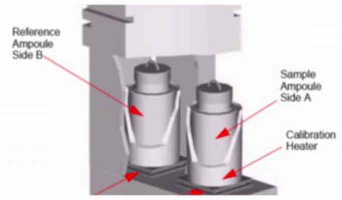
Notes

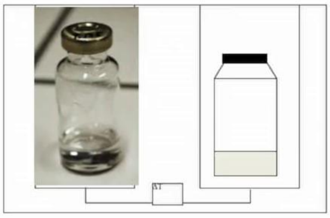
Summary

8m 48s

How do we perform calorimetry measurements?

Reference and Baseline





After putting the reference water in the ampule, we need to seal it well as you can see on the slide. Then we place it into the referenced side of each channel in the instrument. Let’s watch a demo together which shows this process. Different brands may have different design. In TAM Air there are different number of channels for different uses. We use in this demo 8 channel TAM Air instrument. Each channel has sample size and reference side marked as A and B respectively. First of all we open the plastic black lid, use a steel hook to hand the heat sink plug out. Then we put the reference in, making sure it is going to the bottom, sitting right on top of the sensor. After all these we can place the plug back and close the lid.

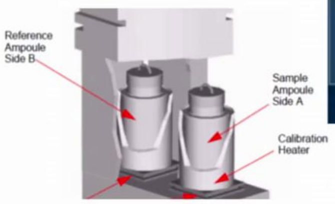
Notes

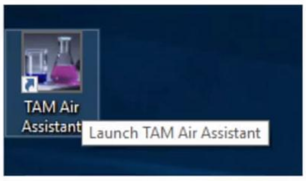
Summary

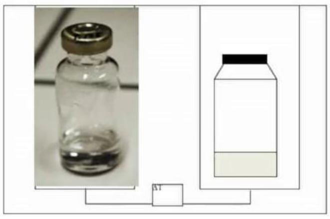
9m 00s

How do we perform calorimetry measurements?

Reference and Baseline





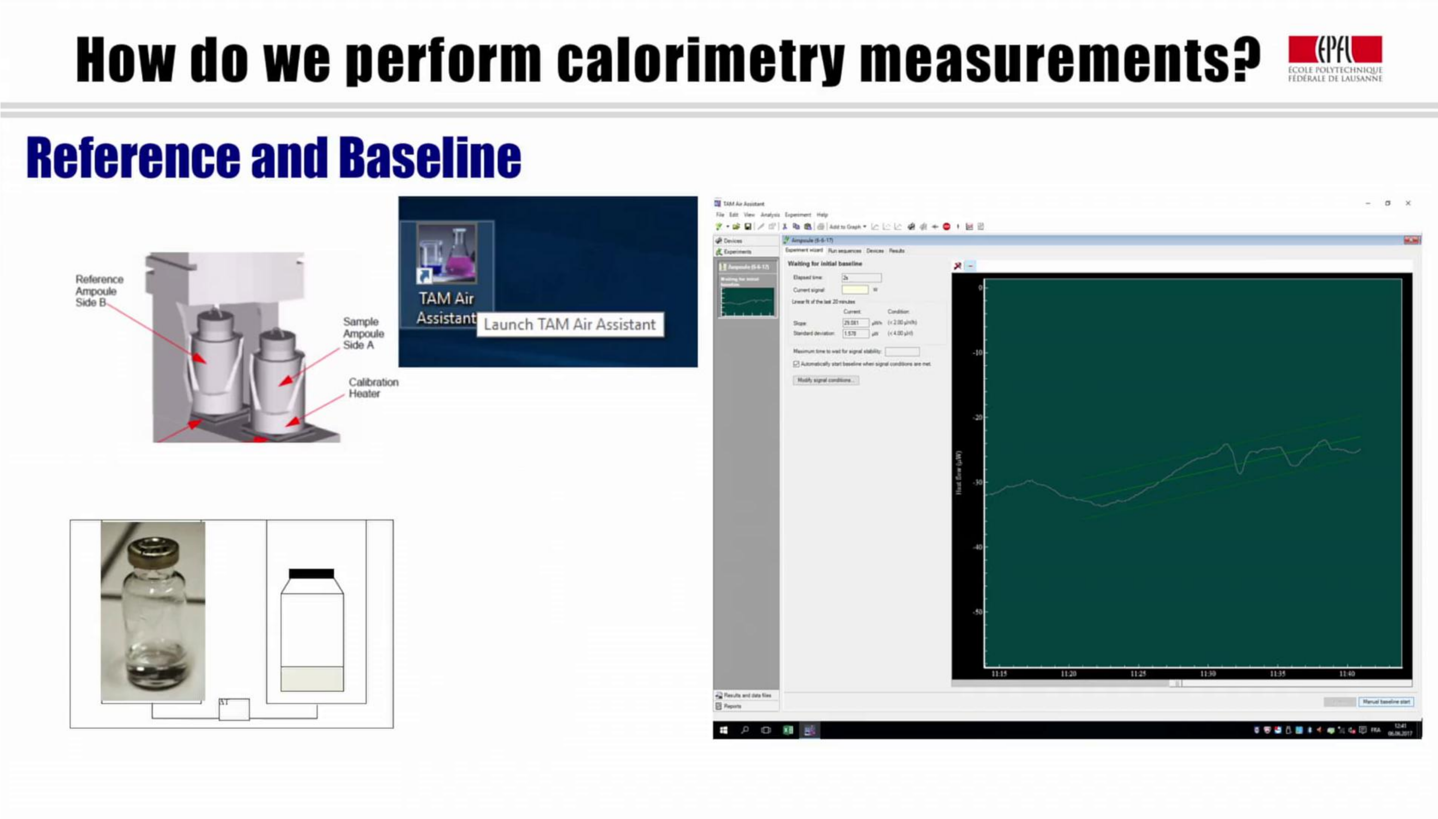


To start the initial baseline, we will need to create a new experiment. In the case of TAM Air, the software being used is called TAM Air assistant. You can see this icon on the slide.

Notes

Summary

10m 01s



Double click to open the software and on the home page, you can click on "experiment" in the new menu or click on the green icon on the top left. After putting the name of the sample and operators name, the experimental wizard will be activated. It will guide you through a number of steps such as selecting the calorimeter and channels. In the next window, you will be reminded to put the reference water inside. And also you need to put the baseline duration and signal stability condition. Different conditions tell the end of the baseline when different conditions are met. Usually at twenty degree the baseline with this condition takes around thirty minutes. If the temperature difference between the reference water and the instrument is higher, then this time it will of course be longer. In the end you can see a window shows the recorded baseline. Until the baseline recording is finalized, you will be instructed to put the samples into the calorimeter.

Notes

Summary

10m 14s

Now is the time to prepare our samples. In order to get reasonable results for calorimetry, representative raw materials is critical. We need to avoid the phases change due to carbonation or humidity. Briefly, three suggestions can be used for getting good raw materials. Keep raw materials sealed, use only recent batches, and sample the amount you plan to use from a big container to avoid always opening the container.

Notes

Summary

11m 25s

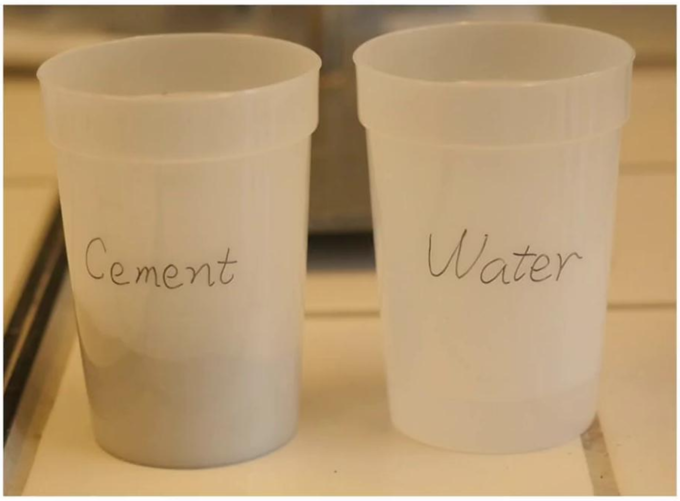
How do we perform calorimetry measurements?

Sample preparation

Weight components based on mixture design

Water: 32 g

Cement: 80 g



In this section, we are going to cast the cement paste with water to cement ratio of 0.4. For one ampule, usually we use approximately ten gram of cement paste. This amount will be changed with different types of materials. One principle is to have high enough signal in order to lower the error to signal ratio. Here we weighed 32 grams of water and 80 grams of cement powders in 250 ml plastic containers.

Notes

Summary

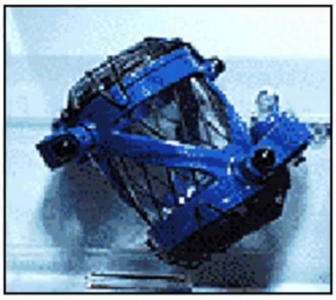
11m 58s

How do we perform calorimetry measurements?

Sample preparation

Sample formulating

Make sure homogeneity



Powder mixer (TURBULA shaker-mixer)

In our case we only have cement powder but if you have several different kinds of components of materials, to get homogeneous examples, it is better to first dry mix them. We can choose dry hand mixing or machine mixing before casting.

Notes

Summary

12m 31s

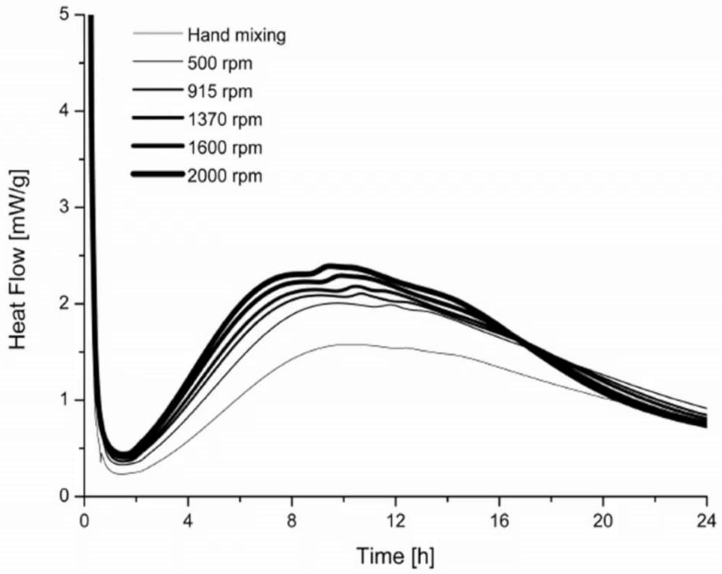
How do we perform calorimetry measurements?

Sample preparation

Keep the same mixing speed

Mixing energy is constant

Time is important



For mixing the sample, it is not mandatory to use one specific type of mixer but the most important thing is to keep using the same mixing speed and duration time. The figure shows the difference when different speeds are used. Because of the different shear rates as mixing energy, the samples which are mixed with higher mixing speed show higher heat flow.

Notes

Summary

12m 51s

How do we perform calorimetry measurements?

Sample preparation

Keep the same mixing speed

Mixing energy is constant

Time is important

Paste mixer (LABORTECHNIK RW 20.n)

Before casting, we need to prepare a mixer, a suitable stirring paddle for different sample sizes and a stopwatch.

Notes

Summary

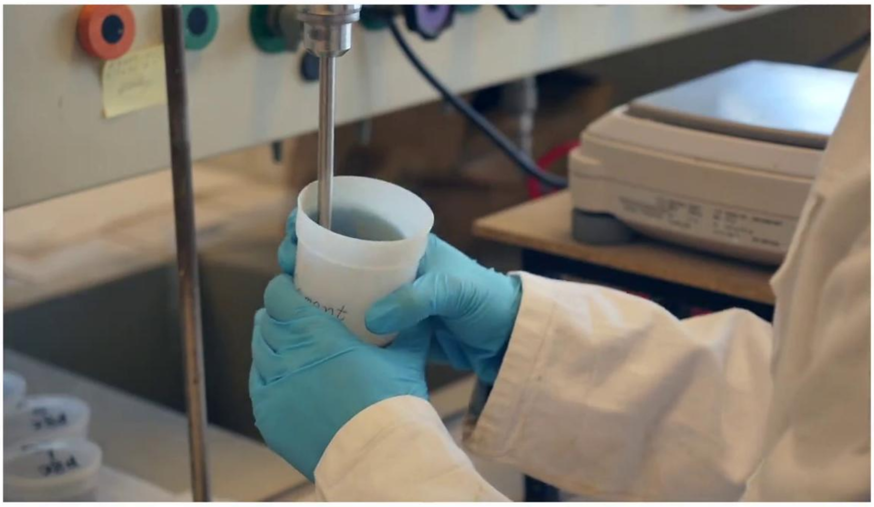
13m 21s

Sample preparation

Keep the same mixing speed (1600 rpm)

Mixing energy is constant

Time is important (2 mins)



In our protocol, we use mixing speed of 1600 rpm and the mixing time is two minutes. Here is another demo which shows how we can make the sample for calorimetry test. First of all we need to adjust to the position of the paddle to make sure we have a good mixing efficiency. We put the water into the cement and quickly put the 250ml plastic container under the mixer. While mixing, we need to move up and down or left and right to make sure the sample is homogenized. Don't forget to write down the time you pour the water inside.

Notes

Summary

13m 31s

How do we perform calorimetry measurements?

Sample Handling

Weight cement paste

Input slowly in the ampule

After the cement paste is ready, we will need to put a certain amount of paste inside the ampoule. The weight of the paste in the ampoule is important in order to later normalize the total heat release. In this step, we will need to prepare a glass ampoule, a pipette and a balance.

Notes

Summary

14m 16s

How do we perform calorimetry measurements?

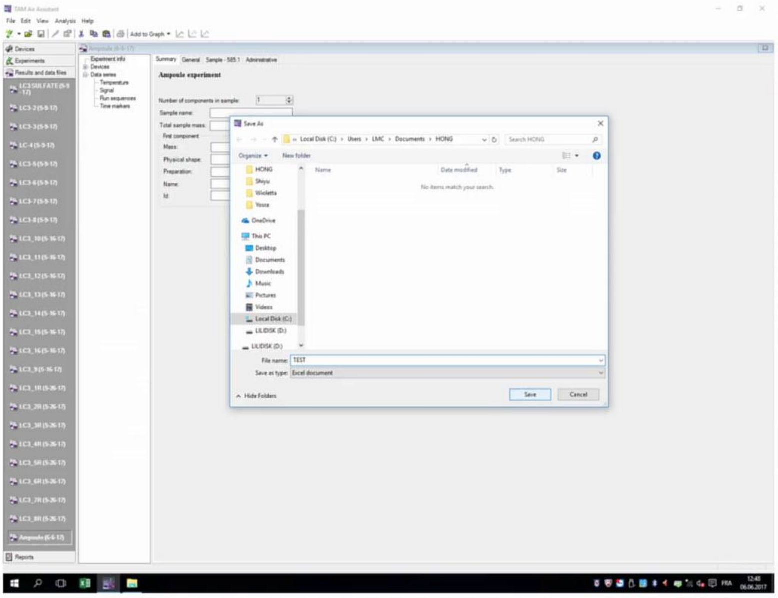
We have another demo showing how we usually do for this step. For ex-situ preparation, the sample needs to be fluid enough, otherwise you will have a some difficulty to put it inside of the ampoule. We cut a bit of the pipette, place the empty ampoule on the balance and tare the balance. Take some paste with the pipette, clean the outside with a tissue. Slowly place the pipette inside of the ampoule and adjust the position and squeeze the paste out. Keep doing this until you reach the mass you need. Write down the exact mass. After we finish weighing we slightly tap the sample and then seal the sample with a lid by using our cap clipping tool. Then we can lower the ampoule in the sample side of the channel the same way as we did for the reference water. Here we have some good and bad examples for the sample preparation. Since the sensor is on the bottom of the ampoules, it is a better to put the sample to the bottom to make sure that the heat generated is completely collected by the sensor.

Notes

Summary

14m 38s

How do we stop the experiments and get results?



Now our experiment is going on. We can use the experiment wizard to check how the experiment is going. When the experiment is finished we need to do the final baseline. Basically it is the same as the initial baseline and there is another wizard that will guide you for all the steps. Just remember before you do the baseline you need to take out of the sample and leave the reference inside. To export the data you need to select which experiment you want to have and click “export” in the file menu. After selecting the information which you want to have, you can export the data as CSV file or Excel file. In this file you can have the time for the experiment, heat flow and cumulative heat release. Cumulative heat release is obtained by calculating the integration of the heat flow. Don't forget to add the time during the sample preparation.

Notes

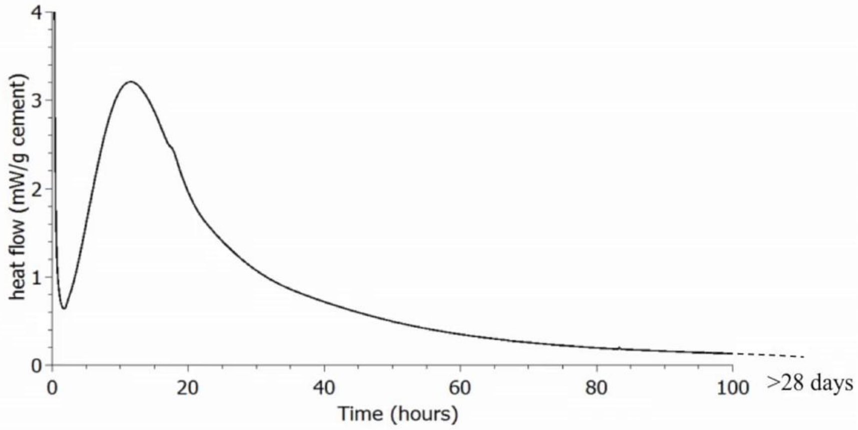
Summary

15m 52s

How do we understand the data?

Results collection

- Output of isothermal calorimetry is the heat flow
- Four/five stages/periods in cement hydration
- Different stages represents different chemical processes



The last part of the section we will have a look together at the heat flow result of a normal Portland cement. Conventionally the whole heat flow curve goes through four or five stages of cement hydration. During each of them there are different mechanisms behind it. Therefore it will help us to understand the hydration properties of cement.

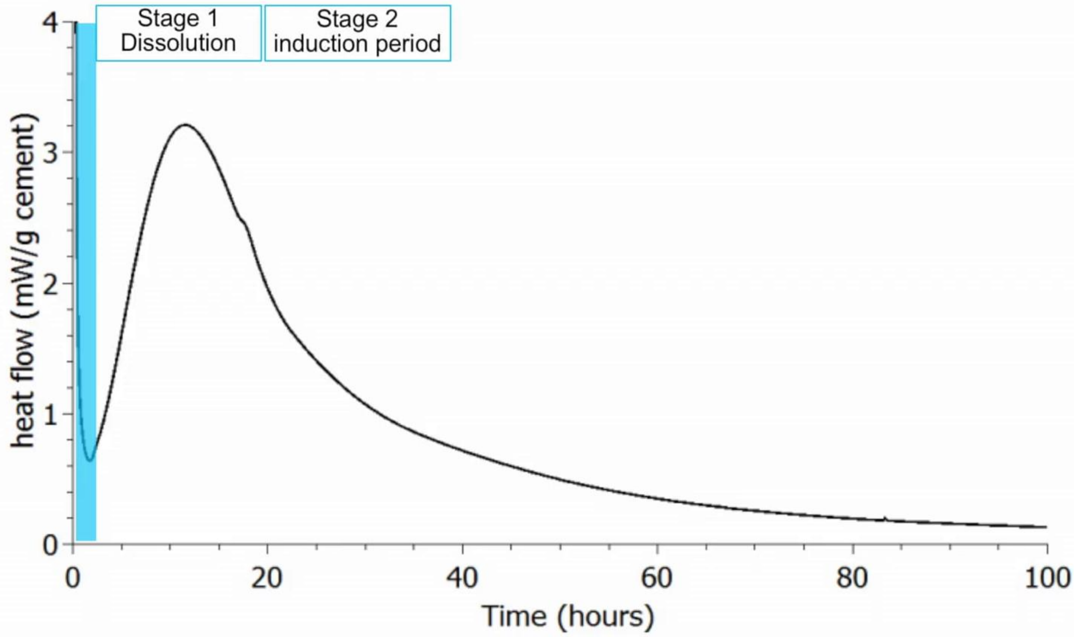
Notes

Summary

16m 54s

How do we understand the data?

Results collection



The first two stages are called dissolution period and induction period. These two stages are associated to the dissolution of ions from solids. The dissolution rate controls the kinetics and the dissolution is higher when the ion concentration in the solution is lower. After some time when the iron concentration goes higher, the dissolution rate slows down. Factors such as the fineness of the particles, the density of critical defects, temperature and undersaturation will all influence the duration of these 2 stages.

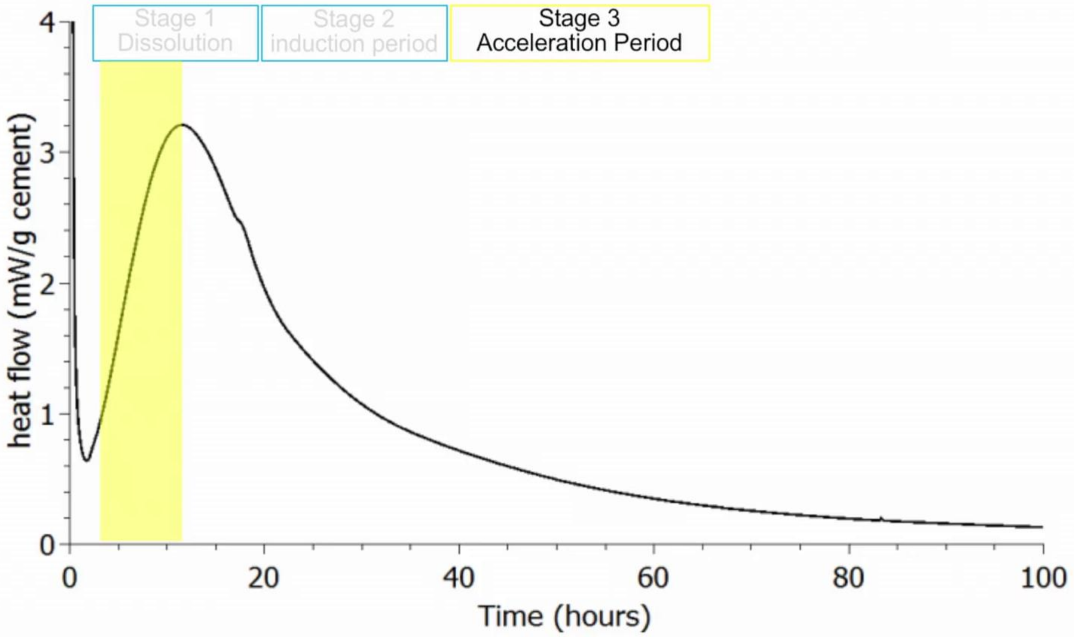
Notes

Summary

17m 20s

How do we understand the data?

Results collection

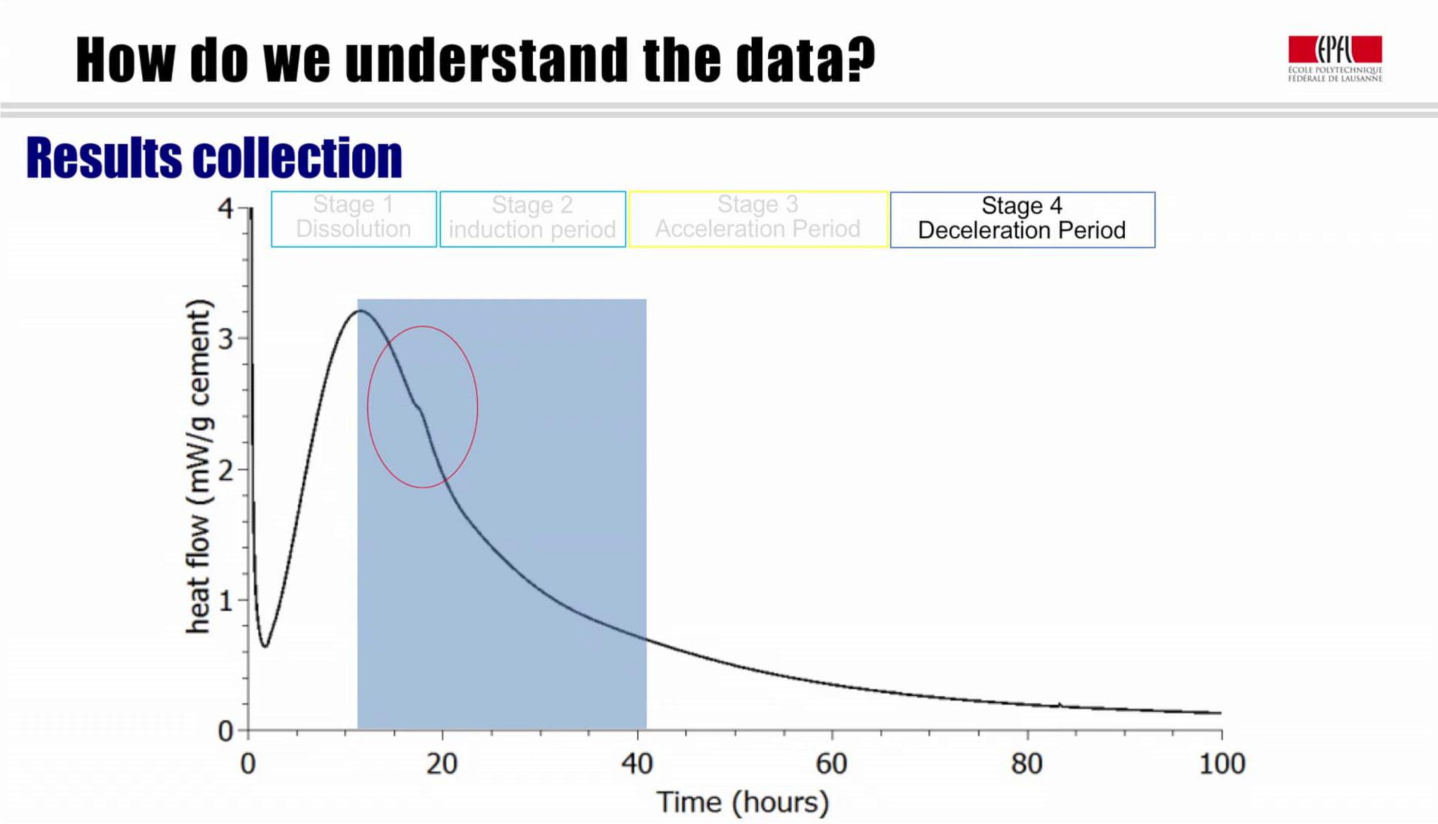


After the first 2 stages, there is an important stage called the acceleration period. This is the main peak of C3S hydration and the rate of acceleration is controlled by the precipitation and nucleation of CSH. CSH precipitates when the degree of supersaturation reaches the maximum value. This is the period which is affected by the mixing rate, fineness of the particles, temperature and the amount of a supplementary cementitious materials.

Notes

Summary

17m 54s



The fourth stage is called the deceleration period. In this period, the heat flow rate starts to decrease. We can see a shoulder which represents the second reaction of aluminate. This one can be used for adjusting the amount of gypsum. The more gypsum we put inside the later we see the aluminate peak.

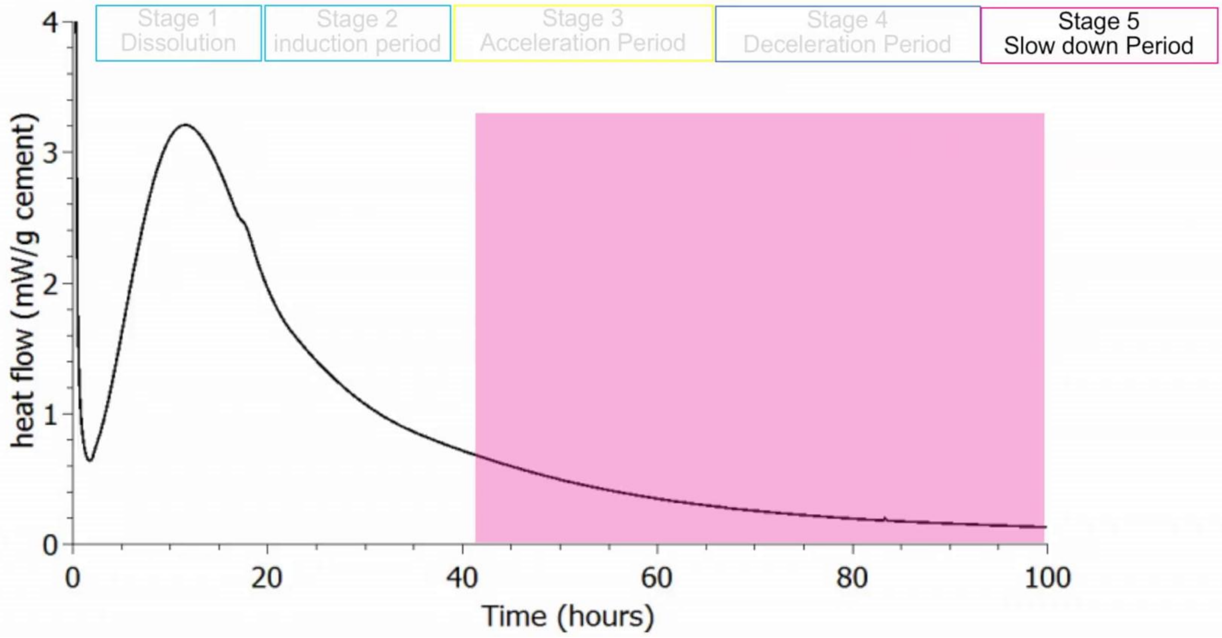
Notes

Summary

18m 26s

How do we understand the data?

Results collection



Sometimes people combine the fourth stage and fifth stage together since during these days the heat flows are always decreasing.

Notes

Summary

18m 48s

Summary

Advantages:

- Very repeatable at early age
- Easy to test at different temperatures
- Easy to measure the effect of SCMs and admixtures
- Can be combined with other techniques

Drawbacks:

- Low signal after several days
- Caution required if testing samples that may generate erroneous data
- Small samples used in the tests

As a summary, here is a list of advantages and disadvantages of these isothermal calorimetry measurements. One thing you may need to pay attention to is that these measurements are still very repeatable at early age. But after several days because of the low signal the test is not very reliable. That is all for this module. Thank you.

Notes

Summary

18m 57s