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1 Summary

Isothermal heat conduction calorimetry is a useful method for determining the heat production rate and the developed heat during cement hydration. It may be used for several different purposes: 1. To determine the total heat of hydration. 2. To determine the rate of heat production in concretes. 3. As a general tool to investigate the hydration process. From the studies presented in this report it is concluded that the heat production rate per mass of cement is quite similar for cement pastes and cement mortars (and then probably also for concretes) of the same water-cement ratio. Also, the way that a cement paste is mixed does not much influence the reaction rate.

Two measurement procedures that are alternatives to solution calorimetry and (semi-)adiabatic calorimetry are presented in this report. The methods described are similar to the Cembureau Test Method of 1977. Both methods use rather small hand mixes and the small samples are quickly charged into the calorimeter to be able to measure the thermal power as early as possible from the start of the reaction.

2 Introduction

This is the result report from the first part of NORDTEST project 1534-01 to develop a method based on isothermal heat conduction calorimetry to measure the heat of hydration of cement, mortar and micro concrete. This method is to be an alternative to the calorimetric methods in use.

In the nordic cement industry there are principally two calorimetric methods used to determine heat of hydation of Portland cement: the solution calorimeter and the (semi-)adiabatic calorimeter. For the solution calorimeter there exists a number of standards (DIN 1164-8, ASTM C186-98, prEN 196-8, SS B1 1960 etc.) and for the semi-adiabatic calorimeter there are French standards (NFP 15-436) and Brittish standards (BS 4550). There has also been NORDTEST projects using semi-adiabatic calorimetry (NT Build 388 and NT Build 480).

This report has a rather wide scope. It both gives a general background of the usefulness of isothermal heat conduction calorimetry for the study of cement hydration, describes procedures for measurements on cement hydration, and discusses calibration and other important issues in a number of appendices.

The measurement methods proposed will be used in the second part of this project to compare isothermal calorimetry to solution calorimetry and semi-adiabatic calorimetry.[1]

A note for quick-readers:

- Sections 4 and 5 give the proposed measurement methods for isothermal calorimetry to be used in the second part of this project.
- The first appendix gives a list of possible uses of isothermal calorimetry in cement science.
- The rest of the appendices discusses various aspects of isothermal calorimetry.

3 Principle of isothermal heat conduction calorimetry

The method comprises the measurement of thermal power (heat production rate) and specific thermal power (heat production rate per gram cement) of the cement hydration reaction at essentially constant temperature. The primary result of a measurement with an isothermal heat conduction calorimeter is the thermal power as a function of time. This result is often rather detailed and one can usually pinpoint the exact time when the main reaction starts, find multiple peaks etc. Because of this, isothermal calorimetry can have many different uses, some of which are described above.

The instrument used is an isothermal heat conduction calorimeter. In such an instrument the heat produced in the sample is conducted away from the sample so that the sample stays at essentially isothermal conditions. The thermal power is measured by a heat flow sensor.

The heat production rate is not as dependent on water-cement ratio, mixing technique and aggregate as are many other measurement techniques used for cement, mortar and concrete. These issues can therefore be treated in less detail than done in ES 196-1 and other standards. This is further discussed in Appendix 3 and 4.

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[1] References to the use of the TAM Air (Thermometric AB, Järfälla, Sweden) isothermal heat conduction calorimeter will be made in footnotes. It is a state-of-the art instrument suitable for cement hydration studies that has been used in both the first and the second parts of this study. Note that the TAM Air is not surrounded by any patents and that the general technique is well known and has been used in cement science for nearly a centrury.

4 Method 1. Measurement of two and seven days heat of hydration of cement by isothermal calorimetry (alternative to solution calorimetry)

4.1 Introduction

The method described here is an alternative to solution calorimetry for the determination of the heat of hydration of cement. It has many similarities to the method proposed by Cembureau (1977) and it has the advantage over solution calorimetry in that it can be used for all types of cements. It also gives the thermal power during the whole reaction, and the same or almost the same method may be used for many other purposes (cf. section 5 below). A difference compared to solution calorimetry is that isothermal calorimetry cannot measure the heat exactly from from the time of mixing. In the method proposed here it takes about two minutes from the water is added to the sample is in the measurement instrument. However, the heat produced during the first minutes is very small compared to the heat produced during three or seven days (cf. Appendix E).

The standard conditions for this method are as follows:

- pure cement paste
- w/c=0.40
- hydration temperature: 20°C

4.2 Laboratory

The laboratory where the preparation of specimens take place shall be maintained at a temperature of (20±2)°C.

4.3 Device for mixing

Mixing should be made in a small transparent beaker of plastics or glass using a mixing device of plastics or stainless steel.

4.4 Balance

The calibrated balance used should have a precision of 0.01 g or better.

4.5 Sample vials

Vials of borosilicate glass sealed with Teflon coated rubber seals should be used. Other types of vials (ampoules) may also be used as long as any reaction between the cement paste and the sample or the thermal properties of the vial does not influence the measured result.

4.6 Thermostated isothermal heat conduction calorimeter

The calorimeter should have a temperature stability over 24 h of better that ±0.3 K. The baseline stability should be better than 10 μW over 24 h.

4.7 Calibration of calorimeter

Each calorimeter shall be calibrated with an electrical heater placed either in the sample position or on the sample holder. The calibration should be made in such a way that the standard deviation of the calibration coefficient (ε) from a series of calibrations should be less than 1% of the calibration coefficient.

The time constant (τ) may be determined from calibrations with an old cement paste sample with low reaction rate or calculated from masses and heat capacities of the parts and materials used (Appendix H).

The baseline of each calorimeter shall be determined regularity.

4.8 Measurement procedure

The measurement is made in the following steps (the described procedure is for a multi-channel calorimeter):

1. Cement and water should have been stored in amounts of less than 1 kg at (20±2)°C for at least 24 h before the measurement.
2. The following items are prepared for the measurement: laboratory note book, cement, water, mixing beakers, mixing devices, glass vials, caps (and capping device if this is used), devices to charge samples into glass vials (e.g. plastic funnels) and other devices necessary for the calorimetric experiments (e.g. hooks for the vials).
3. Weigh up 10±0.05 g cement in the eight mixing jars.
4. Start calorimeter data collection and count-up timer at the same time to keep track of the time (minutes and seconds).
5. Tare an empty vial.
6. Add 4±0.025 g water directly to *one* cement (a calibrated automated pipette is recomended).
7. Note time when water was added (minutes and seconds).
8. Mix carefully for 30 seconds. Make sure that there is no dry cement on the bottom of the jar.
9. Add cement paste to the tared vial.
10. Determine and note mass of cement paste. The mass of cement paste should be 4-8 g.

11. Seal vial and load into calorimeter.
12. Note time when vial was loaded into the calorimeter (minutes and seconds). There should be no more than 200 seconds between mixing and charging.
13. Repeat steps 5-12 for all samples

A few notes on the above procedure:

- Note that one has to have separate beakers, mixing devices, funnels etc. for each sample.
- It is advantageous if the sample is as close to 20°C as possible when the sample is charged. Therefore do not heat the sample with your hands. Use cotton gloves.
- The calorimeter should not have a low upper range for this type of measurement as it then will take a long time before the thermal power goes below the maximal level.[2]

4.9 Evaluation procedure

For the evaluation one needs the calibration coefficient ε (W/V), the time constant τ (s) and the baseline U_{bl} (V). It is here assumed that the primary output from the calorimeter is in volts, but other units may also be used (Appendix I). The thermal power P (W) is calculated from the measured voltage U (V) with the following equation:

$$P = \varepsilon(U - U_{\mathrm{bl}} + \tau\frac{\mathrm{d}U}{\mathrm{d}t}) \tag{1}$$

The $\mathrm{d}U/\mathrm{d}t$-part does only play a role at the very beginning of the measurement.

All diagrams should be made so that time zero is time of mixing. All integrations should be made from the time of charging of the sample into the calorimeter (essentially the same as from the time of mixing as the thermal power (cf. Eq. 1) should be zero (=baseline) before the sample is charged).

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[2] The TAM Air has two ranges (60 mW and 600 mW); the upper range should be used for this measurement.

5 Method 2. Measurement of heat production rate of cement paste, mortar and micro concrete by isothermal calorimetry at different temperatures (alternative to semi-adiabatic and adiabatic calorimetry)

5.1 Introduction

The method described here is an alternative to semi-adiabatic and adiabatic calorimetry for the determination of the heat of hydration of cement. It may be used both with the standard conditions given below and as a general tool to investigate mortar/concrete hydration. It has many similarities to the method proposed by Cembureau (1977). In the method proposed here it takes 2-5 minutes from the water is added to the sample is in the measurement instrument.

The standard conditions for this method as used as in the second part of this project are as follows:

- cement mortar with an unreactive aggregate with a maximal diameter of 2 mm.
- w/c=0.50
- cement/aggregate-ratio 2.0
- hydration temperatures: 20, 30, 40, 50 and 60°C

Other condictions may also be used.

5.2 Laboratory

The laboratory where the preparation of specimens take place shall be maintained at a temperature of (20±2)°C.

5.3 Device for mixing

Mixing should be made in a small transparent beaker of plastics or glass using a mixing device of plastics or stainless steel.

5.4 Balance

The calibrated balance used should have a precision of 0.01 g or better.

5.5 Sample vials

Vials of borosilicate glass sealed with Teflon coated rubber seals should be used. Other types of vials (ampoules) may also be used as long as any reaction between the cement paste and the sample or the thermal properties of the vial does not influence the measured result.

5.6 Thermostated isothermal heat conduction calorimeter

The calorimeter should have a temperature stability over 24 h of better that ±0.3 K. The baseline stability should be better than 10 μW over 24 h.

5.7 Calibration of calorimeter

Each calorimeter shall be calibrated with an electrical heater placed either in the sample position or on the sample holder. The calibration should be made in such a way that the standard deviation of the calibration coefficient from a series of calibrations should be less than 1% of the calibration coefficient.

The baseline of each calorimeter shall be determined regularity.

5.8 Measurement procedure

The measurement is made in the following steps (the described procedure is for a multi-channel calorimeter):

1. Cement, aggregate and water should have been stored in amounts of less than 1 kg at (20±2)°C for at least 24 h before the measurement.
2. The following items are prepared for the measurement: laboratory note book, cement, aggregate, water, mixing beakers, mixing devices, glass vials, caps (and capping device if this is used), devices to charge samples into glass vials (plastic funnels) and other devices necessary for the calorimetric experiments (e.g. hooks for the vials).
3. Weigh 20±0.1 g cement and 10±0.05 g fine aggregate in the mixing beakers and mix them.
4. Start calorimeter data collection and count-up timer at the same time to keep track of the time (minutes and seconds).
5. Tare a vial
6. Add 5±0.025 g of water to one of the cement+aggragate mixes and mix by hand for 30 s. Make sure that all cement is mixed. Note time when water was added (minutes and seconds). See note below on mixing.
7. Charge the tared vial with sample and determine the sample mass.
8. Seal vial and load into calorimeter.

9. Note time when vial was loaded into the calorimeter (minutes and seconds). There should be no more than 300 seconds between mixing and charging for the standard procedure.
10. Repeat steps 5-7 for all samples

A few notes on the above procedure:

- Note that one dhould have separate beakers, mixing devices, funnels for charging etc. for each sample.
- It is advantageous if the sample is as close to the temperature of the calorimeter as possible when the sample is charged (to decrease the time that the thermal power cannot be determined). This is obviously more difficult when measurements are made at non-ambient temperatures. One may try to thermostat the different materials so that the mixed sample has the temperature of the measurment when it is being charged into the calorimeter (cf. Appendix J). Do not heat the sample with your hands. Use cotton gloves.
- Mixing by hand is the standard procedure. There may be cements for which longer mixing by a mechanical mixer is neccesary.
- The calorimeter should not have a low upper range for this type of measurement as it then will take a long time before the thermal power goes below the maximal level.[3]
- The maximal aggregate size that should be used in the TAM Air is about 5 mm diameter.

5.9 Evaluation procedure

For the evaluation one needs the calibration coefficient ε (W/V) and the baseline U_{bl} (V). It is here assumed that the primary output from the calorimeter is in volts, but other units may also be used (Appendix I). The thermal power P (W) is calculated from the measured voltage U (V) with the following equation:

$$P = \varepsilon(U - U_{\mathrm{bl}}) \tag{2}$$

It is not neccesary to make a Tian correction.

All diagrams should be made so that time zero is time of mixing. All integrations should be made from the time of charging of the sample into the calorimeter (essentially the same as from the time of mixing as the thermal power (cf. Eq. 2) should be zero (=baseline) before the sample is charged).

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[3] The TAM Air has two ranges (60 mW and 600 mW); the upper range should be used for this measurement.

A Various uses of isothermal heat conduction calorimetry for the study of cement hydration

This section summarizes various applications of isothermal calorimetry for the study of cement hydration. The range of applications is very wide and the list below is by no means conclusive.

A.1 Determination of three and seven days heats of hydration

This measurement is made to compare cements and classify them according to their rate of reaction (heat development rate). It is described in detail in section 4. This type of measurement by isothermal calorimetry is an alternative to solution calorimetry.

A.2 Heat of hydration as a function of temperature

These type of measurements (cf. section 5) are made to assess the influence of temperature on the heat production from cement paste, mortar and concrete. Such information can be used to calculate temperature distributions in massive constructions, and determine the time for deforming. Figures 1 and 2shows measurements on a cement paste with w/c=0.5 at three temperatures. It is seen that the thermal powers, and thus the rate of reaction, increases with temperature.

In Fig. 3 the thermal power is plotted as a function of the produced heat. This plot therefore shows the rate of reaction as a function of reacted amount. It is seen that all three curves peak at the same time and shows the same weak second peak. The produced heat is a measure of the degree of hydration.

A.3 Determination of admixture retardation

Most plasticizers retard the cement hydration and isothermal calorimetry is an good method to assess the retardation time as a function of temperature, admixture concentration etc. Figure 4 gives an example.

A.4 The influence of contaminants on cement hydration

Water and aggregate can contain substances that influences the rate of cement hydration. There have also been cases when cement trucks have been contaminated by other products, e.g. fertilizers, that influence the rate of hydration.

Figure 5 shows the result from measurements at 20°C on a mortar containing different fractions of a mixture of soil and saw dust. The base recipe contained 50

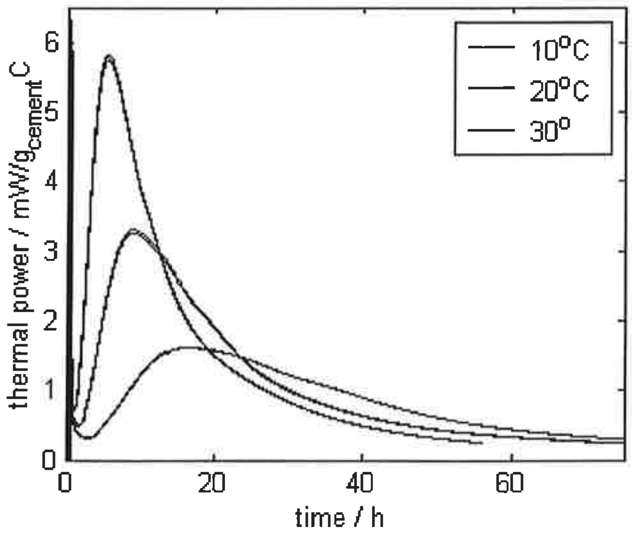

Figure 1: Thermal power of cement hydration at three temperatures: 10, 20 and 30°C. The samples were cement pastes with w/c=0.5 For each temperature the results of four simultaneous measurements of samples from the same mix are plotted.

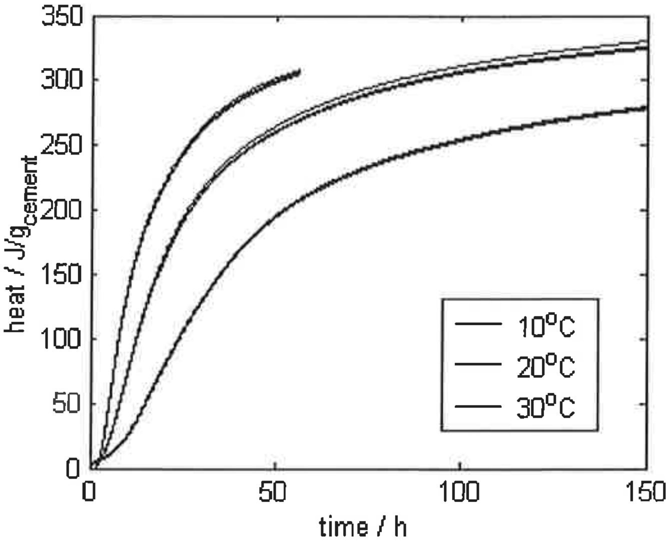

Figure 2: Heat produced from cement reaction at three temperatures.

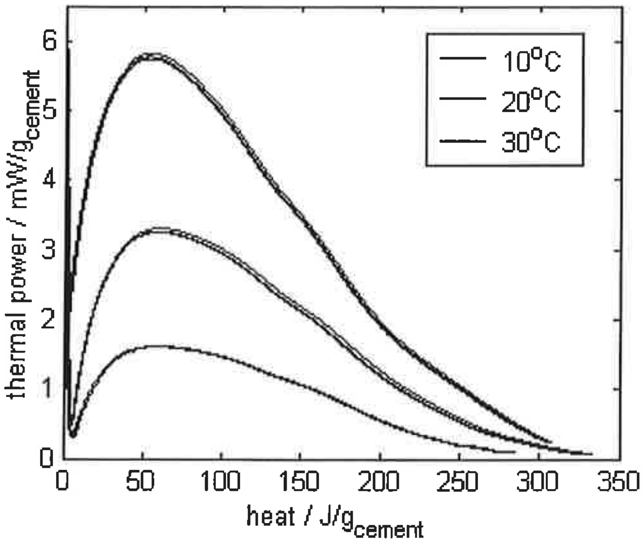

Figure 3: Thermal power (proportional to the rate of reaction) ploted as function of produced heat (proportional to the reacted amount).

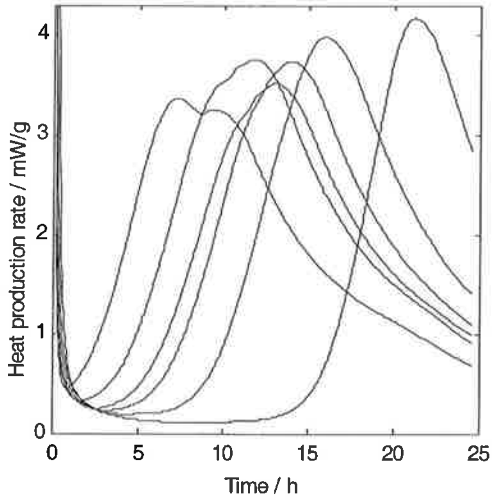

Figure 4: This figure shows the result of measurements on six cement pastes with different concentrations (0; 0.1; 0.15; 0.2; 0.3; 0.5%) of an admixture.

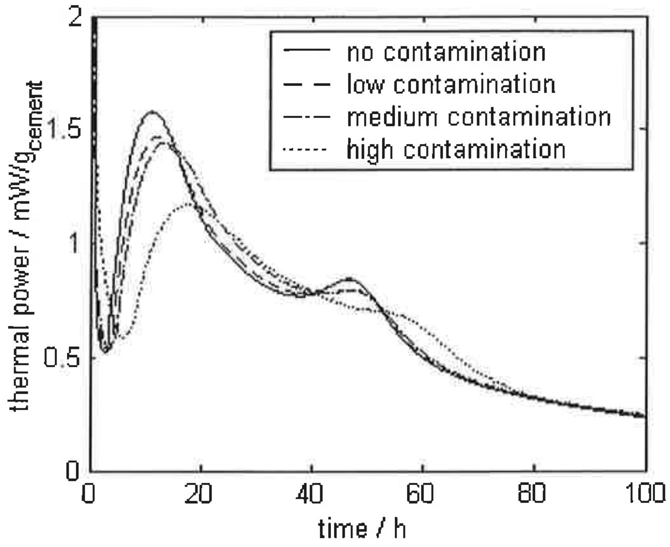

Figure 5: The result from a measurement on four cement mortars with different proportions of a contaminant.

g cement, 150 g sand and 30 g water (w/c=0.6). To this mixture the contaminant mixture was added in four concentrations: 0, 4, 12 and 29% of the cement mass. It is seen in the figure that the contaminant mixture retarded the hydration, but that the hydration still continued at almost the same rate as without the contaminant.Figure 6 shows the produced heat as a function of time. Here it is evident that there is a slight delay in the reaction. Note that the calorimetric measurement shows the reaction rate which for an unknown concrete (especially with contaminants like sawdust present) does not give any information about the *absolute* strength development that is also a function of structure, aggregate etc.

This example shows that isothermal calorimetry is an interesting method to judge the influence of contaminants on cement hydration, whether the purpose is to judge if a certain aggregate is acceptable or find the source of a problem.

A.5 Studies of early reactions

Directly after water has been added to cement reactions start. All applications described above refer to the main reaction which at 20°C starts at about 3 h after mixing. To study the earlier reactions there are two options:

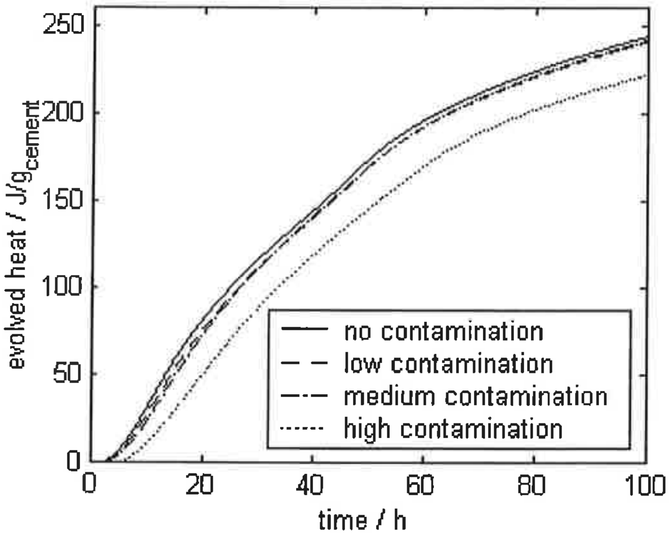
250
200
150
100
50
0
evolved heat / J/g$_{cement}$
0
20
40
60
80
100
time / h
no contamination
low contamination
medium contamination
high contamination

Figure 6:

- Charge directly after mixing and correct the signal from the calorimeter with the Tian equation (maybe with two time constants).
- Charge only the cement into a vial connected to a mixing device. Inject water when cement is at equilibrium and mix the sample inside the vial while it is in the calorimeter. Correct the signal with the Tian equation (maybe with two time constants).

B A comparison between different types of calorimetry for cement hydration studies

B.1 Isothermal calorimetry

The heat production in the sample is monitored while the sample temperature is unchanged. The most common type is the heat conduction (flow) calorimeter is which the heat produced in the sample is measured as it is conducted out from the sample through heat flow meters. There are today several types of commercial instruments available. No cement standards exist for isothermal calorimetry, although Cembureau have issued recommendations how to use it (Cembureau 1977) and there have been a few manufacturers of such instruments.

B.2 Adiabatic calorimetry

In this type of calorimetry the sample is perfectly insulated so that all heat produced is used to heat the sample. The temperature increase of the sample is measured and the rate of temperature increase is a measure of the heat production rate in the sample. So called adiabatic shields are usually used to hinder the heat form leaving the sample.

B.3 Semi-adiabatic calorimetry

This is a simpler type of insulated calorimeter in which the insulation is not perfect so a certain fraction of the heat produced is allowed to escape from the sample. In practice the sample is simply placed in an insulation made of polystyrene. One example of a semi-adiabatic calorimeter is "hökassen" (NT Build 388).

B.4 Solution calorimetry

In this method the total heat of hydration at a certain time is determined as the difference between the liberated heat when an un-hydrated sample and the sample under investigation is dissolved in a mixture of hydrofluoric acid and nitric acid. This old measurement technique is described in ASTM C185, prEN 196-8, SS B1 1960 etc. It is time consuming, costly and dangerous, but still in use.

B.5 Comparison between isothermal and adiabatic calorimetry

Isothermal calorimeters have many advantages over adiabatic calorimeters:

- Isothermal calorimeters directly measure the heat production rate that is proportional to the rate of the reaction (adiabatic calorimeters measure temperature (change) that is recalculated to give heat produced).
- In isothermal calorimetry it is not necessary to know the heat capacity of the sample, as is required in adiabatic calorimetry.
- Isothermal calorimeters are very stable and need not be calibrated more than a few times a year (adiabatic calorimeters are often calibrated before each run).
- Isothermal heat conduction calorimeters for cement hydration studies are more sensitive than adiabatic calorimeters.
- The temperature never increases to unrealistic temperatures in an isothermal calorimeter. (final temperatures during measurements in adiabatic calorimeters are very high, e.g. 80°C; far above what is desirable in real constructions).
- The engineer does not need adiabatic heat curves, but instead heat curves for different constant temperatures as this is the information used in calculation of maturity and strength growth in concrete, as well as the risk of thermal cracking.

Most calorimeters in use in cement and concrete science are instruments that are either home built or manufactured only for this special use. The type of modern isothermal calorimeter we plan to use in this project is commercially available and is used in pharmaceutical industry, microbiological laboratories, defense research establishments etc. It is therefore a less expensive instrument. Isothermal calorimetric experiments are easy to perform and need little operator time (in contrast especially to the conduction calorimetric method described on the previous page).

The only possible drawback with isothermal calorimetry is that only small samples may be used. For measurements on large samples of concrete one therefore needs adiabatic or semi-adiabatic calorimeters. Most measurements may however be made on cement pastes, mortar or micro-concrete since normal coarse aggregate does not influence the heat development in the cement paste (approx. 30% of the concrete). Calorimetric measurements on a real concrete could also be done isothermally by sieving the large aggregate away before the measurement.

Adiabatic and semi-adiabatic calorimeters are sometimes advocated because the temperature increases during a measurement, just like it does in a real construction. This is, however, not of any advantage since there are very different temperature increases in different parts of a massive construction. The truth is that the isothermal measurement is the most well defined calorimetric measurement, and to completely describe the hydration of a cement paste or a mortar the best way is to make isothermal measurements of its hydration at different temperatures.

C The influence of aggregate on cement hydration

As noted in Appendix B it is not possible to have large aggregate in the small samples for isothermal calorimetry. The maximal aggregate size for a TAM Air 20 ml glass ampoule in the order of 5 mm, but one should note that the larger the aggregate is, the larger will also the spread in the result be. In cement calorimetry we want to measure the rate of cement hydration. Do we need to have the aggregate in our calorimetric samples? Would it be possible to make calorimetric measurements only on cement paste or only on mortar (with a maximal aggregate size of 2 mm)?

How can the large aggregate influence the hydration? I see three possible ways:

- If the aggregate is dry it may absorb water lowering the water-cement ratio. It may also be wet so that it raises the water-cement ratio. Normal Swedish aggregate has a quite low porosity and small changes in water-cement ratio will not influence the cement hydration much.
- It carries on its surface contaminants that influences the hydration. If one suspects that this is the case the water that should be used for mixing the mortar could be used to leach out these contaminants prior to the mixing.
- It is extremely reactive, but such aggregate should not be used.

A number of tests on the influence of the aggregate on cement hydration has been performed as part of this work. The idea was to see if there was a difference between no aggregate and fine aggregate as it can be expcted that the fine aggregare with its larger surface area should influence the hydration more than the large aggregate. Different types of small size aggregates (sand, gravel) were used. All measurements were made with Cementa Byggcement with a water-cement ratio of 0.5. For each measurement a cement paste was mixed and divided into three parts. One was charged into two ampoules as it was (cement paste), to one part an equal mass of aggregate was added to the cement paste, to the last part half the mass of aggregate was added to the cement paste. The two mortars were charged into three ampoules each. It should be noted that the second type of sample with equal masses of aggregate and cement paste was very difficult to mix into a mortar by hand; it contained an extreme fraction of fine aggregate.

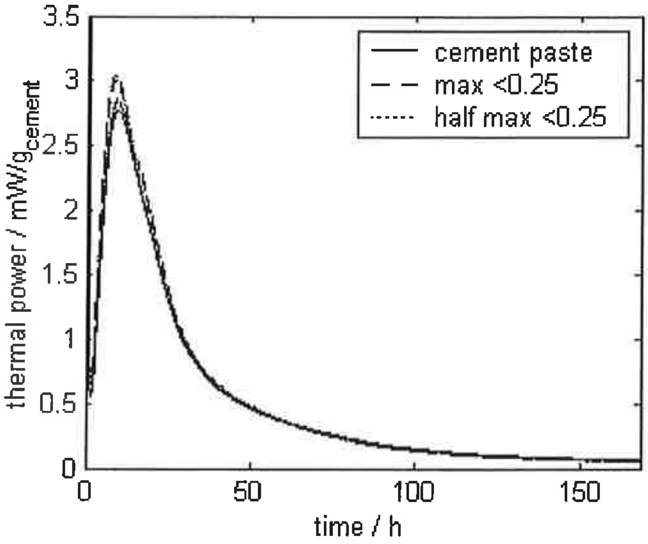

Figure 7: All results from one measurement with the same cement paste, but very different amounts of aggregate (fine sand).

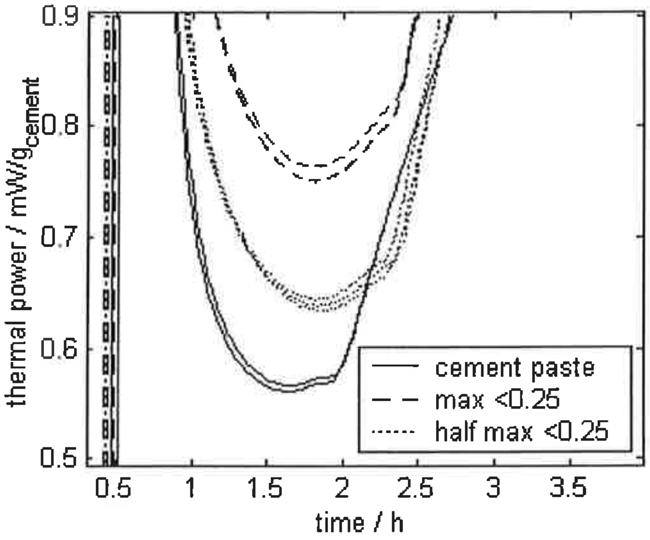

Figure 8: Close up of start of the main cement hydration. The same data as shown in the previous figure.

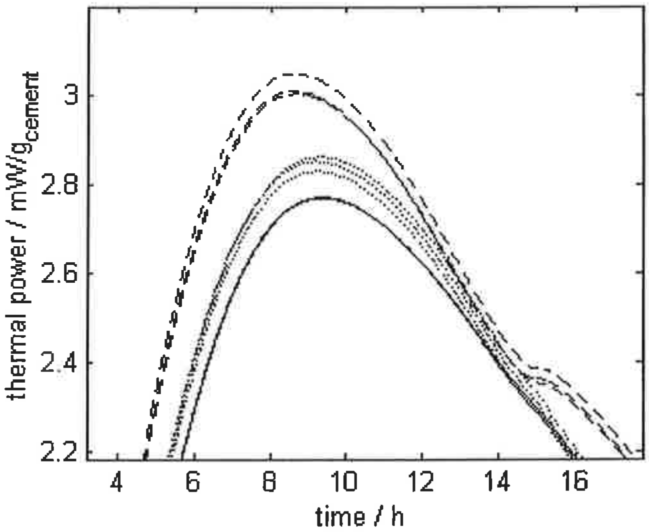

Figure 9: Close up of the peak of the measurement shown in Fig. 7.

Figures 7-9 shows typical results from these measurements. Figure 7 shows that the results are rather similar for both cement paste and mortar. Figure 8 shows that the main reaction in the cement paste starts about 20 minutes earlier in the cement paste that in the mortars. However, in another measurement the cement paste hydration started about 12 minutes later than the hydration of the cement mortars, so this small difference seems to be variable. Figure 8 also shows that the thermal activity during the dormant period is higher in the mortars that in the cement paste, but as this is during a relatively short time it does not much influence the total heat. Finally, Fig. 9 shows that the maximal thermal power is slightly higher for the mortars than for the cement paste. It also shows that there is a second peak for the samples with the largest fraction of aggregate.

The differences seen between the samples with and without aggregate are quite small. This suggests that one may determine the heat production rate of a concrete by making measurements on cement paste or cement mortar with only fine aggregate. Table 2 in Appendix F also shows that the heat integrals are about the same with and without aggregate.

For the large majority of cases I believe that it is safe to make measurements on cement mortar containing aggregate with a diameter of 2 mm or less. The heat production per unit of mass of concrete also containing the larger aggregate is then:

$$\Pi = \frac{P}{m_\mathrm{s}} \cdot \frac{m_\mathrm{c} + m_\mathrm{w} + m_\mathrm{au}/f}{m_\mathrm{c} + m_\mathrm{w} + m_\mathrm{au}} \tag{3}$$

Here, P_s (W) is the measure thermal power from the sample, m_s (g) is the mass of the calorimetric sample, m_c (g) is the mass of cement used in the mix, m_w (g) is the mass of water use in the mix, m_au (g) is the mass of the agregate used in the mix, f is the mass fraction of the aggregate that was used for the calorimetric sample, and Π (W/g) is the specific thermal power from the mortar/concrete sample with all the aggregate. When a sieve is used to sort out the larger aggregate from the smaller that can be used in the calorimetric sample, then f can be calculated like:

$$f = \frac{m_\mathrm{passed}}{m_\mathrm{passed} + m_\mathrm{not\ passed}} \tag{4}$$

Here, m_passed (g) is the mass that passed the sieve and $m_\mathrm{not\ passed}$ (g) is the mass that did not pass the sieve.

D Can glass vials be used for cement hydration measurements?

Cement paste is extremely alkaline and can dissolve (etch) glass. I have therefore made measurements with cement paste and cement mortar in glass vials and in polyethylene bags to see if there is a difference in the measured thermal power. Three types of samples were run:

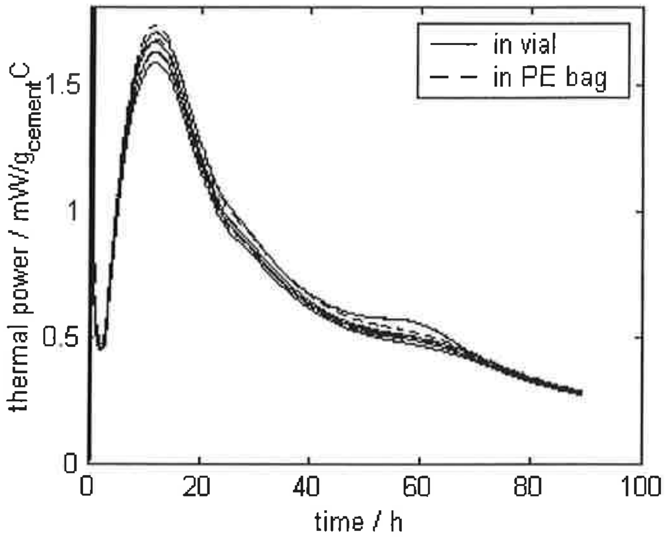

Figure 10: The result of measurements of cement paste hydration. Four samples directly in glass vials and four samples in polyethylene bags with parafin oil as heat transfer medium.

1. The samples were charged directly into the vials.
2. The samples were charged into polyethylene bags that were placed in glass vials. This did give somewhat lower thermal powers and a third type of samples were then used to see if this could be caused by the limited thermal contact between the plastic bag and the glass vial.
3. The samples were charged into polyethylene bags that were placed in glass vials. About 1 ml of paraffin oil was placed as a heat transfer medium on the bottom of the vial. This type of sample gave the same result as did the samples charged directly into vials.

In the following only types 1 and 3 are discussed. Figure 10 shows the result of measurements with a cement paste of water-cement ratio of 0.5. Table 1 gives evaluated heats that shows that there is no difference between measurements in vials and in polyethylene bags. It is therefore possible to charge cement paste and cement mortar directly into glass vials for measurements.

	heat / J	heat / J
in glass vial	148.0±2.7	146.7±1.2
in polyethylene bag	146.7±1.0	-

Table 1: Mean values and standard deviations of the integrals of thermal power from 140 minutes after mixing (start of main reaction) to 5000 minutes. In the rightmost column one of the samples in a glass vial has been excluded as it shows a slightly different shape of the hydration curve (the one with more pronounced second peak in Fig. 10).

E Integration limits for heat of hydration

A most common calorimetric measurement for cement is the determination of the heat of hydration during the first three or seven days of hydration. For the three types of calorimetric methods used (cf. Appendix B) different integration limits must be used:

- For isothermal calorimetry as described in this report a cement paste or a mortar is mixed outside the calorimeter and then transferred into the calorimeter. Depending on the circumstances the time from the start of the reaction (addition of the water to the cement) to the charging of the vials into the calorimeter can be from two to 30 minutes for an isothermal calorimeter[4]. The longer time refers to a case where several different pastes are mixed separately, but charged into the calorimeter at the same time. If one is interested in knowing the true heat from the early reactions one should of course work with short times between mixing and charging. After a sample has been charged into the calorimeter it will take in the order of 30 minutes before the true thermal power is directly measured. This time can be substantially shortened by the use of the Tian equation which calculates the true thermal power in the sample from the measured signal.
- For semi-adiabatic and adiabatic calorimeters the sample is usually large and mixed outside the instrument and then transferred to the instrument. The time for this is very much dependent on the type of instrument. It will then take some more time before the sample has thermally stabilized itself. All in all the time between mixing and knowing true values is usually in the order of 30-60 minutes.
- The solution calorimetric method is quite different from the above methods as one only gets information about the produced heat from time zero (start of mixing) to the time when one ends the measurement. This is thermodynamically very elegant, but the measurement

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[4] For the TAM Air procedures in sections 4 and 5 it should take approx. two minutes to get the sample into the calorimeter.

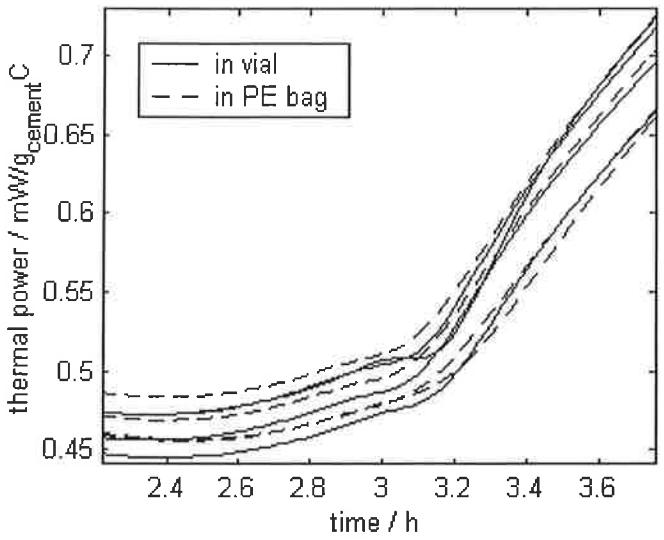

Figure 11: A close up of the start of the cement hydation in Fig. 11.

is difficult to make and one does not get any information on what happens during the time until the measurement is stopped.

For isothermal calorimetry there is a possibility to integrate from the start of the main hydration as this time is clearly seen as a knick-point on the diagram, as in Fig. 11. Here, it is clearly seen that all eight measurements have this knick-point at about 3 h. I have defined the starting time of the main hydration as the inflexion point (cf. Fig. 12).Figure 13 shows a results from a measurement in which the sample was charged about two minutes after mixing. The dashed line (with Tian correction) is show a somewhat higher total heat than the solid line (without Tian correction). This is because the Tian correction takes away the heat in the ampoule that is there because it did not have the same temperature as the calorimeter when it was charged. The logarithmic scale makes this most visible at the start of the measurement, although the difference exists for the whole measurements (after the initial part the thermal power changes so slowly that the Tian equation does not make much difference).

F Reproducible mixing

The mixing procedures prescribed in cement, mortar and concrete standards are rather detailed. However, I have found that for the small mixtures (10-100

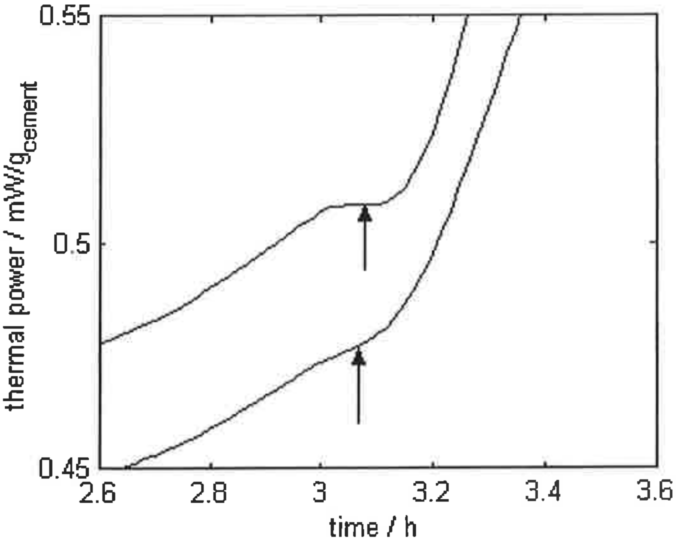

Figure 12: The arrows shows how I have defined the starting time of the main cement reaction as the inflexion point.

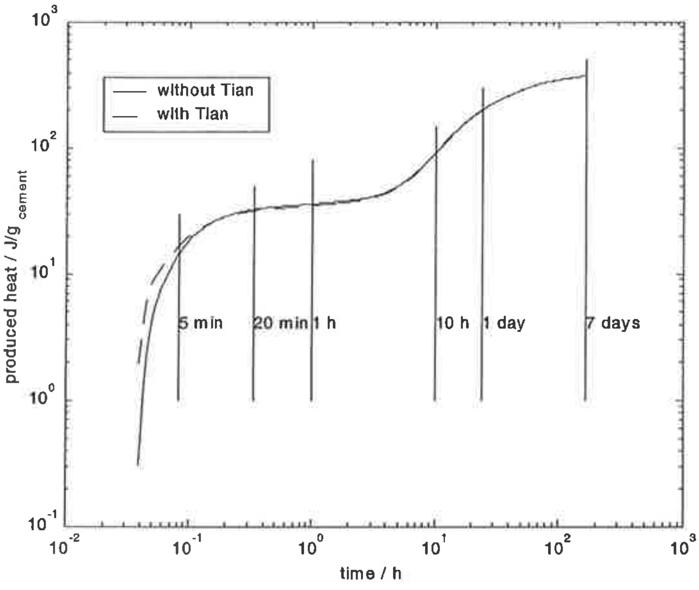

Figure 13: The result from a measurement with quick charging in a log-log diagram to show the differences at early times (not that the scale grossly overexagerates the differences in the beginning of the measurement).

	start react.	Q, start-10 h	Q, start - 3 days	main peak
	h	J/g_{cement}	J/g_{cement}	mW/g_{cement}
mortar w/c=0.5	2.92±0.01	33.2±0.4	198±4	1.64±0.03
paste w/c=0.5	3.03±0.05	32.1±1.0	206±6	1.65±0.05
three mortars w/c=0.5	2.55±0.01	50.0±0.2	257.6±6.6	2.50±0.10
one paste w/c=0.5	2.33±0.02	49.3±0.2	269.9±2.4	2.50±0.004

Table 2: Results from two mixes with the same water-cement ratio. All figures are mean and standard deviation of four measurements.The three mortars on line three were mixed by hand 15 s, 1 min and 2 min.

g) of cement paste or mortar that is used in the methods described above one minutes mixing by hand gives reproducible results. The last two lines of Table 2 show one example of this (the top two lines also show this as the mixing of the cement paste is supposed to be much more efficient when there is an aggregate present as in the mortar).

There may be cements with high filler concentrations etc. for which hand mixing is not sufficient. One may then use small electric mixers (kitchen type).

G Basics of isothermal calorimetry for cement hydration

When cement is mixed with water a series of chemical reactions starts, ending with the hardened cement paste. All reactions, including the ones involved in cement paste hydration, produce heat. The measurement of the heat produced by cement hydration by isothermal calorimetry is therefore a method to monitor and study the hydration processes.

An isothermal calorimeter measures the thermal power (heat production rate) P (unit: W) from the cement hydration reaction. Let us assume that the aggregate does not influence the hydration reaction. Then for a cement paste sample with a water-cement ratio w/c (g/g) and a mass m (g) the thermal power is proportional to the enthalpy of hydration Δh (J/g) and the degree of hydration α:

$$P = \Delta h \frac{m}{w/c+1} \frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{5}$$

Under isothermal conditions and for a certain cement paste the thermal power is a function of time or the degree of hydration (either may be used):

$$P = f_1(t) = f_2(\alpha) \tag{6}$$

Under non-isothermal conditions the thermal power can only be described as a function of temperature T (K) *and* the degree of hydration. This is done by assuming that the thermal power at a certain degree of hydration follows an

Arrhenius' relationship:

$$P = P_0(\alpha)\exp(\frac{-E_\mathrm{a}}{RT}) \tag{7}$$

Here, E_a could be a function of α, but one usually takes this as constant.

The degree of hydration can be determined in different ways. For the present type of measurement it is useful to define it as the heat of hydration Q (J) divided by the maximal heat of hydration (when all cement has reacted):

$$\alpha = \frac{Q}{Q_\mathrm{max}} \tag{8}$$

The heat is the integral of the thermal power:

$$Q(\tau) = \int_0^\tau P\mathrm{d}t \tag{9}$$

An isothermal calorimeter measures thermal power which is proportional to reaction rate. From such a measurement we can therefore see how the cement hydrates. This is useful for many different purposes, as discussed below. However, it should be noted that there are two types properties of which isothermal calorimetry *in general* does not give information about: rheology and strength.

It should be noted that Δh in the above equations is not a constant. It will change during the course of the cement hydration and it will be he weighed mean of the Δh:s of all different types of reactions taking place simultaneously.

H Use of the Tian equation for cement hydration studies

The measured signal from a heat conduction calorimeter is not the true thermal power produced in the sample as there is a time lag for the heat to pass through the heat flow sensor. The Tian equation removes this time lag and gives as output the true thermal power produced at each instant in the sample:

$$P = \varepsilon(U + \tau\frac{\mathrm{d}U}{\mathrm{d}t}) \tag{10}$$

Here, P (W) is the thermal power, U (X) is the measured output, ε (W/X) is the calibration coefficient, and τ (s) is the time constant. The measured output can have different units - here denoted by X - volts being the most common, but the output from an A/D-converter or mm measured on a recorder paper could also be used.

It is unnecessary to use the Tian equation if the process studied only changes slowly compared to the time constant τ which may be calculated by the following equation:

$$\tau = \frac{C}{k} \tag{11}$$

	C , J/K	c , J/K/g
ampoule holder	12	-
glass ampoule	13	-
cement	-	0.75
water	-	4.18
aggregate	-	0.75

Table 3: Thermal properties for time constant calculations.

Here, C (J/K) is the total heat capacity of the sample (including ampoule and ampoule holder etc.) and k (W/K) is the thermal conductance of the heat flow sensor. The heat capacity C may be calculated by summing the heat capacities of all n parts on the sample-side of the heat flow sensor:

$$C = \sum_{i=1}^{n} C_i \tag{12}$$

For cement paste and mortar in the TAM Air with glass ampoules the values in Table 3 may be used. The thermal conductance of the TAM Air heat flow sensors is 0.68 W/K. The time constant may also be found from dynamic calibration curves.

Figure 14 shows an example of a Tian-corrected curve measured on 10 g cement paste. It shows that part of a cement paste hydration curve where the most rapid changes take place except for the very early reactions. The difference is small and it is safe not to use the Tian correction for most applications. The sample in this example has a time constant of about 65 s. One drawback with using the Tian equation is that one has to collect data at a quite high rate (minimum 5 s time interval). If one does not use the Tian correction any initial disturbances can be considered to be gone after about 5τ (1% of initial disturbance left), 7τ (0.1%), 9τ (0.01%). [5]

For the above example (Fig. 14) the integrals from the time the samples are charged into the calorimeter (about 25 minutes after mixing in this case) to are 315.15 and 314.93 $\mathrm{J/g_{cement}}$, respectively, without and with the application of the Tian equation. Starting the integration at a later time gives somewhat lower heat integrals, e.g. 309.72 and 307.52 J/g for integration from 1 and 2 hours after charging. The conclusion from this is that if the goal of a measurement is to look at the main hydration it is not important to use the Tian equations. On the other hand, if one is interested in the integral (cf. the solution calorimetric method) it is important to start measuring as early as possible from the mixing, use the Tian equation, and start the integration as early as possible.

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[5] For cement hydration with 5 g of cement paste in a TAM Air the time constant is about 50 s.

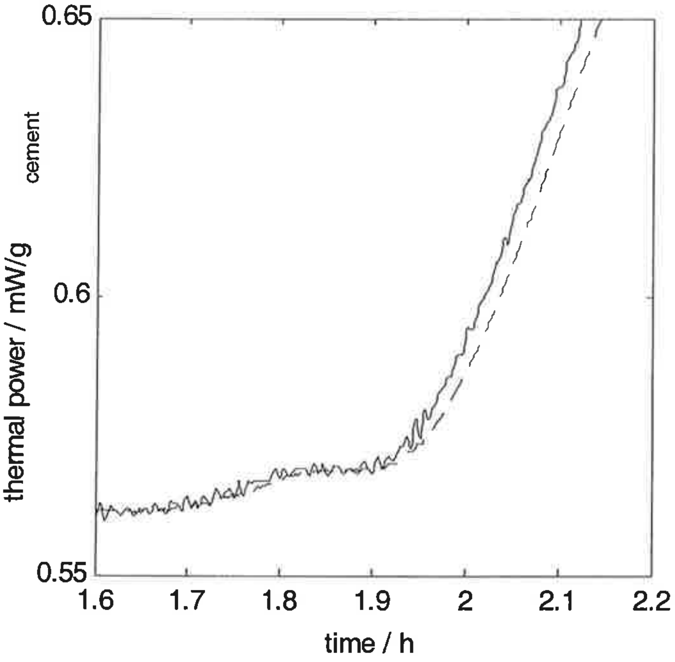

Figure 14: An example of Tian correction. The dashed curve is the original measured curve and the solid curve is Tian corrected.

I Calibration of isothermal heat conduction calorimeters

Today the only simple and precise way of calibrating isothermal heat conduction instruments for cement hydration measurements are by electrical calibration. In such a calibration an electrical current is passed through a resistance (heater) placed in the calorimetric ampoule or on he ampoule holder. If the current I (A) and the resistance is R (Ω) the produced thermal power (P, W) can be calculated as:

$$P = I^2 R \tag{13}$$

If the corresponding output from the calorimeter at steady-state is U_c (X) the calibration coefficient ε (W/X) is calculated by:

$$\varepsilon = \frac{P}{U_\mathrm{c}} \tag{14}$$

Here, X denotes the units of the data logger (usually V, mV, μV etc, but it can also be the direct output form an A/D-converter).

Electrical calibration is good, but the results can be several percent wrong if proper precautions are not taken. The main rule is to make the calibration case as similar as possible to the measurement case. Place the heater as close as possible to the place where heat will be produced during a measurement. Use thin electrical leads (but not too thin as this will give heating in the leads).

J A method to start a measurement at the correct temperature

It is a problem, especially, if one is working with calorimeter at another temperature than the laboratory, that the sample does not have the same temperature as the calorimeter when it is charged. Below is presented a method to calculate the temperature of the water so that the final mix is quite close to the temperature of measurement. The used nomenclature is according to Table 4.

The mean weighted temperature of all components (incl. vial etc.) should be equal to the temperature of the calorimeter:

$$\frac{T_\mathrm{w} m_\mathrm{w} c_\mathrm{w} + T_\mathrm{a} m_\mathrm{a} c_\mathrm{a} + T_\mathrm{a} C_\mathrm{x}}{m_\mathrm{w} c_\mathrm{w} + m_\mathrm{a} c_\mathrm{a} + C_\mathrm{x}} = T_\mathrm{c} \tag{15}$$

This may be rearraged to:

$$T_\mathrm{w} = \frac{T_\mathrm{c}(m_\mathrm{w} c_\mathrm{w} + m_\mathrm{a} c_\mathrm{a} + C_\mathrm{x}) - T_\mathrm{a} m_\mathrm{a} c_\mathrm{a} + T_a C_\mathrm{x}}{m_\mathrm{w} c_\mathrm{w}} \tag{16}$$

If water with this temperature is used to mix the cement paste of mortar the temperature of the mix should be similar to that of the calorimeter.

c_s	specific heat capacity of cement and aggregate	0.75 J/g/K
c_w	specific heat capacity of water	4.2 J/g/K
C_x	heat capacity of vial and ampoule holder[6]	J/K
m_s	mass of solids (cement, aggregate)	g
m_w	mass of water in pase/mortar	g
T_a	temperature in lab (temp. of solids)	°C
T_c	temperature in calorimeter	°C
T_w	temperature of water in cement/mortar	°C

Table 4: Nomenclature used in method to calculate temperature of water when mixing paste and mortar.

K How isothermal is an isothermal heat conduction calorimeter?

Isothermal heat conduction calorimetry is essentially isothermal, not exactly isothermal, as the heat produced in the sample will heat the sample slightly so that one gets the temperature gradient that gives the conduction of heat away from the sample. Wadsö ("Temperature changes within samples in heat conduction calorimeters" Thermochim. Acta 366 (2000) 121-127) has given equations to calculate the maximal (center) temperature increase in a sample during a measurement. For most purposes the following equations may be used:

$$\Delta T = \frac{P}{k} \tag{17}$$

Here, ΔT (K) is the temperature difference between the heat sink and the sample, P (W) is the produced thermal power, and k (W/K) is the thermal conductance of the heat flow sensors[7]. For well designed measurements in well designed isothermal heat conduction calorimeters the temperature increase should be less than 0.1 K, i.e. the measurement can be seen as *essentially* isothermal.

L Research needs

Below are listed a number of questions that should be looked into to gain a better understanding of isothermal calorimetry as a tool for the study of cement hydration.

L.1 Hydration as a function of w/c

Water-cement ratio (w/c) is the most important parameter in concrete production as it greatly influences both strength and rheology. However, its influence on the hydration rate is not at all as marked and one would probably find that

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[7] For the TAM Air k=0.33 W/K which gives a temperature increase of approx. 0.05 K with a 5 g cement paste sample.

using slightly different w/c (e.g. 0.55 instead of 0.50) one would get essentially the same results from a calorimetric measurement.

There are a number of factors of interest here:

- For normal w/c there is more water than the cement needs to fully harden. Low w/c pastes are self desicating as there is not enough water proesent for a full hydration of the cement.
- More water means that the cement particles are further away from each other.
- The surface of a concrete is often exposed to more water from watering and rain than the interior.

It would be interesting to make measurements of hydration as a function of water supply (incl. different w/c and wetting of surfaces). A combination of isothermal calorimetry and RH-measurements could be of interest.

L.2 Internal mixing vs. external mixing for the study of early reactions

It is possible to mix cement pastes and mortars down in the calorimeter, at least at high w/c. This should be investigated further.

L.3 Relative strength development as a function of produced heat

It has been shown that there is a rather linear relation between the strength development and the produced heat. However, it is not known when this relation starts as there can be no such relation before the cement paste has any strength, i.e. before the main reaction starts, even if some heat is produced.

M Practical questions to be answered in the second part of this project

1. How important is it to measure the heat production rate from the time of mixing when one is interested in the temperature of a massive construction? Problems with measurements at non-ambient temperatures.
2. How important is the comntrol of the water-cement ratio?
3. How important is the contro of the mixing process?
4. How important is the possible influence of aggregate on cement hydration (moisture content, porosity)?
5. What precision, reproducibility is needed for isothermal calorimetry?