



Danish Centre for Green Concrete

Physical and Thermodynamic Properties of Green Concrete

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Aalborg University, October 2002

Title: Physical and Thermodynamic Properties of Green Concrete
Author: Jacob Thrysoe
Date: October 2002
ISBN: 87-7756-695-5

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Preface

This report is a result of the work carried out in the Ph.D.-project "Physical- and Thermodynamic Properties of Green Concrete" at Aalborg University, Department of Building Technology and Structural Engineering. The Ph.D.-project has not yet been formally closed down and the present report is meant as an overview and a documentation of the activities completed until the autumn of 2002.

The report is divided into three parts:

Chapter I, Introduction: A status of the project and an easy-to-read overview of the two central experimental parts of the project. Activities carried out during the project period is described.

Chapter II, Differential Pressure Analysis: A review of the main experimental part of the project, the *Differential Pressure Analysis*, including a description of experimental set-up and procedures. The theory and ideas behind the DPA-measurements are shown.

Chapter III, Isochor Volumeter: A review of the work carried out on and the ideas behind the *Isochor Volumeter*. The apparatus, the experimental set-up and the procedures put forward are described.

The Ph.D.-project was started 1st of January 1999, with an expected end of 31st of December 2001. The project period was extended two weeks until the 14th of January 2002 due to maternity leave.

If it were possible I would like to thank my supervisor during the project period, Professor *Per Freiesleben Hansen*^{*}, for always being inspiring, creative and deeply involved in the project. Unfortunately this is not possible anymore since Per Freiesleben Hansen deceased on the 25th of August 2002:

All honour to his memory

Research Professor Ole Mejlhede Jensen^{*} is appointed as new supervisor on the Ph.D.-project.

Jacob Thrysøe

Aalborg, 31st of October 2002

^{*} Aalborg University, Department of Building Technology and Structural Engineering.

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Chapter I

INTRODUCTION

This introduction provides an easy to read overview of the experimental parts of the project; a more detailed description is placed in Chapter II and Chapter III. Activities carried out during the Ph.D.-project period are described along with information about which material that has been produced and where further information about the project can be found.

1.1 Status of the Ph.D.-project

As described in the project plan for the Green Concrete Contract, the obligation of Aalborg University was research into the following areas:

BK 5.1:

Investigation of the physical binding condition of adsorbed and chemically bound water in *Green Concrete* subjected to fire, including a mapping of decomposition reactions and pressure build up in these materials during fire in the temperature range 100-500°C.

... A central element in these investigations will be the **DPA**-equipment (Differential Pressure Analysis) that has been developed at the *Institute of Building Technology and Structural Engineering* at Aalborg University and further developed as a part of the Ph.D.-project "Physical- and Thermodynamical Properties of Water Phases in Hardening Portland Cement Systems" [1].

BK 5.2:

Investigation of chemical shrinkage in and thermal activation energy of hardening green cements and binders; this includes a mapping of the dependence of the activation energy of curing temperature, maturity and particle distribution.

... A central element in these investigations is a newly developed instrument, Isochor Volumeter (HYDRATEMETER), with which it is possible to carry out accurate determination of the reaction scheme in dense pasta systems, including a differential determination of the thermal activation energy.

To be able to measure the above-mentioned physical parameters it was an essential part of both projects to develop new experimental equipment and experimental procedures. The "apparatus development phase" took up most of the Ph.D.-project time. Both instruments were completed and proved by test by the "financial" end of the project; the DPA-apparatus has been used in a wide range of experimental test series and the mode of operation of the HYDRATEMETER has been proven.

This report is to be seen as an up to the minute summary of the Ph.D.-project and as a documentation of the work and activities carried out during the project period. Status of the Ph.D.-project, autumn 2002:

- BK 5.1:**
- Development of the DPA-instrument completed.
 - Investigation of decomposing reactions and pressure build-up in different cement binders carried out and completed.
 - Final reporting in the form of a Ph.D.-project is not completed.
- BK 5.2:**
- Development of the HYDRATEMETER-apparatus completed.
 - Experimental tests with cement and other binders completed to some extend.
 - Final reporting in the form of a Ph.D.-project is not completed.

Both instruments are situated at the Institute of Building Technology and Structural Engineering at Aalborg University, Denmark.

1.2 Differential Pressure Analysis - DPA

The Differential Pressure Analysis (DPA) apparatus is designed for measurements of equilibrium pressure above a test specimen at a given temperature; the system is Isochor and the limits of operation is 538°C and 340 atmosphere. By measurements of coherent values of temperature and equilibrium pressure above the test specimen through a wide temperature interval, thermodynamic properties can be calculated, including enthalpy H^θ and entropy S^θ . When investigating Portland Cement systems at high temperatures, the instrument can be used for determination of thermodynamic properties, decomposition reactions and pressure build up above the cement paste. The DPA-apparatus is illustrated in Figure 1 and a photograph is shown in Figure 2.

The DPA-apparatus consists of an oven in which the test specimen is placed; a high temperature pressure transducer seal of the oven chamber to the surroundings using a copper disc as a gasket on the contact surface between the oven and the pressure transducer. The temperature in the chamber is measured by thermocouples placed in the oven. A data logger is controlling the heating sequence, measurements of pressure and temperature and collection of data. The data logger is programmed via a computer terminal and experimental results can be followed in real time.

When used for examination of cement paste this has to be pulverised and thereafter pounded down into a small stainless steel container that fits into the chamber of the oven. Approximately 1.2 g of cement paste can be examined in an experiment. An automatic internal transducer calibration is done before any experimental run.

Investigating cement paste samples, reliable measurements can be carried out from 150°C; the heating sequence is done in steps of 5-10°C. The aim is to obtain a near equilibrium pressure condition above the test specimen at a given temperature; the time at each temperature to reach equilibrium is found to be approximately 15 minutes.

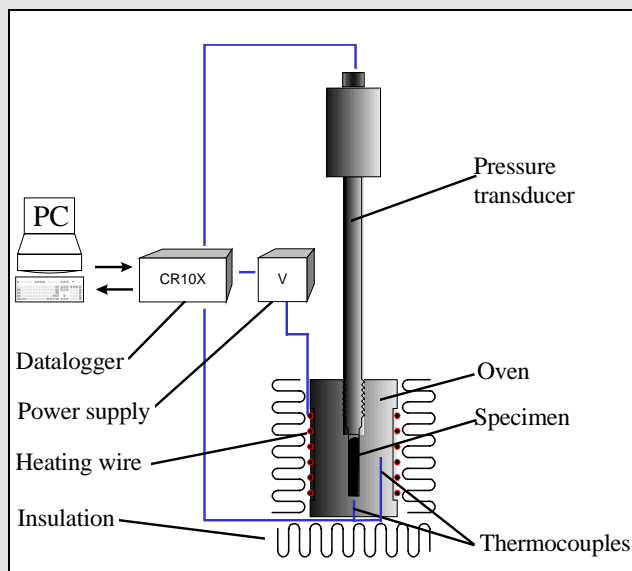


Figure 1 Illustration of the DPA-apparatus. The data logger is measuring coherent values of temperature and pressure above a cement paste specimen subjected to high temperatures. The data logger is controlling the heating sequence of the oven.

Figure 2 Photo of experimental set-up.

1.3 Isochor Volumeter - HYDRATEMETER

The Isochor Volumeter (HYDRATEMETER) is a new instrument designed for continuous and very accurate measurements of small volume changes during physical or chemical processes in reacting systems; the instrument can thus be used for investigation of chemical shrinkage of hardening Portland cement systems. The HYDRATEMETER is illustrated in Figure 3 and a photograph is shown in Figure 4.

The system consists of a control-cell, which is connected to a sample-cell through a narrow capillary tube. During an experiment, the entire system is completely filled by liquid, and the pressure of the system is kept constant by controlling the temperature of the control-cell; a volume change in the sample-cell can thus be measured as a temperature rise in the control-cell. If for example Portland Cement is placed in the sample-cell, the chemical shrinkage during the hydration process can be followed by a simple temperature measurement in the control-cell. The system has proven to be a very accurate measurement of even small volume changes in the sample-cell. At the present stage the resolution of experiments are about $25 \cdot 10^{-9}$ litre.

To control the hydration temperature, the sample-cell is submerged into a thermostated bath. Since the sample is completely filled with water during an experiment, the dry packing of the powder into the sample-cell determines the water/powder-ratio of the sample.

The entire system is evacuated before an experiment and trapped atmospheric air is flushed out by water vapor. By a special valve, air-free water is let in through the duct in the top of the instrument; the water fills up the system in a few seconds and the duct is cold-welded by clipping. The system pressure is then raised to a predefined level (normally around 10 bars) and the measurements begin.

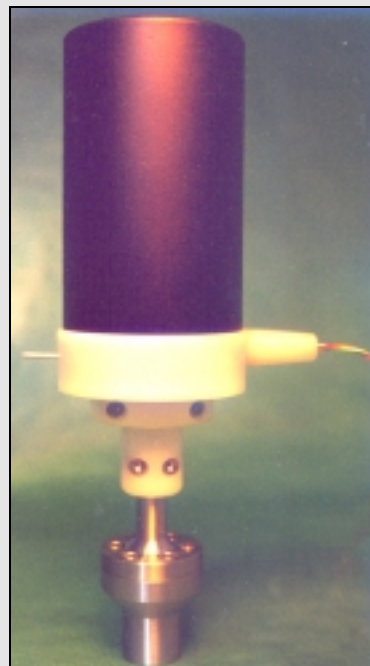
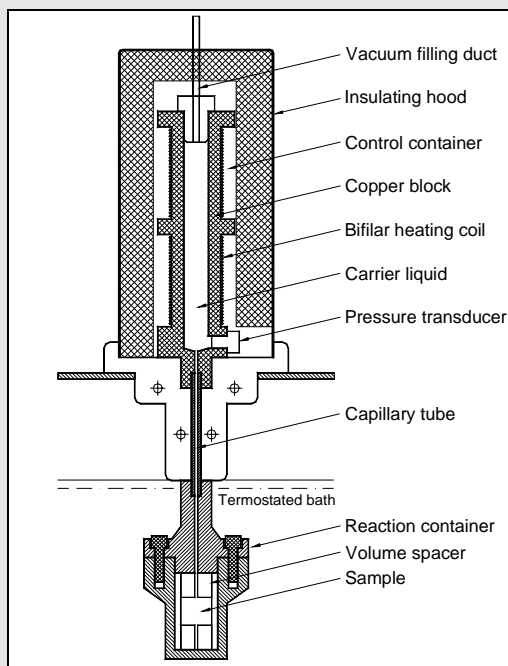


Figure 3 Illustration of the HYDRATEMETER. During experiment the sample-cell is submerged into a thermostated bath. **Figure 4** A photo of the HYDRATEMETER. Surrounding the control-cell is an insulating hood.

1.4 Activities carried out during the project

1.4.1 Ph.D.-courses

In Table 1 the Ph.D.-courses completed during the project period are listed.

Table 1 Ph.D.-courses completed. AAU = Aalborg University; DTU = Technical University of Denmark; AP = Aalborg Portland.

Title	Place	Modules	Time
Thermodynamic	AAU	4,0	Feb.-Jun. 1999
Porøse materialers struktur og egenskaber	AP	3,5	Mar.-Aug. 1999
Hydration and Microstructure of High Performance Concrete	DTU	1,5	Aug. 16-25 1999
Philosophy of Science and Technology	AAU	1	25-27 Oct. 1999
Writing and reviewing of Scientific Papers	AAU	1,5	23 Mar. and 20 May 1999
Professional Communication	AAU	1	20, 22 and 23 Apr. 1999
Design and Analysis of Experiments	AAU	2	1, 8, 15, 22 and 29 Oct., 5 Nov. 1999

1.4.2 Visit to Aberdeen University

From October 2000 to February 2001 I spent four month visiting The Department of Chemistry at Aberdeen University in Scotland. Professor *F.P. Glasser* was kindly my supervisor for that period guaranteeing a professional and rewarding stay. Dr. *Eric Lachowski* helped me using both X-ray Diffraction and Scanning Electron Microscopy.

The DPA-apparatus was brought to Aberdeen and cement paste samples was simultaneously examined using DPA, X-ray Diffraction and Scanning Electron Microscopy.

1.4.3 Research and Development Centre at Aalborg Portland

At the Research and Development Centre at Aalborg Portland a series of experiments was carried out from May 2001 to December 2001.

Pastes based on respectively pure clinker minerals and Aalborg Portland White Cement was simultaneously examined using DPA, Differential Thermo Gravimetry (DTG) and Quantitative X-ray Diffraction (QXRD).

1.5 Further information

The experimental work carried out during the project period has generated a large amount of data and some written material. The intention is to document the entire work in a Ph.D.-project in the near future, but if needed, further information can be required using one of the following addresses:

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1.6 References

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Chapter II

DIFFERENTIAL PRESSURE ANALYSIS - DPA

2.1 Theory

When subjected to high temperatures, concrete undergoes physical and chemical changes. The internal structure of the concrete matrix is to some extent damaged [11] [16] [4] [8]. Water held in the paste at normal temperatures, e.g. room temperature, will gradually evaporate. Decomposition of calcium silicate hydrates into other forms and calcium hydroxide into calcium oxide, causes chemically bound water to be released during the heating sequence. The pore structure and porosity of the cement paste will be changed. Gradients of pore pressure cause diffusion of evaporable water through the cement paste matrix. Transportation of heat and vapor through the cement paste matrix causes pore pressure build up which in some cases may lead to a condition, where explosive spalling of the concrete occurs [2] [3] [7] [15] [10].

2.1.1 Explosive spalling

Severe consequences can be observed when filler materials are used making up a dense matrix. In [13] an extensive survey of high-strength concrete (HSC) properties at elevated temperatures has been made with some important conclusions:

- HPC has a higher rate of strength loss than normal concretes up to 400°C.
- HPC is more susceptible to explosive spalling when exposed to high temperatures (above 300°C) than normal concrete.

In [17] it is concluded that concrete specimens containing 10% silica fume are stable for thermal treatment up to 300°C, after which appearance of micro cracks appears. Higher content of silica fume leads to internal cracks already after 105°C. Both pore pressure and thermal stresses are believed to play a role when high temperatures result in explosive spalling. In [13] Bazant argues that the main driving force of the explosive spalling is the release of stored energy due to thermal

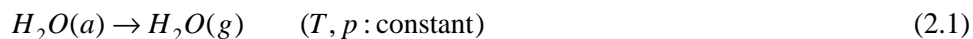
stresses; the pore pressures build up serve “only” as a triggering mechanism that is able to open a crack in the fire exposed concrete specimen. Although the pore pressure cannot drive the explosion, explosive spalling does not occur in unsaturated concrete according to Bazant [13]. Other researchers in [13], Anderberg and Ahmed, argue that the primary mechanism is the vapor pressure, especially when the spalling occurs explosively; thermal stresses large enough to cause spalling occurs primary at corners and convex surfaces.

2.1.2 Principle of Differential Pressure Analysis

When heated, water will evaporate from the surface adsorbed water phases and a shift in equilibrium vapor pressure adjusts at constant pressure and temperature. The evaporation is controlled by the thermodynamic properties of the adsorbed water phase; enthalpy $H_{T, adsorbed}$ and entropy $S_{T, adsorbed}$ are used for describing these properties, where:

- $H_{T, adsorbed}$: heat of evaporation or binding energy; a measure of how much energy is needed for evaporation of the adsorbed water phase.
- $S_{T, adsorbed}$: a measure of the order of the molecules in the adsorbed water phase; a low entropy indicates an ordered system which ultimately transforms into a solid.

The equilibrium pressure condition emerging above a heated cement paste specimen at a given temperature is investigated by considering the reversible phase transmission when a vaporisable adsorbed water phase $H_2O(a)$ is transformed into a ideal gaseous phase $H_2O(g)$:



With equilibrium between the two phases in a one-component system, Clayperons equation is valid [12] [1]:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \quad (Pa / K) \quad (2.2)$$

The molar volume of vapor V is much larger than the molar volume of liquid. For water at 25°C the molar vapor volume V is 1700 times larger than the molar volume V_{Liquid} of liquid water at the boiling point [12]. Therefore V_{Liquid} is disregarded, and with assumed behaviour as a perfect gas, then:

$$V_{\text{vapor}} - V_{\text{liquid}} \cong V_{\text{vapor}} = \frac{RT}{p} \quad (2.3)$$

By inserting Equation 2.3 into Clayperon's equation and then with $dp/dT = d/\ln(p)$ and $dT/T^2 = -d(1/T)$ the relation between the equilibrium pressure of the vapor phase and the equilibrium temperature is expressed by the Clausius-Clapeyron equation:

$$\frac{d \ln(p)}{d(1/T)} = -\frac{\Delta_r H_T}{R} \quad (2.4)$$

The enthalpy of the liquid phase can be determined by the reaction enthalpy:

$$H_{T,\text{adsorbed}} = H_{T,\text{vapor}} - \Delta_r H_T \quad (2.5)$$

The enthalpy of the vapor phase is given by, [5]:

$$H_{T,\text{vapor}} = H_{298}^\theta + c_p(T - 298.15) \quad (2.6)$$

Hence the reaction enthalpy can be calculated from experimental measurements of coherent values of equilibrium pressure and corresponding temperature above the test specimen.

The approach given above is less exact near the critical point, which for water is at 374,15°C and 218 atm; the heat of evaporation is zero at this point and the specific volume of liquid is indistinguishable from the specific volume of vapor.

Using Equation 2.4, a mapping of the natural logarithm of the equilibrium pressure against the inverse to the temperature, results in a straight curve, with the slope of $-\Delta_r H_T/R$, as illustrated in Figure 5:

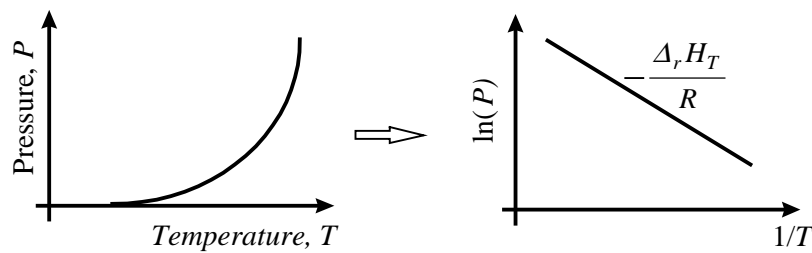


Figure 5 Conversion of measured values of P and T to a $\ln P$ $1/T$ mapping.

At equilibrium Gibb's free energy is 0:

$$\Delta_r G_T = \Delta_r H_T - T \cdot \Delta_r S_T = 0 \quad (T, p: \text{constant}) \quad (2.7)$$

Thereby the reaction entropy can be calculated:

$$\Delta_r S_T = \frac{\Delta_r H_T}{T} \quad (2.8)$$

The relationship in equation 2.8 between $\Delta_r S_T$, and $\Delta_r H_T$, implies that by using Equation 2.4 both the reaction entropy and the reaction enthalpy can be investigated by measurement of pressure P vs. temperature T over a cementitious system in equilibrium.

Equivalent to determination of the enthalpy the entropy of the gas phase is determined by [5]:

$$S_{T,vapor} = S_{298}^{\theta} + c_p \cdot \ln\left(\frac{T}{298.15}\right) - R \cdot \ln\left(\frac{P}{101325}\right) \quad (2.9)$$

2.1.3 Decomposition reactions

By removing evaporable water from the cement paste before experimental run, decomposition reactions can be monitored during a heating sequence; the only source for establishing a vapor pressure in the closed container is water combined in the solid hydrates. An increase in vapor pressure thus indicates a decomposition reaction taking place due to the increasing temperature of the system.

2.2 Applied instrumentation

The High Temperature DPA-apparatus consists of an oven in which the test specimen is placed. A High Temperature Pressure Transducer is used to seal of the chamber to the surroundings by using a copper disc as gasket between the oven and the seating of the pressure transducer; thus the pressure can be measured above the test specimen at relatively high temperatures and high pressures. Parallel to the pressure measurements, temperature in the chamber is measured by thermocouples placed in the oven. Controlling of the heating sequence, measurements of pressure and temperature and collection of data is done by a data logger. The DPA-

apparatus with support systems is illustrated in Figure 6. In Figure 7 a photo of the experimental set-up is shown.

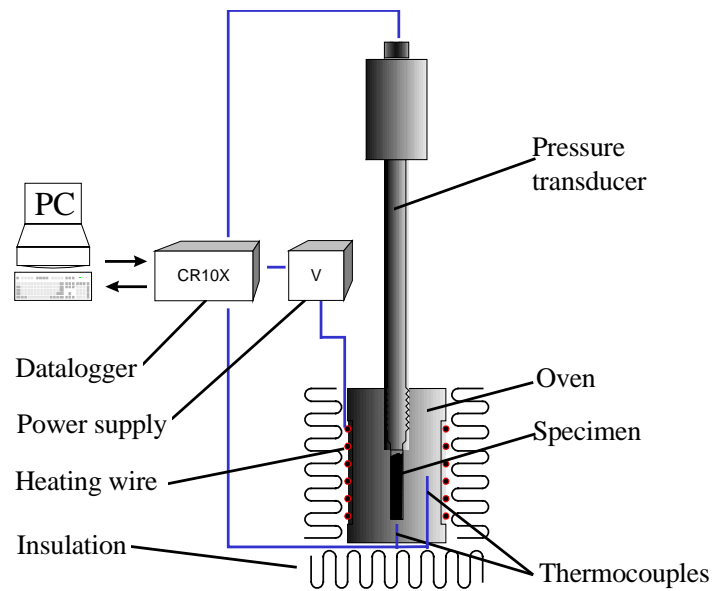


Figure 6 Illustration of the DPA-apparatus. The data logger is measuring coherent values of temperature and pressure above a cement paste under heating. The data logger is controlling the heating sequence of the oven.

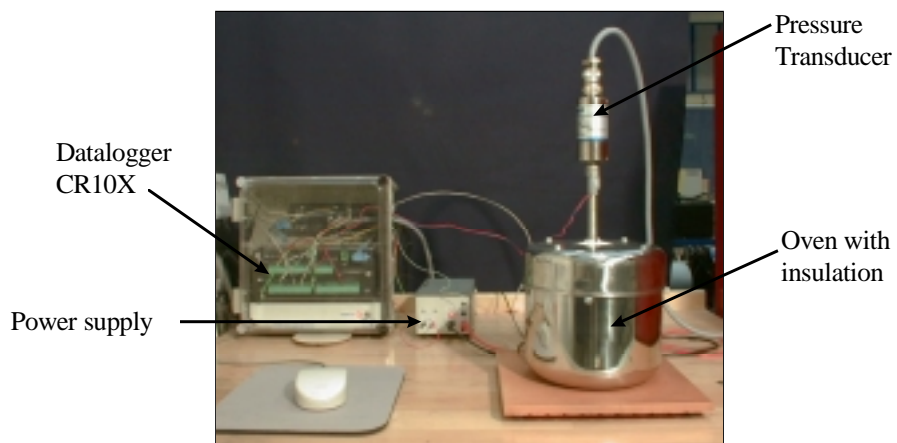


Figure 7 Photo of experimental set-up.

2.2.1 Electric oven

The basic unit of the DPA-apparatus is the electric oven. The oven is made of stainless steel. Constantan wire, with 16Ω resistance, is used as heating wire. The wire is attached to the oven with high temperature putty. In Figure 8 the oven with heating wire is shown, along with a 3D-illustration, showing the test chamber and placement of the pressure transducer.

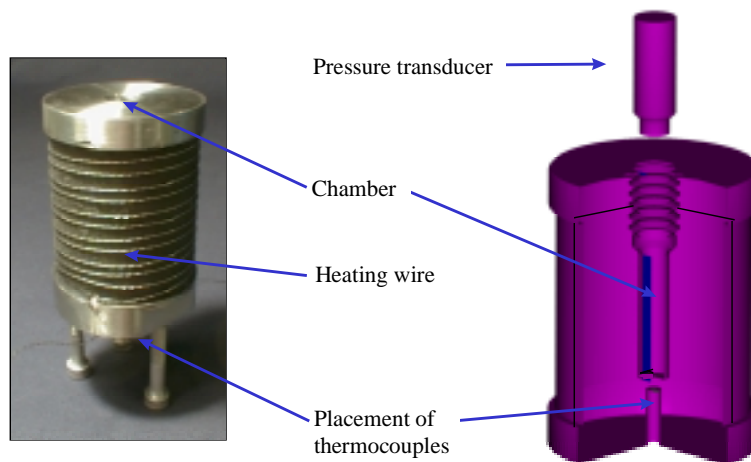


Figure 8 To the left a photo of the oven in which the test specimen is placed. To the right an illustration of the oven and placement of the pressure transducer and thermocouples.

2.3 Preparation of experiments

2.3.1 Preparation of cement paste specimen before experimental run

A crushed sample of cement paste is carefully pounded down into a small stainless steel container using a brass bar. Approximately 1.2 g of cement paste can be used in an experiment. After pounding the filled container is weighted with precision of 1/1000 of a gram.

2.3.2 Preparation of DPA-apparatus

Before an experimental run, the DPA-apparatus has to be cleaned thoroughly. Any leftovers can influence the outcome of the preceding experiments. To secure a per-

fectly closed system, chemically pure charcoal powder is applied to the surface of the copper ring. The charcoal does not influence on the experimental results.

2.3.3 Placement in DPA-instrument

The container is placed into the DPA-instrument and the pressure transducer is turned in. A special momentum key is used to give a maximum moment of 52Nm. The pressure transducer is connected to the data-collection unit.

Before an experiment can start, a reading of the internal transducer calibration circuit has to be made. This reading is used in calculation of the measured pressure. The experiment is started via the computer.

2.3.4 Experimental run

The instrument heat up the specimen to 100°C before the experiment begins. From 100°C the heating sequence is done in steps. A period of 15 min. in each step to reach equilibrium has been chosen. The instrument then heat up rapidly to the preceding temperature and hold that for 15 min. The temperature rise per step is chosen to be in the range 5°C-10°C, depending on the resolution of results and the time available for an experiment. From 150°C the pressure measurements are reliable.

Other methods of heating the test specimen can be applied, whereas two have been considered and tried out; a continuous heating sequence with a predefined temperature increment pr. min. The temperature increment then has to be small enough to ensure equilibrium conditions during heating. Another approach is to heat up in steps as suggested above, and then await an equilibrium condition to arise. This is obtained by programming the data logger to survey the process and step up the temperature when no pressure increment has been detected for a predefined time interval. The time needed at each level is not the same during the temperature interval.

During experimental run, the transducer has to be re-tightened at 250°C and at 400°C. The momentum used for re-tightening is approximately 52Nm at 250°C and 25Nm at 400°C. An experiment lasts approximately from 14 - 22 hours. To that 2-3 hours should be added for cooling down the instrument.

2.4 Experimental series

Experiments has been carried out to validate the results obtained by High Temperature DPA measurements; comparison by use of reference measurements by well known experimental procedures are done using Quantitative X-Ray Diffraction (QXRD) and Differential Thermo Gravimetry (DTG).

Cement pastes with different water/cement-ratios and varying pozzolan additions were investigated by DPA and decomposition reactions and heat of evaporation throughout the considered temperature interval were derived. The following experimental series have been carried out:

- **Validation and reference measurements:**
 - **Pure clinker minerals:** Pastes made on pure C_3S , C_2S and C_3A were cured for 56 days at 20°C ; the pastes were then heated to different temperatures in the DPA-apparatus and subsequently examined by QXRD and DTG.
 - **Cement paste:** White Portland cement paste with a w/c-ratio of 0.45, both with and without addition of 25 weight-% silica fume was heated to different temperatures using DPA and subsequently examined by QXRD and DTG.
 - **Cement paste:** Same experiments as above but by using DPA, X-ray Diffraction and Scanning Electron Microscopy.
- **Effect of w/c-ratio and pozzolan addition:** Cement pastes with w/c-ratios of 0.30 and 0.60 were examined in the DPA-apparatus. Pozzolan additions in the form of silica fume and fly ash were used with contents of respectively 0, 5, 25 and 50 weight-%.

2.4.1 Examples of experimental results

Two typical examples of experimental results derived from DPA-measurements are shown in Figure 9 and Figure 10.

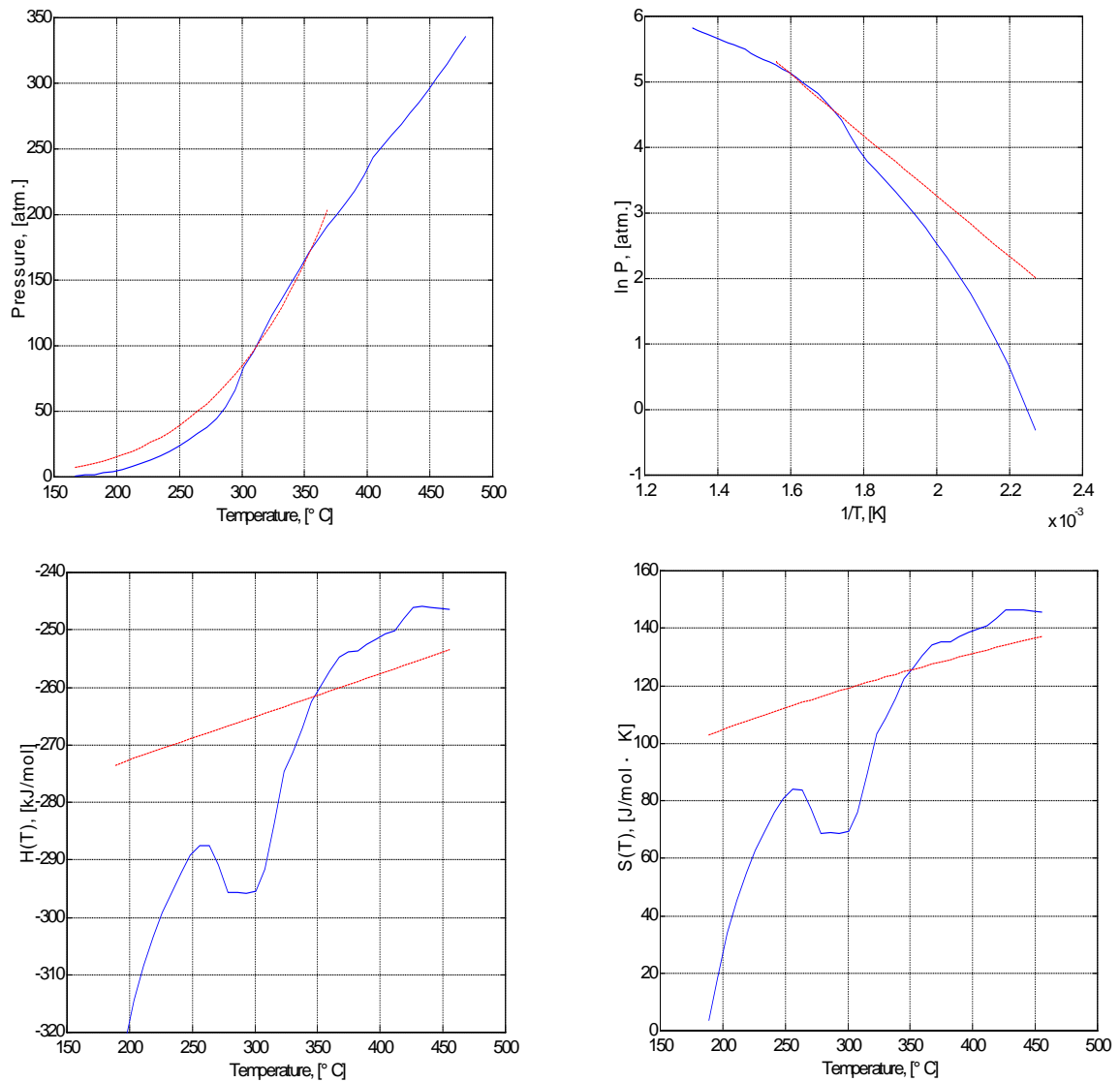


Figure 9 DPA-measurements on cement paste with a w/c-ratio of 0.30 based on Aalborg Portland White Cement and 25 weight-% silica fume heated to 105°C before experimental run. For comparison the red line is drawn up from theoretical data of pure water at the given temperatures [19].

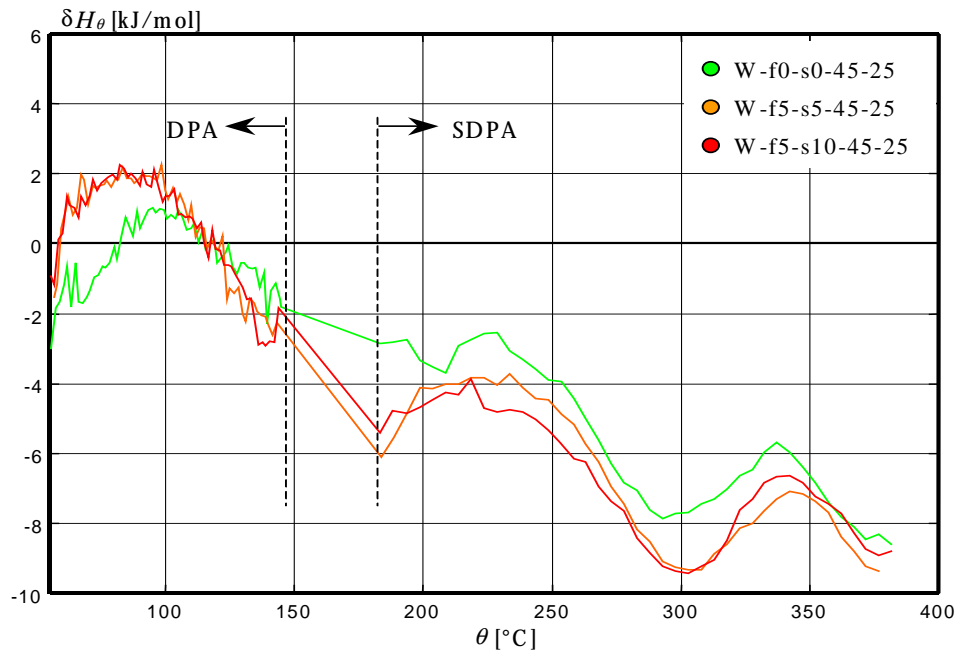


Figure 10 Experimental results from a parallel testing of three different cement pastes with a water/powder-ratio of 0.45 cured at 20.6°C for 25 days. The results are shown as the difference between the theoretical Enthalpy of pure water at the given temperature and the one calculated via DPA measurements above the cement pastes. Both a Low Temperature DPA-apparatus [6] and the High Temperature DPA developed during this project was used. W = White Aalborg Portland cement; f = percentage of Fly Ash; s = percentage of Silica Fume.

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Chapter III

ISOCHOR VOLUMETER - HYDRATEMETER

The Isochor¹ Volumeter (HYDRATEMETER) is a new instrument designed for accurate measurements of chemical shrinkage in hardening cement paste systems. The apparatus was originally invented by Professor *Per Freiesleben Hansen* and Research Professor *Ole Mejlhede Jensen* from Aalborg University, Denmark. The Isochor Volumeter is under patent pending². Since the instrument was originally designed for use in the area of cementitious materials it was given the acronym "HYDRATEMETER".

The development from an idea through different prototypes and finally into a fully working instrument was done as a part of this Ph.D.-project in collaboration with Ph.D.-student Peter Simmelsgaard from Aalborg University. The process of taking an idea up from a principal stage to a useable instrument turned out to be far more difficult and demanding than first expected; the apparatus was finished and tested shortly before the official ending of this Ph.D.-project.

In the following a short presentation of the principle behind the apparatus will be given, and a few results presented. Furthermore a method to determine the activation energy of hardening cement-based systems will be presented.

3.1 Background

Conventional concrete has typically a water/powder-ratio (w/p-ratio) of 0.40 - 0.60, whereas High Strength and High performance concretes, which are widely used in today's construction, has w/p-ratios as low as 0.20 - 0.30. To make the concrete flowable and durable, superplasticizer is used together with mikrosilica. This new

¹ Isochor: constant volume.

² More information about the patent pending can be given by contacting Research Professor Ole Mejlhede Jensen at Aalborg University, Department of Building Technology and Structural Engineering.

material concept results in concretes with extremely low permeability and consequently new demands towards better and more accurate measuring techniques.

Portland cement is mainly made up of four clinker minerals:

- 1) $3\text{CaO}\cdot\text{SiO}_2$
- 2) $2\text{CaO}\cdot\text{SiO}_2$
- 3) $2\text{CaO}\cdot\text{Al}_2\text{O}_3$
- 4) $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$

When reacting with water different hydrates are formed, which all influence on the properties of the final binder phase. All hydration reactions are characterised by reaction products that have a smaller volume than the reactants. The hydration of a Portland cement typically results in a volume reduction - a *Chemical Shrinkage* - of about 5 cm^3 per 100 g reacted cement.

Since the magnitude of the chemical shrinkage is dependent on the hydrates developed, a continuous measurement of the chemical shrinkage during hydration can provide vital information on the properties of a given cement based binder, including:

- Formation of hydrates and the character of hydrate formation.
- The influence of different process conditions on the hydration.

3.2 Principle of measurement of chemical shrinkage of a hydrating cement binder system

M. Geiker [1] measured the chemical shrinkage of cement paste using an experimental set-up as illustrated in Figure 11. The cement paste specimen is placed in a glass sample-holder closed by a rubber stopper through which centre a water filled capillary tube is connected. During the hydration process the cement paste suck up an amount of water equivalent to the chemical shrinkage. The development of chemical shrinkage at a given time can thus be followed by reading the height of the water column in the capillary tube $h(t)$, see Figure 11. This very simple principle has been widely used in investigations of the reaction kinetics of cement based systems [1] [7].

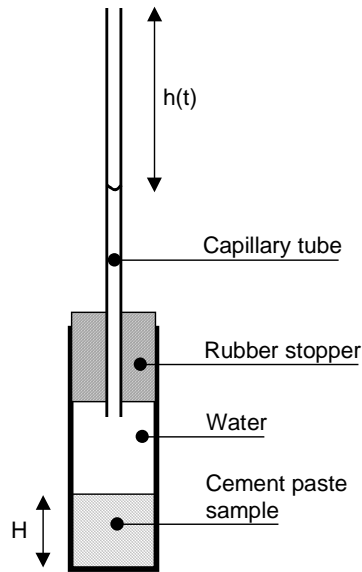


Figure 11 Measurement of chemical shrinkage. The cement paste specimen is placed in a glass sample-holder closed by a rubber stopper through which centre a water filled capillary tube is connected. When hydrating the chemical shrinkage of the cement paste can be followed by observation of the height of the water column at a given time, $h(t)$, in the capillary tube.

When investigating binder systems of new high strength and high quality concretes the measuring set-up as illustrated in Figure 11 is not ideal. The main problem is caused by a far denser binder phase than the one of conventional concrete; in new binder phases both mikrosilica and low w/p-ratios contribute to a dramatic lowering of the permeability. The low permeability blocks the suction of water at an early stage of hydration; further chemical shrinkage cause gas filled pores to be developed inside the hydrating binder phase. In Figure 12 the chemical shrinkage of respectively a "conventional" and a "new" binder phase are illustrated.

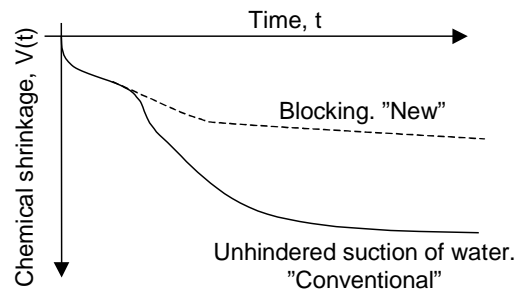


Figure 12 Illustration of how the chemical shrinkage is developing in different binder systems. In normal cement based systems, "conventional", an unhindered suction of water into the binder phase takes place. If the binder phase, at a given time, is becoming too dense, as in modern high strength and high quality concrete, "new", a blocking mechanism will set in leading to development of gas filled pores in the hardening cement paste.

This problem of measuring the chemical shrinkage of dense binder phases can be solved in one of the following ways:

1. Using a lower sample height H , see Figure 11. The drawback of lowering the sample height is a reduced sample volume, which again require a more accurate measurement of the volume change.
2. Raising the driving pressure difference, which in the experimental set-up as shown in Figure 11 is equal to the atmospheric pressure. Hereby the development of gas filled pores can be limited.

3.3 A new measuring technique

The *Isochor Volumeter*, the HYDRATEMETER, is based on a "control"-cell and a "sample"-cell, which are connected by a capillary tube, as illustrated in Figure 13. During an experimental run, the sample-cell is submerged into a thermostated bath, whereby the curing temperature can be controlled.

The control-cell is made by a copper cylinder. On the outer surface of the copper cylinder a heating wire is attached by epoxy glue making it possible to control the temperature of the control-cell accurately and independent of the sample-cell. A pressure transducer is fitted to the control-cell, facilitating pressure measurement in the system, see Figure 13.

During an experimental run the pressure of the system is kept constant by controlling the temperature of the control-cell. A volume reduction in the sample-cell,

caused by chemical shrinkage of for example hydrating cement paste, is thereby measured as a temperature rise in the control-cell; to keep a constant pressure the water in the control-cell has to be thermally expanded by raising the temperature. Registration of even very small volume changes in the sample-cell is thus converted into a simple temperature measurement.

The system is stiff and a temperature change of 1°C in the control-cell provides a pressure increase of 4-5 bar in the entire system. The continuous measurement/control of the volume-dose provides an accuracy of 0.001 - 0.01 mm³.

3.3.1 Experimental set-up

The HYDRATEMETER is illustrated in Figure 13 and Figure 14. A CR10X data logger is used for data-sampling and control of experimental run. Four HYDRATEMETER's has been constructed during the research period.

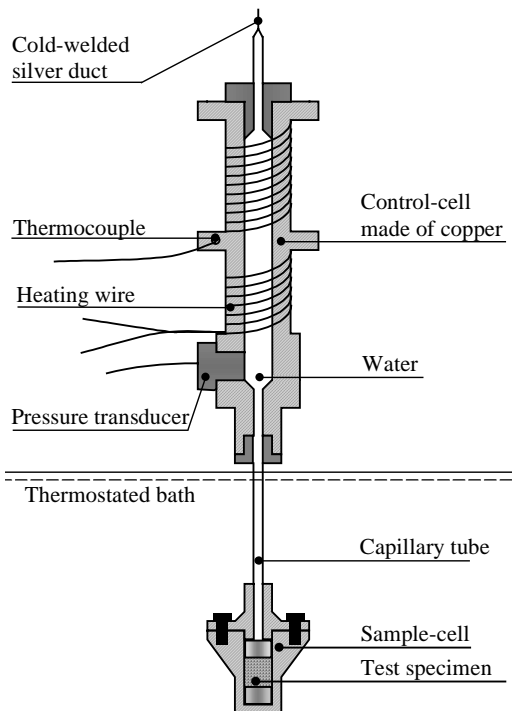


Figure 13 Illustration of the HYDRATEMETER. The apparatus consists of two cells connected by a capillary tube. The sample-cell is submerged into a thermostated bath. As the entire system is kept at a high and constant pressure (isobar), the chemical shrinkage of the cement paste sample is measured as a

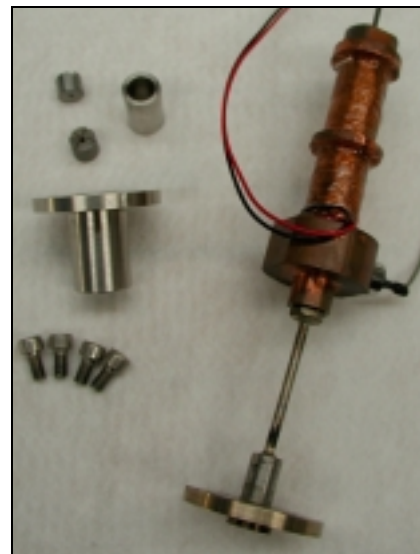


Figure 14 Control-cell, sample-cell and capillary tube. The control-cell is made by copper attached with heating wire and a pressure transducer. The sample-cell is shown separated; the volume is 3.5 ml but can be varied by insertion of different spacers as shown.

The shown system is constructed for measurements of chemical shrinkage at 10 bars system pressure. The control-cell has a volume of 3.5 ml and is made for measurements of chemical shrinkage in cement paste samples with weights of 0.5 - 2 g. The temperature of the control-cell is typically in the range of 25-65°C during an experiment.

When starting up an experiment, the entire system has to be totally empty of water. This is done by heating all parts in an oven at 105°C for 24 hours. Thereafter all parts are put together using special gaskets in all the critical joints (which most of the joints are!). The gaskets have to harden, where after the binder sample (in the form of un-reacted powder) is placed into a sample-holder that fit into the sample-cell. Sample-holders of different sizes make it possible to investigate binders at different w/p-ratios; the dry packing of the binder determines the w/p-ratio. The sample-cell is then closed using both a gasket and special screws. Now the HYDRATEMETER is ready for measuring the chemical shrinkage of the binder sample in the sample-cell, by the following procedure:

1. The sample-cell is submerged into a thermostated bath and the system is evacuated using a vacuum pump attached to the silver duct in the top of the system, see Figure 13. When vacuum is reached, as indicated on an attached vacuum-meter the system is closed off from the vacuum pump using a special valve.
2. Another valve controlling a reservoir of de-aired water is immediately turned open and de-aired water now momentarily fills up the entire system with water through the silver duct in the top of the instrument. Thus the sample binder is in contact with water and hydration is initiated.
3. When the system is totally filled with water, after a few seconds, a special nipper is used on the silver duct to seal of the system making a cold-welding, as illustrated in Figure 13.
4. With a totally air-free and stiff liquid system, the temperature of the control-cell is raised until the internal pressure off the entire system is about 10 bars. Hereafter the actual measurements begin.

The entire operation from adding water to the actual measurements begin takes about 20 seconds ensuring that it is possible to measure the hydration reactions from the very beginning.

3.3.2 Experimental results

In Figure 15 a curve from an experiment using the HYDRATEMETER is shown. The hydrating cement is a White Aalborg Portland cement with a w/p-ratio of 0.40 cured at a temperature of 25°C. The result is shown in [ml/100 gram cement].

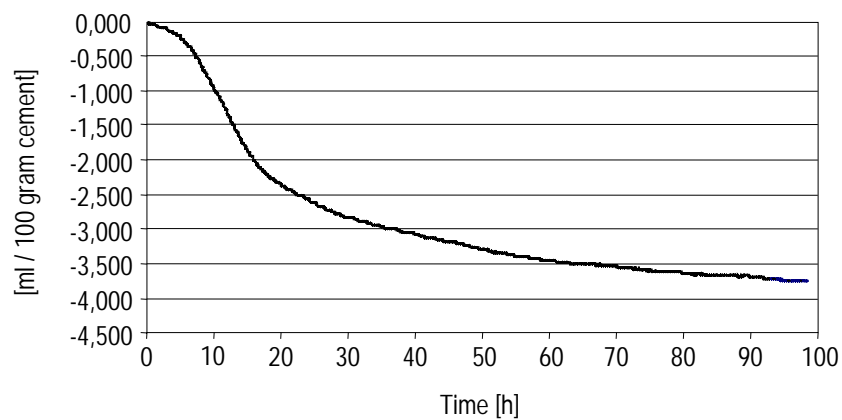


Figure 15 Chemical shrinkage of a white Aalborg Portland cement. The sample had a w/p-ratio of 0.40 and was cured at 25°C.

In Figure 16 the chemical shrinkage of a White Aalborg Portland cement is shown; in the "zoom" window the curve is scaled up to illustrate the resolution of the HYDRATEMETER. The resolution is about $25 \cdot 10^{-9}$ litre (25 nano-litre). The resolution can be compared to the process of 100 g hydrating cement, which has a total chemical shrinkage of about 5 ml or a factor of 200000. Normally an amount of 1 g can be fitted into the specimen chamber, and the resolution is thus about 1:2000.

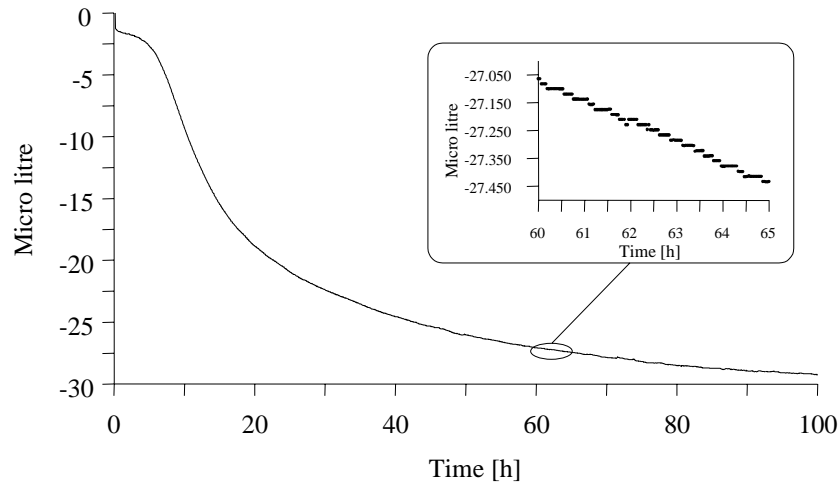


Figure 16 Illustration of the resolution of the measurements done by the HYDRAMETER.

3.4 A new technique for measuring activation energy

The HYDRAMETER can be used for *differential* determination of the *activation energy* of a cement-based system.

The activation energy is the basic parameter in what is called the *maturity concept*. The maturity concept has been introduced for indirect prediction of the properties of cement paste (strength, degree of hydration or heat of hydration) when the curing conditions are taking place at different temperatures, compared to a reference temperature [7].

3.4.1 The maturity concept

The maturity concept is based on the assumption that the rate of hydration $d\alpha/dt$ for a given degree of hydration α approximately can be described as a function $f(T)$ of the temperature T [2] [8]; this is formulated in the following differential equation [4]:

$$\frac{d\alpha}{dt} = g(\alpha) \cdot f(T) \quad (3.1)$$

where

t is the time

Equation 3.1 states, that a change in the hydration rate due to a temperature change is independent of the degree of reaction. Identical concretes, cured to the same maturity, have equal degree of hydration, despite which combination of temperature and time lead to the actual maturity [4]. After separation and integration:

$$G(x) = \int_0^{\alpha} \frac{d\alpha}{g(\alpha)} = \int_0^{\tau} f(T(t))dt \quad (3.2)$$

If the hydration process is to be compared to an isotherm hydration process at the same degree of hydration, $G(\alpha)$ is the same for both processes, and:

$$\int_0^{\tau} f(T(t))dt = \int_0^{\tau_0} f(T_0)dt = f(T_0) \cdot \tau_0 \quad (3.3)$$

By Equation 3.3 the maturity of the temperature-varying system can thus be determined as:

$$M_0 \equiv \tau_0 = \int_0^{\tau} \frac{f(T(t))}{f(T_0)} \quad (3.4)$$

The temperature function $f(T)$ has to be determined accurately. Different temperature functions have been proposed from the suitability of the function to describe the relationship between an experimentally measured property and the maturity calculated by Equation 3.4. The most used maturity concept in Denmark for the last 20 years is the *Freiesleben Hansen* maturity model [3], which describes the maturity M_{20} at the reference temperature 20°C as:

$$M_{20} = \int_0^{\tau} H(\theta) dt \quad (3.5)$$

where

$$H(\theta) = \frac{\text{hydration rate at } \theta^{\circ}\text{C}}{\text{hydration rate at } 20^{\circ}} \cong \exp\left[\frac{E_a}{T} \left(\frac{1}{293} - \frac{1}{273 + \theta}\right)\right] \quad (3.6)$$

E_a is a characteristic activation energy:

$$= \begin{cases} 33500 \text{ J/mol } \theta \geq 20^{\circ}\text{C} \\ 33500 + 1470(20 - \theta) \text{ J/mol } \theta < 20^{\circ}\text{C} \end{cases}$$

Using Equation 3.5 the maturity equivalent to a reference temperature of 20°C of a concrete cured under a given temperature history can be calculated. It follows

that a correct determination of E_a for the system is vital for using the maturity concept. The above given activation energies is based on measurements on conventional cement paste binders. It is believed that the HYDRATEMETER can be used to measure the activation energy accurately for new types of cement binders.

3.4.2 Differential determination of the activation energy

The activation energy E_a describes the temperature effect on the rate process of a hydrating cement system. Generally the temperature effect on a rate process can be described by the Arrhenius temperature function, which describe the rate of reaction k with temperature [6]:

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \quad (3.7)$$

Using equation 3.7 the rate of reaction k_2 at a temperature T_2 compared to the rate of reaction rate k_1 at a temperature T_1 is:

$$\frac{k_1}{k_2} = \frac{A \cdot \exp\left(\frac{E_a}{RT_1}\right)}{A \cdot \exp\left(\frac{E_a}{RT_2}\right)} = \exp\left(\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \quad (3.8)$$

If the rate constants are known the activation energy can thus be calculated:

$$E_a = R \cdot \frac{\ln\left(\frac{k_1}{k_2}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (3.9)$$

By following a special experimental procedure the HYDRATEMETER can be used for determination of E_a in new dense cement binders. Knowing that k is dependent on the reaction temperature the activation energy can be continuously monitored by alternating the curing temperature $\pm 1-2^\circ\text{C}$ around the reference curing temperature examined (for example 20°C as in Freiesleben Hansens maturity model); the curing temperature is controlled by the thermostated bath, see Figure 13. Thereby k equals the derivative of the *time - chemical shrinkage* curve. k is determined left and right of the point on the time axis where the temperature has changed. The principle is illustrated in Figure 17.

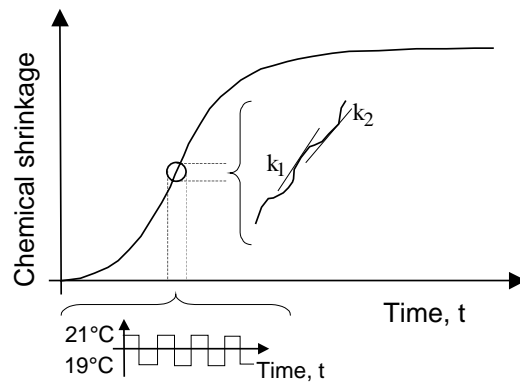


Figure 17 Illustration of the principle of differential determination of the thermal activation energy. When alternating the temperature of the thermostated bath $\pm 1-2^{\circ}\text{C}$ around a given temperature, the rate of reaction k can be determined at two temperatures very close to the one examined. Hereby the activation energy can be calculated.

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