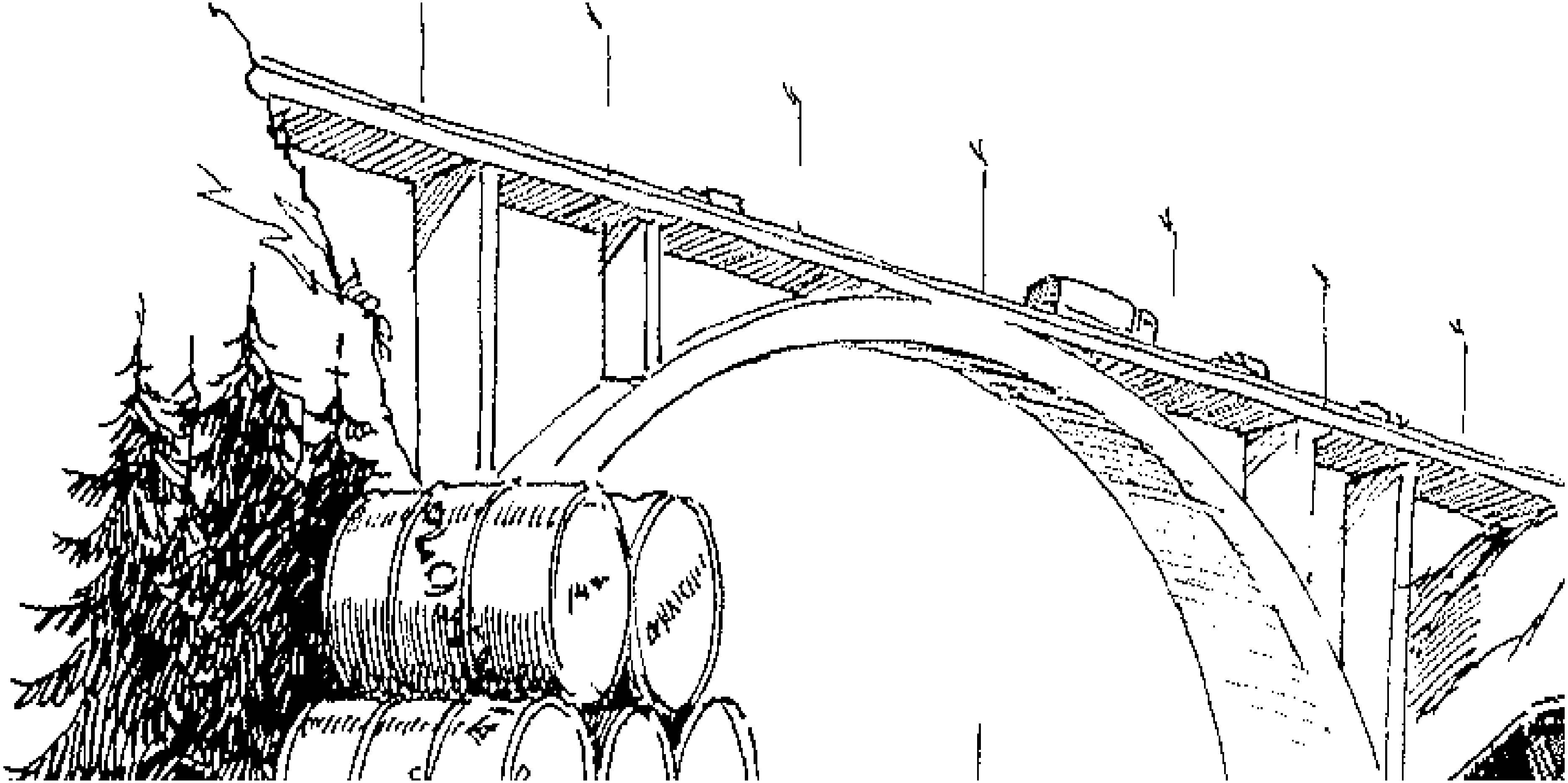
Moderní metody termické analýzy pro cementové směsi a životní prostředí

Jaroslav Kolejka

TA Instruments

- Isothermal Calorimetry
- Simultaneous Thermal Analysis
- High Pressure Sorption Analysis



Calorimetry – universal technique

- Virtually all chemical and physical processes result in either heat production or heat consumption.
- Heat production or consumption of a sample can be directly measured by calorimetry
- Calorimetry is a non-specific technique making it ideal for studying almost all kind of biological, physical and chemical processes.

Microcalorimetry

A heat flow calorimeter measures heat flow

$$dQ/dt$$

Heat flow is directly related to the heat production (or consumption) rate in a sample

$$P$$

P and *dQ/dt* is measured in

$$W = J/s$$

A microcalorimeter is a calorimeter that can measure heat production in the µW range

Heat production (or consumption)

$$P = \Delta H \cdot k \cdot f(c)$$

Heat production (or consumption)

$$P = \Delta H \cdot k \cdot f(c)$$

Enthalpy
→
Thermodynamic information

Heat production (or consumption)

$$P = \Delta H \cdot k \cdot f(c)$$

Enthalpy
→
Thermodynamic information

Reaction rate
→
Kinetic information

Heat production (or consumption)

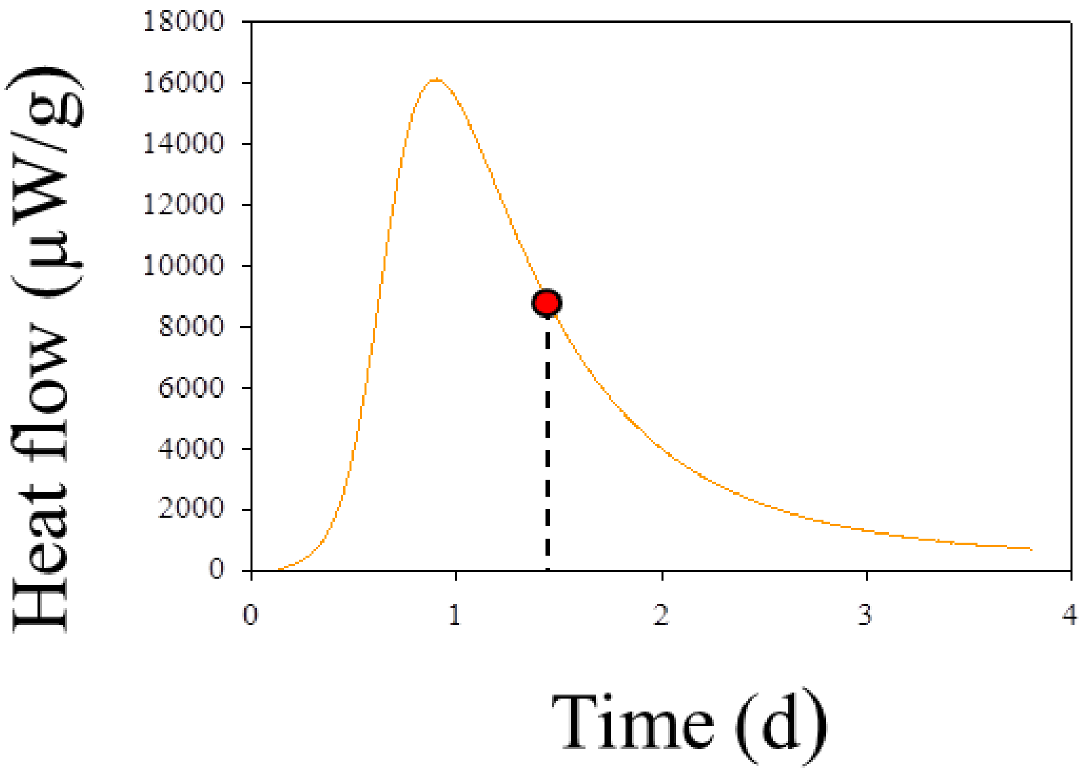
$$P = \Delta H \cdot k \cdot f(c)$$

Enthalpy
→
Thermodynamic information

Reaction rate
→
Kinetic information

Concentration
→
Analytical information

Heat flow of reaction



The heat flow is directly related to the rate of the process/reaction.

The measured heat flow is the sum of all ongoing processes

TAM Air isothermal multichannel calorimeter

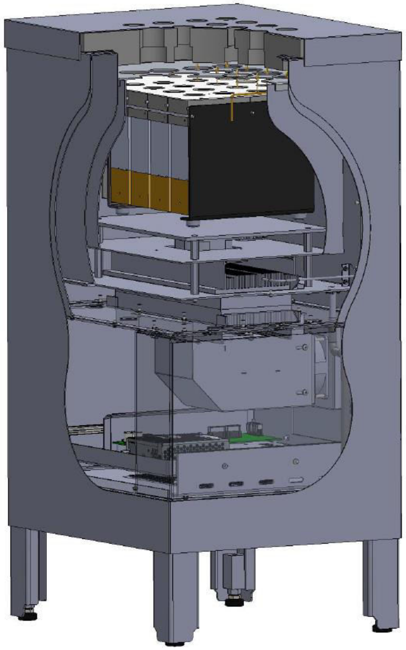
TAM Air consists of a thermostat and a calorimeter

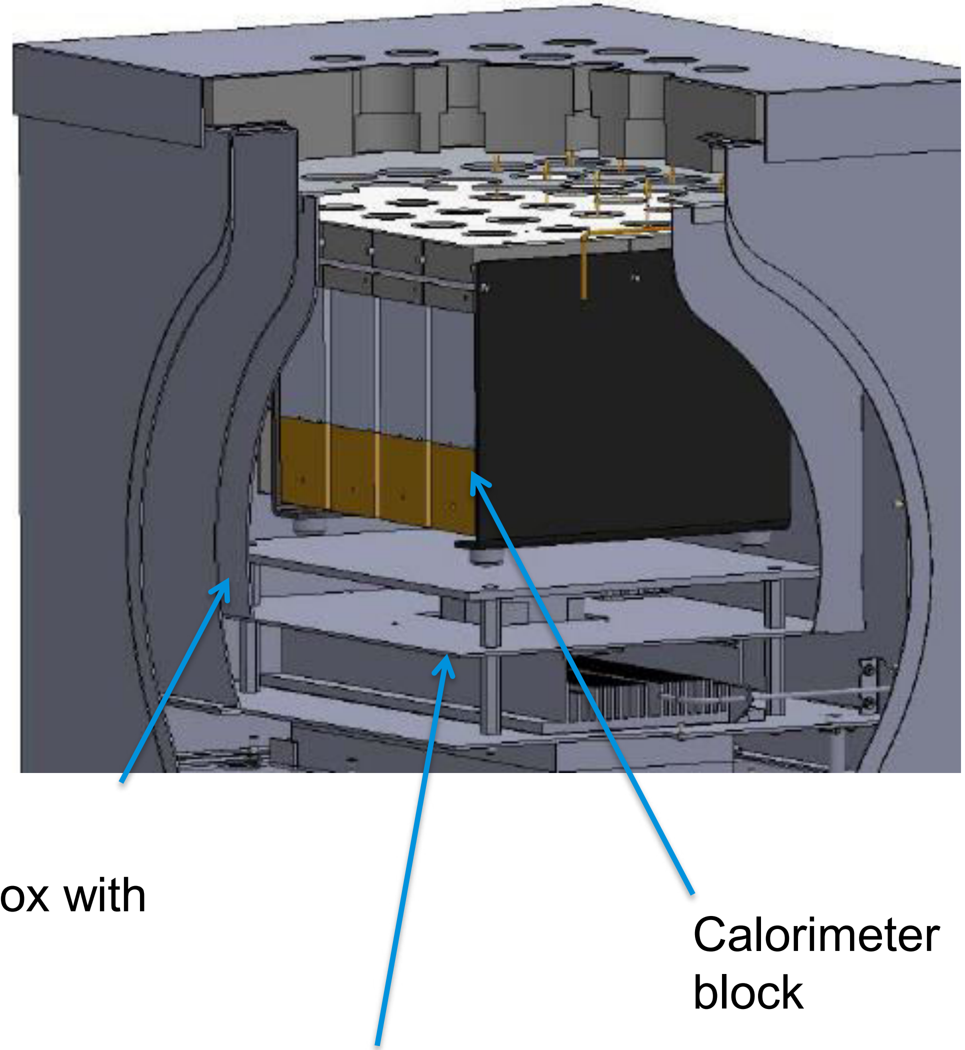
- The air based thermostat precisely controls the calorimeter temperature and effectively minimize outside temperature disturbances.

- The calorimeters are held together in a single removable block, with either 8 or 3 individual calorimeters

- Each calorimeter is a twin heat flow calorimeter, consisting of a sample and a reference side

The thermostat





Thermostat box with circulating air

Calorimeter block

Temperature control

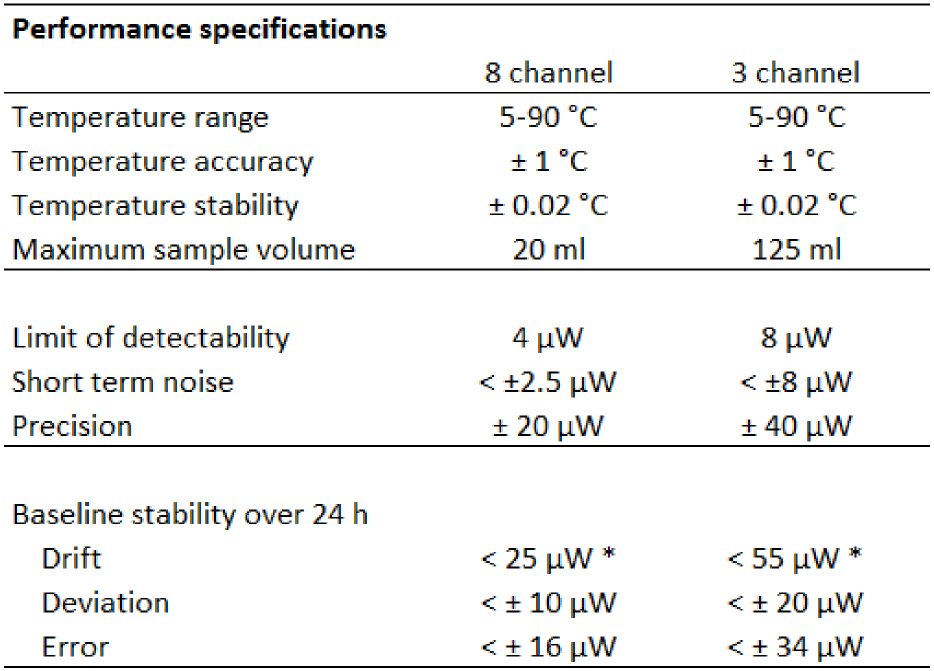
Sample handling

- Static ampoules available in glass, HDPE plastic and stainless steel
- Admix ampoule is available in 20 mL size with and without motor for stirring


Admix Ampoule with manual stirring


Admix Ampoule with stirring motor

TAM Air configurations and specifications



Performance specifications	8 channel	3 channel
Temperature range	5-90 °C	5-90 °C
Temperature accuracy	± 1 °C	± 1 °C
Temperature stability	± 0.02 °C	± 0.02 °C
Maximum sample volume	20 ml	125 ml
Limit of detectability	4 μW	8 μW
Short term noise	< ±2.5 μW	< ±8 μW
Precision	± 20 μW	± 40 μW
Baseline stability over 24 h		
Drift	< 25 μW *	< 55 μW *
Deviation	< ± 10 μW	< ± 20 μW
Error	< ± 16 μW	< ± 34 μW

* Baseline drift specification is based on a 24-hour room temperature cycle and can be extended to be valid for multiple days and up to several weeks

TAM Air 8 Channel
Standard Volume Calorimeter
8 twin type calorimeters, 20mL

TAM Air 3 Channel
Large Volume Calorimeter
3 twin type calorimeters, 125 mL

TAM – Thermal Activity Monitor

5 – 90 °C

Flexible

interchangeable calorimeter blocks depending on sample

Sample sizes

from 20 mL up to 125 mL

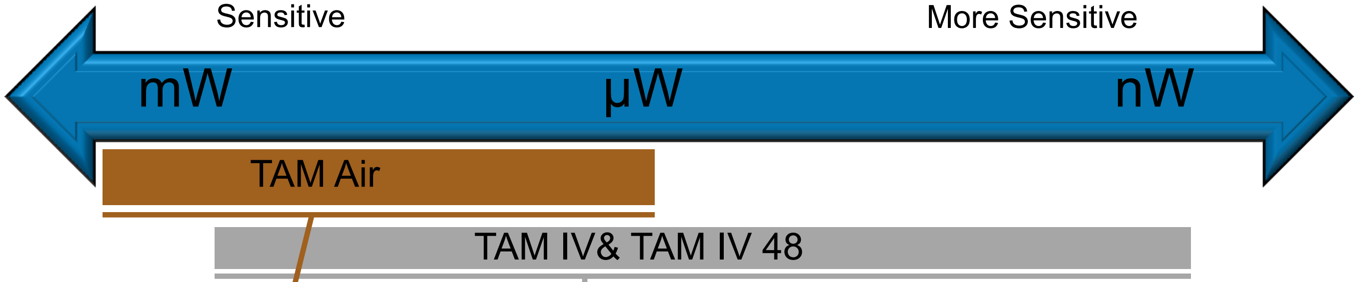
3 channel version

Large samples up to 125 mL

8 channel version

- Samples up to 20 mL
- Possibility to add and mix *in situ*

TAM – Thermal Activity Monitor



Sensitive

More Sensitive

mW

µW

nW

TAM Air

TAM IV& TAM IV 48

5 – 90 °C

Flexible

interchangeable calorimeter blocks depending on sample

Sample sizes

from 20 mL up to 125 mL

3 channel version

Large samples up to 125 mL

8 channel version

- Samples up to 20 mL
- Possibility to add and mix *in situ*

4 – 150 °C

Flexible

one system multiple possibilities

Modular

add functionality by choice of calorimeters, sample handling systems and accessories

Sample sizes

from less than 1 mL up to 125 mL

4 channel version

highest flexibility and sensitivity

48 channel version

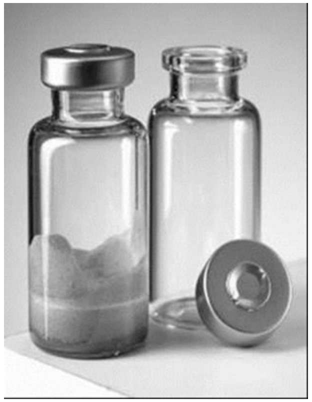
highest throughput

Applications

ISOTHERMAL CALORIMETRY

TAM Air is a powerful tool for the study of cement and concrete hydration processes

Isothermal calorimetry is an excellent tool to measure the total heat of hydration as well as to continuously follow the reaction rates in the different phases of the complex cement hydration process.

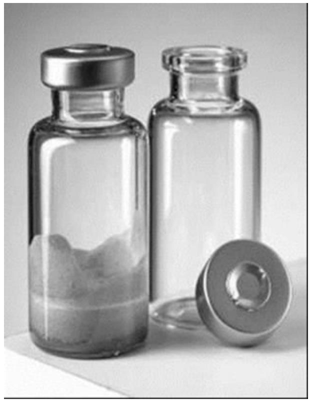


TAM Air is a powerful tool for the study of cement and concrete hydration processes

Isothermal calorimetry is an excellent tool to measure the total heat of hydration as well as to continuously follow the reaction rates in the different phases of the complex cement hydration process.

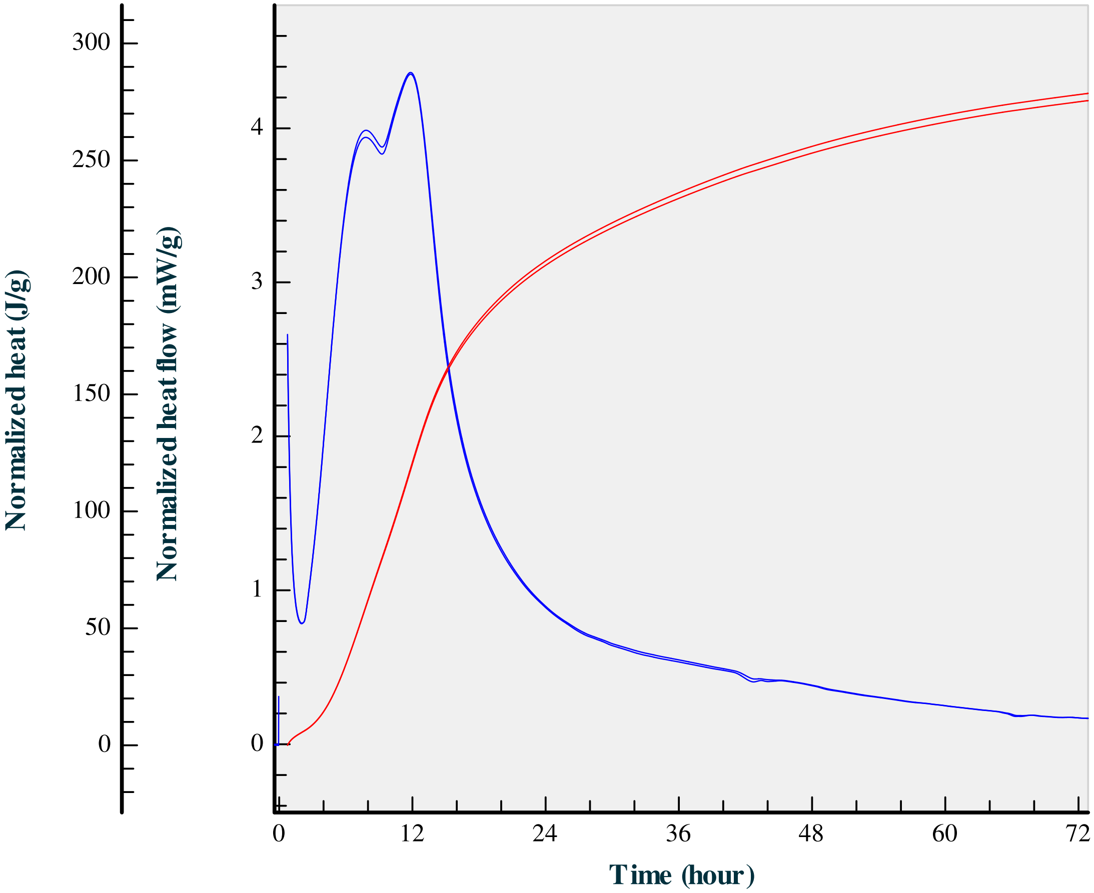
The heat flow profile from a hydrating cement or concrete sample is information-rich and can be used for:

- The development of new cements and admixtures
- Dosing and formulation optimization
- The impact of temperature on the hydration process
- The detection of any incompatibility of materials
- Production and quality control

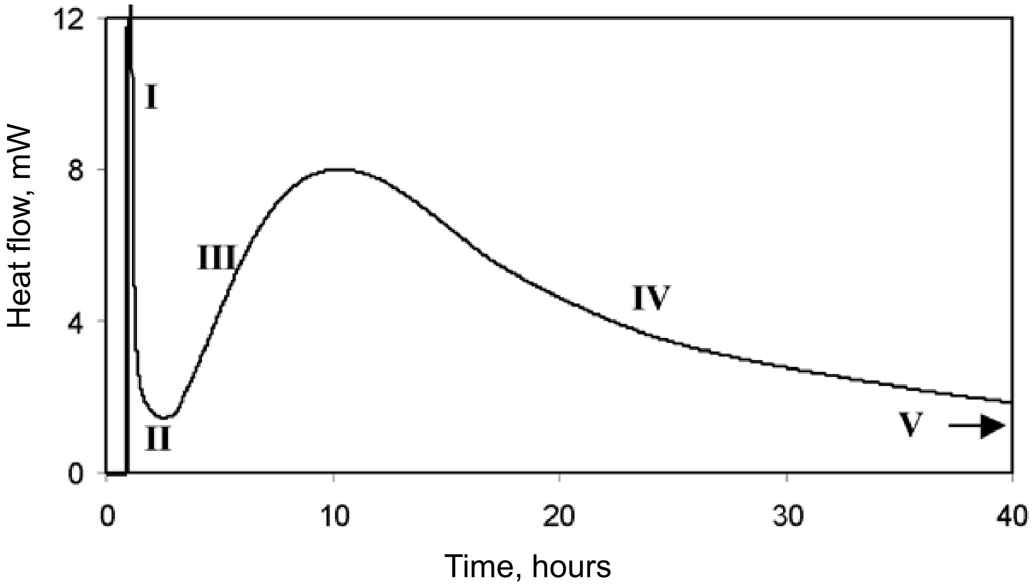


The heat flow signal

- The shape of the heat flow versus time curve reflects the hydration process of cement
- The effect of an admixture is reflected in a change of the hydration curve
- The integrated heat flow time curve, i.e. the energy evolved is related to the extent of hydration



The cement hydration process



I. Rapid initial process – Dissolution of ions and initial hydration
II. Dormant period – Associated with a low heat evolution and slow dissolution of silicates
III. Acceleration period – Silicate hydration
IV. Retardation period – Sulphate depletion and slowing down of the silicate hydration process
V. Long term reactions

ASTM C1702

Standard Test Method for

Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry

7 days heat of hydration
with or without internal mixing

Gives equivalent test results to method C186

Designation: C1702 – 15b

Standard Test Method for
Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry[1]

This standard is issued under the fixed designation C1702; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method specifies the apparatus and procedure for determining total heat of hydration of hydraulic cementitious materials at test ages up to 7 days by isothermal conduction calorimetry.

1.2 This test method also outputs data on rate of heat of hydration versus time that is useful for other analytical purposes, as covered in Practice C1679.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C186 Test Method for Heat of Hydration of Hydraulic Cement

C1679 Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *baseline, n*—the time-series signal from the calorimeter when measuring output from a sample of approximately the same mass and thermal properties as a cement sample, but which is not generating or consuming heat.

3.1.2 *heat, n*—the time integral of thermal power measured in joules (J).

3.1.3 *isothermal conduction calorimeter, n*—a calorimeter that measures heat flow from a sample maintained at a constant temperature by intimate thermal contact with a constant temperature heat sink.

3.1.4 *reference cell, n*—a heat-flow measuring cell that is dedicated to measuring power from a sample that is generating no heat.

3.1.4.1 *Discussion*—The purpose of the reference cell is to correct for baseline drift and other systematic errors that can occur in heat-flow measuring equipment.

3.1.5 *sensitivity, n*—the minimum change in thermal power reliably detectable by an isothermal calorimeter.

3.1.5.1 *Discussion*—For this application, sensitivity is taken as ten times the random noise (standard deviation) in the baseline signal.

3.1.6 *thermal mass, n*—the amount of thermal energy that can be stored by a material (J/K).

3.1.6.1 *Discussion*—The thermal mass of a given material is calculated by multiplying the mass by the specific heat capacity of the material. For the purpose of calculating the thermal mass used in this standard, the following specific heat capacities can be used: The specific heat capacity of a typical unhydrated portland cement and water is 0.75 and 4.18 J/(g·K), respectively. Thus a mixture of A g of cement and B g of water has a thermal mass of $(0.75 \times A + 4.18 \times B)$ J/K. The specific heat capacity of typical quartz and limestone is 0.75 and 0.84 J/(g·K), respectively. The specific heat capacity of most amorphous supplementary cementitious material, such as fly ash or slag, is approximately 0.8 J/(g·K).

3.1.7 *thermal power, n*—the heat production rate measured in joules per second (J/s).

3.1.7.1 *Discussion*—This is the property measured by the calorimeter. The thermal power unit of measure is J/s, which is equivalent to the watt. The watt is also a common unit of measure used to represent thermal power.

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[1] This test method is under the jurisdiction of ASTM Committee C01 on Cement and is the direct responsibility of Subcommittee C01.26 on Heat of Hydration.

Current edition approved Dec. 1, 2015. Published January 2016. Originally approved in 2009. Last previous edition approved in 2015 as C1702 – 15a. DOI: 10.1520/C1702-15B.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

ASTM C1702

Comments on sample size and sensitivity:

- The method states the sample temperature to be within 1 °C of the thermostat temperature.

- A larger sample (method recommend 3-15 g of cement) may not comply with C1702 as heat produced may warm the sample up and hence the measurement cannot be considered isothermal and kinetics can be affected.

- However, sample need to be large enough to generate a reliable signal after 7 days.

ASTM C1702

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- However, sample need to be large enough to generate a reliable signal after 7 days.

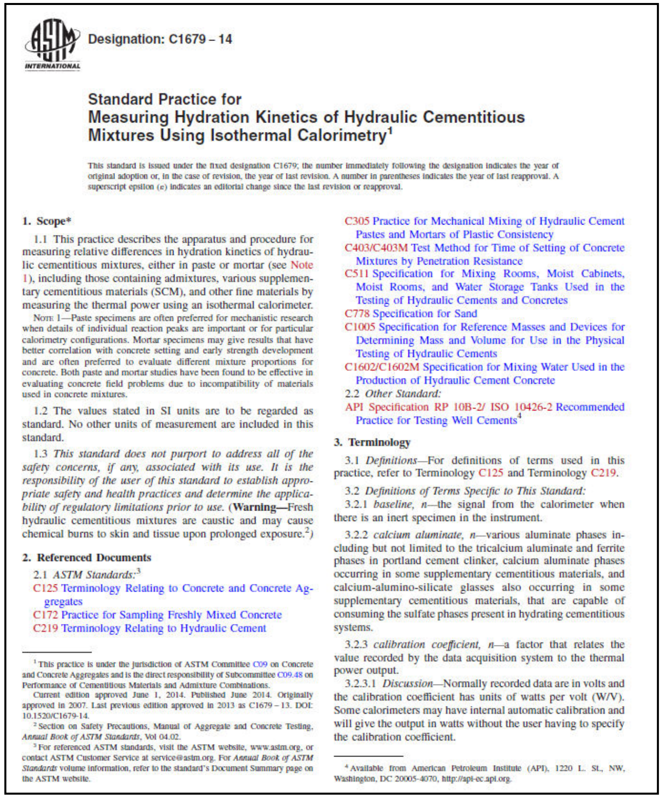
The benefits of TAM Air

- Sensitivity, even smaller samples will give a reliable signal after 7 days
- Choice of two sample volumes
  - 8 channel standard volume for cement/mortar hydration measurements using smaller samples
  - 3 channel large volume for mortar/concrete hydration measurements using larger samples

ASTM C1679

Standard Practice for
Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry

- Measures relative differences in hydration kinetics of cement paste or mortar
- Graphically and mathematically evaluated for retardation and acceleration effects
- Calcium sulphate may be added as a probe



Designation: C1679 – 14

Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry[1]

This standard is issued under the fixed designation C1679; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice describes the apparatus and procedure for measuring relative differences in hydration kinetics of hydraulic cementitious mixtures, either in paste or mortar (see Note 1), including those containing admixtures, various supplementary cementitious materials (SCM), and other fine materials by measuring the thermal power using an isothermal calorimeter.

NOTE 1—Paste specimens are often preferred for mechanistic research when details of individual reaction peaks are important or for particular calorimetry configurations. Mortar specimens may give results that have better correlation with concrete setting and early strength development and are often preferred to evaluate different mixture proportions for concrete. Both paste and mortar studies have been found to be effective in evaluating concrete field problems due to incompatibility of materials used in concrete mixtures.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (**Warning—**Fresh hydraulic cementitious mixtures are caustic and may cause chemical burns to skin and tissue upon prolonged exposure.[2])

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C125 Terminology Relating to Concrete and Concrete Aggregates
C172 Practice for Sampling Freshly Mixed Concrete
C219 Terminology Relating to Hydraulic Cement
C305 Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency
C403/C403M Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance
C511 Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes
C778 Specification for Sand
C1005 Specification for Reference Masses and Devices for Determining Mass and Volume for Use in the Physical Testing of Hydraulic Cements
C1602/C1602M Specification for Mixing Water Used in the Production of Hydraulic Cement Concrete

2.2 *Other Standard:*

API Specification RP 10B-2/ ISO 10426-2 Recommended Practice for Testing Well Cements[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology C125 and Terminology C219.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *baseline, n*—the signal from the calorimeter when there is an inert specimen in the instrument.

3.2.2 *calcium aluminate, n*—various aluminate phases including but not limited to the tricalcium aluminate and ferrite phases in portland cement clinker, calcium aluminate phases occurring in some supplementary cementitious materials, and calcium-alumino-silicate glasses also occurring in some supplementary cementitious materials, that are capable of consuming the sulfate phases present in hydrating cementitious systems.

3.2.3 *calibration coefficient, n*—a factor that relates the value recorded by the data acquisition system to the thermal power output.

3.2.3.1 *Discussion*—Normally recorded data are in volts and the calibration coefficient has units of watts per volt (W/V). Some calorimeters may have internal automatic calibration and will give the output in watts without the user having to specify the calibration coefficient.

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[1] This practice is under the jurisdiction of ASTM Committee C09 on Concrete and Concrete Aggregates and is the direct responsibility of Subcommittee C09.48 on Performance of Cementitious Materials and Admixture Combinations.

Current edition approved June 1, 2014. Published June 2014. Originally approved in 2007. Last previous edition approved in 2013 as C1679 – 13. DOI: 10.1520/C1679-14.

[2] Section on Safety Precautions, Manual of Aggregate and Concrete Testing, *Annual Book of ASTM Standards*, Vol 04.02.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, http://api-ec.api.org.

ASTM C1679

Standard Practice for

Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry

- Provides indications relative to setting characteristics, material compatibility, sulfate balance and early strength development
- Can be used to evaluate effects of composition, proportions and time of addition as well as curing temperature
- Can be used to measure admixture effects

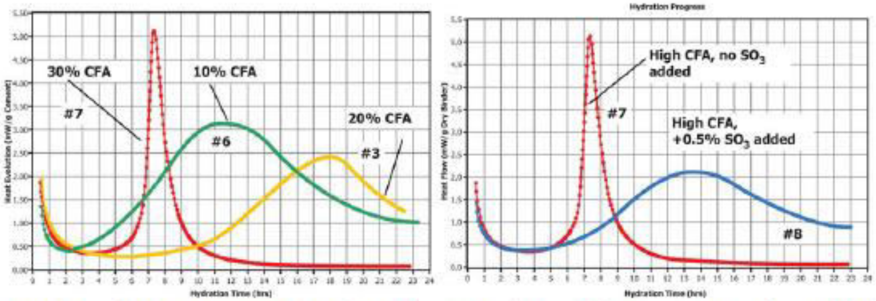


FIG. X6.1 (a) Effect of Fly Ash Dosage on Hydration Kinetics; (b) Effect of SO_3 Addition (as Calcium Sulfate Hemihydrate)

From appendix in ASTM C1679

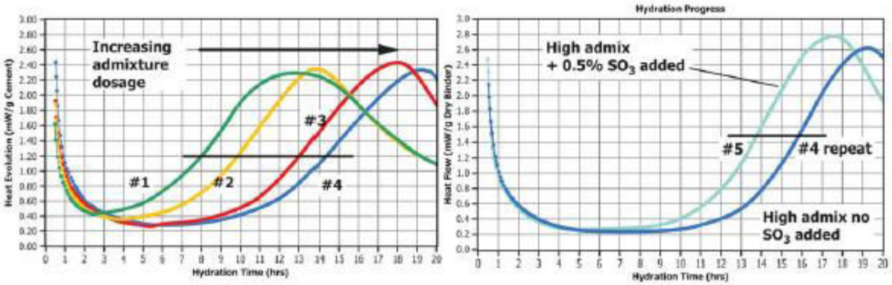
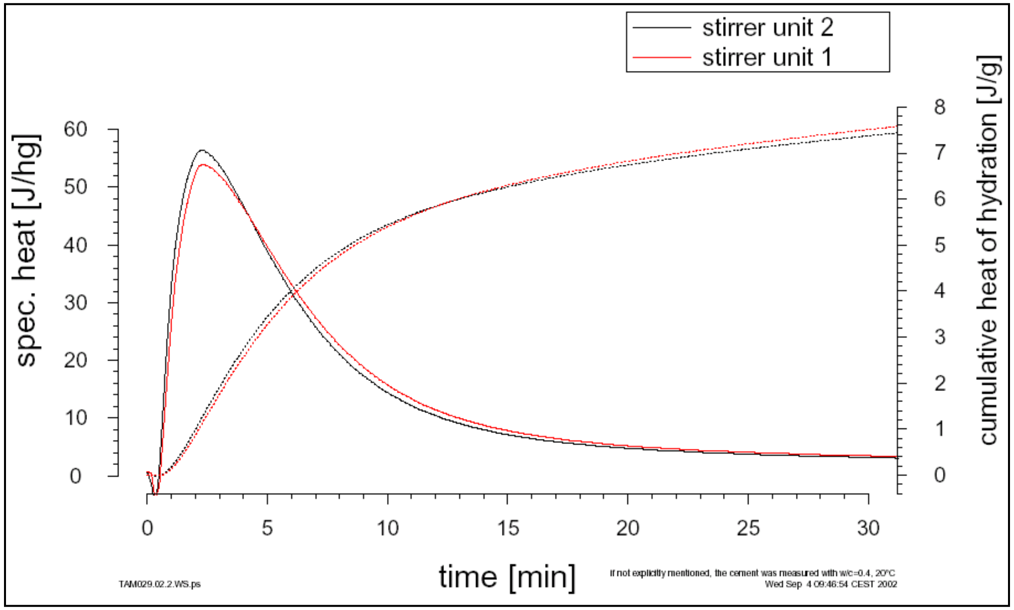


FIG. X5.1 (a) Effect of Admixture Dosage on the Thermal Indicator of Setting Time for This Given Set of Materials; (b) Effect of SO_3 Addition (as Calcium Sulfate Hemihydrate) for This Given Set of Materials

From appendix in ASTM C1679

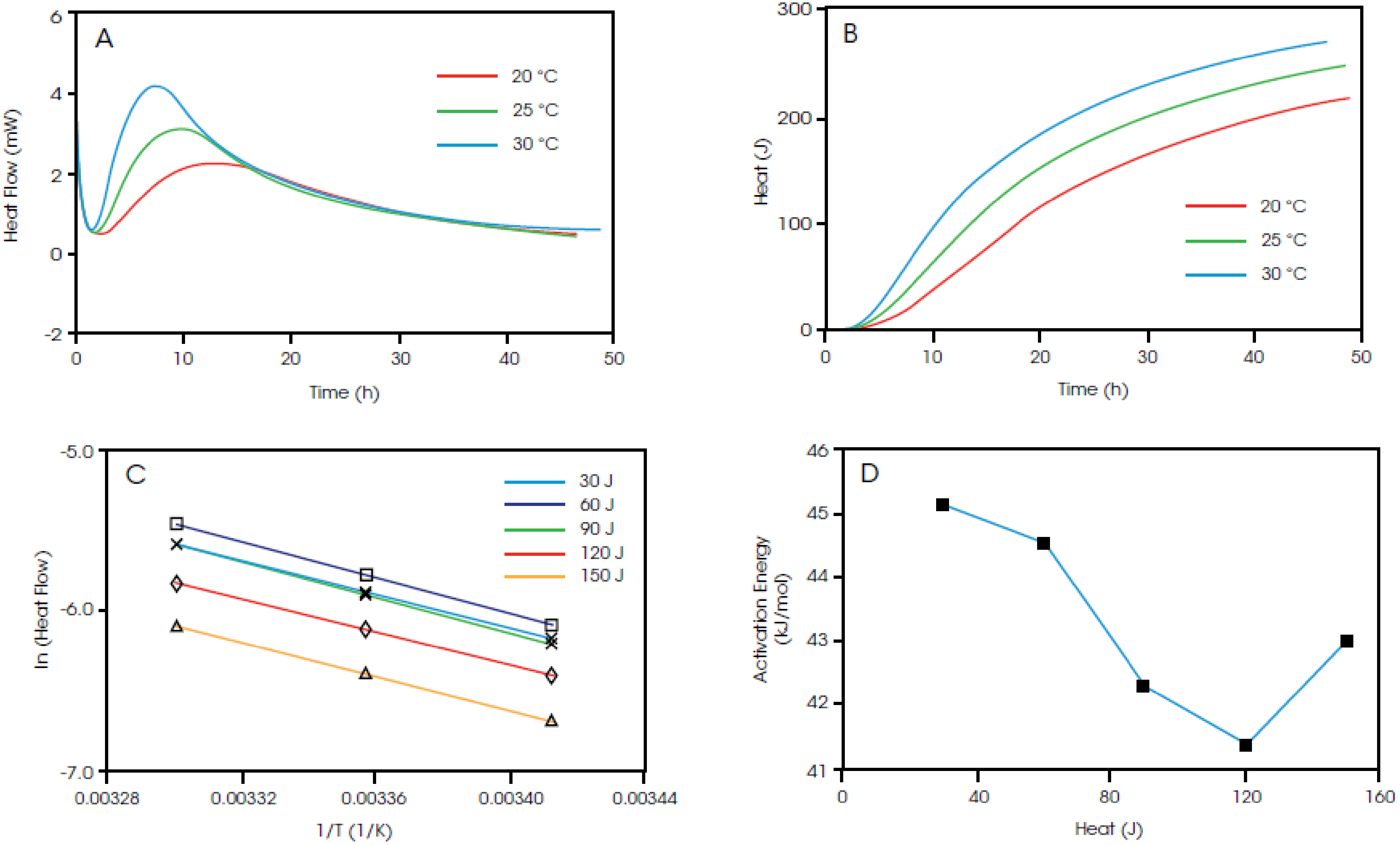
Early hydration using the admix ampoule



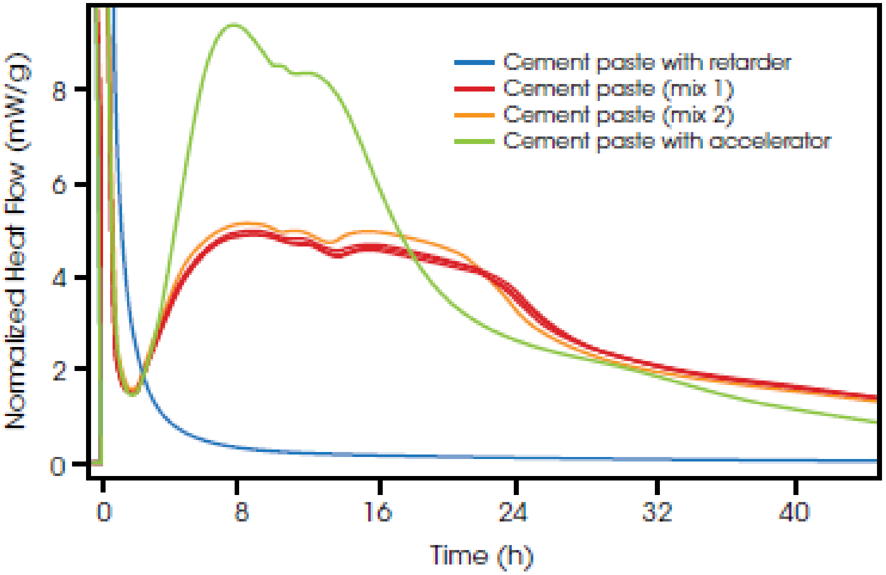
Dr. Moro, Holcim Group Support, Switzerland (2002)

The admix ampoule is used to initiate a reaction inside the calorimeter by injecting the water and/or admixture into the cement in the calorimeter to study the early hydration reaction

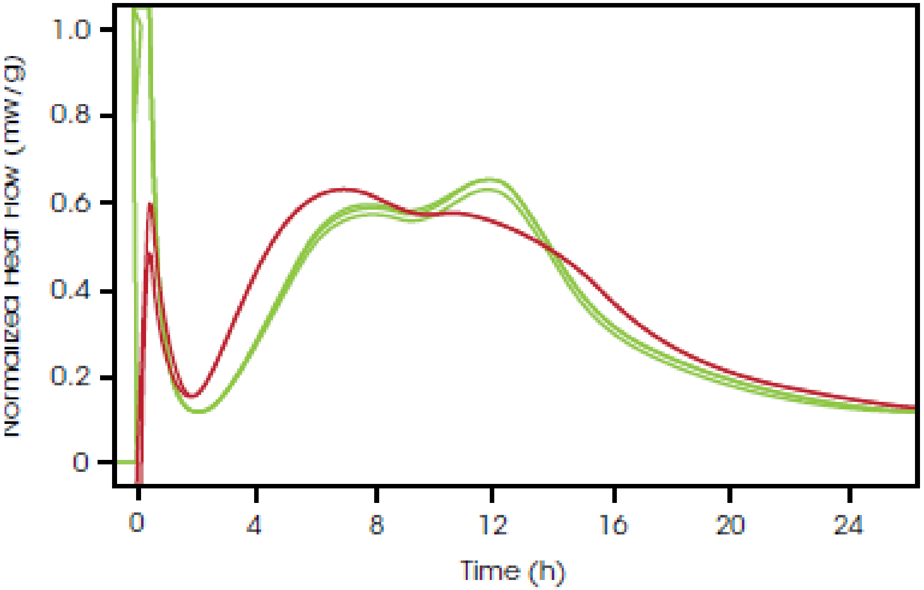
Temperature-dependent processes



Examples of hydration profiles



Cement sample with and without admixtures



Example of a concrete sample and the effect of adding a superplasticizer

TAM Air features and benefits for the measurement of the hydration process

- Choice of two volumes, 20 and 125 mL, to allow measurements of either cement or concrete with optimal performance

- Availability of the admix ampoule for the study of the initial reaction directly when water is added to the cement

- High sensitivity and baseline stability makes it possible to follow the hydration process for weeks

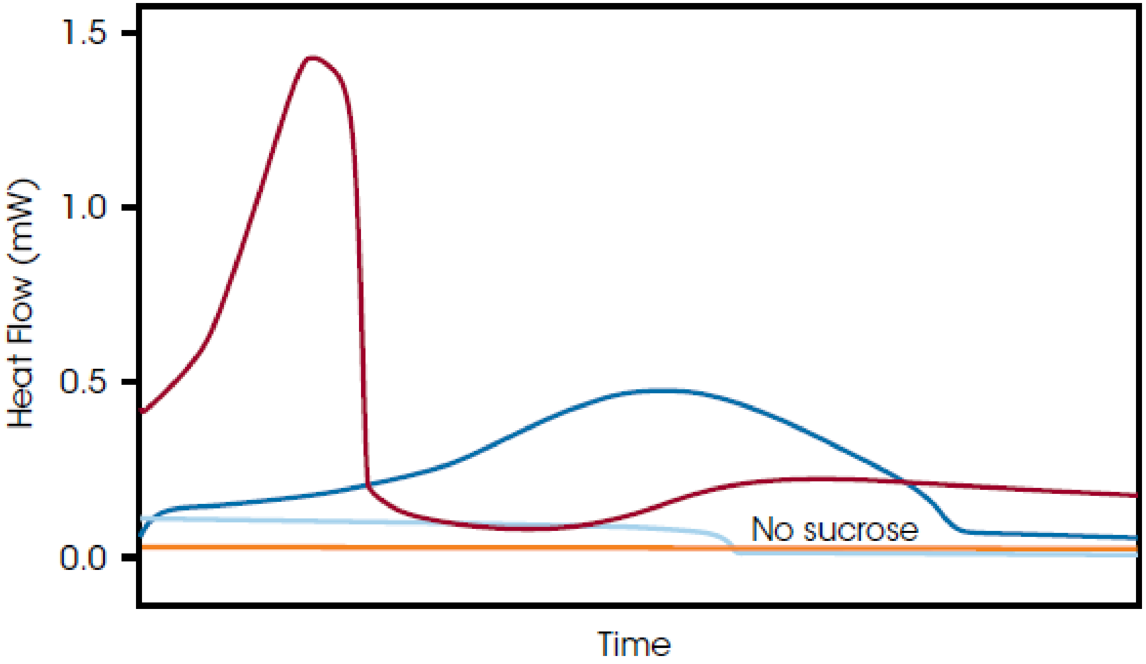
- Multi-sample capacity for simultaneous analysis

- Conforms to the standards ASTM C1702 and C1679

Biological activity in soil

An example of soils from two different locations, with and without sugar amendment.

Sugar amendment of soils are common to study how the microorganisms can utilize the substrate for metabolism and growth



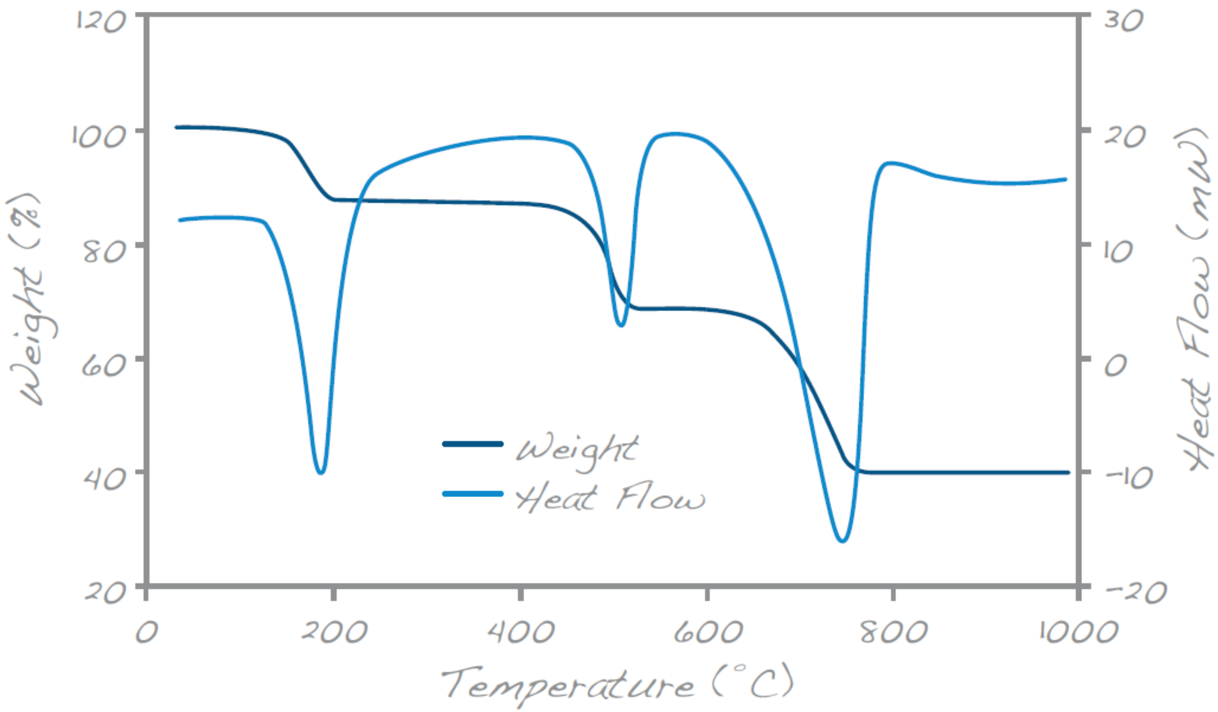
Simultaneous Analysis - Discovery SDT 650

Discovery
SDT 650

- 1500°C
- DSC/ DTA
- Simultaneous TGA

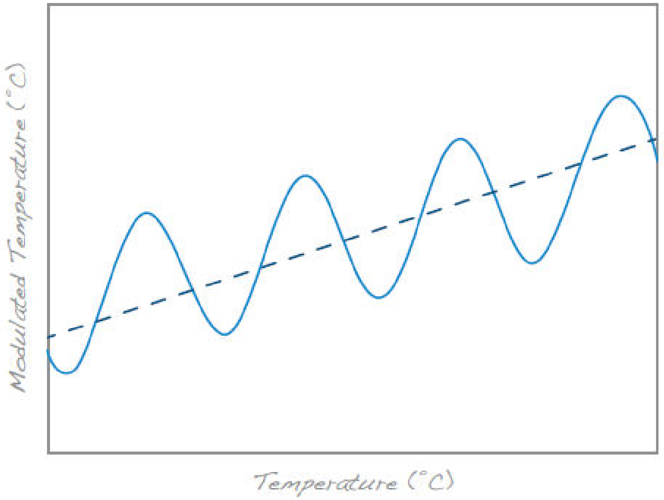
Simultaneous DSC-TGA (SDT)

Simultaneous application of *Differential Scanning Calorimetry (DSC)* and *Thermogravimetry (TGA)* of a material will measure both *heat flow* and *weight change* as a function of time, temperature and atmosphere in a single experiment.



Advanced Mode: MDSC® and MTGA™

Modulated Techniques
MDSC® & MTGA™



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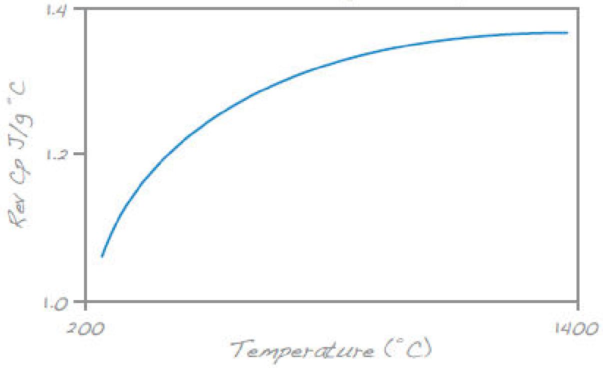
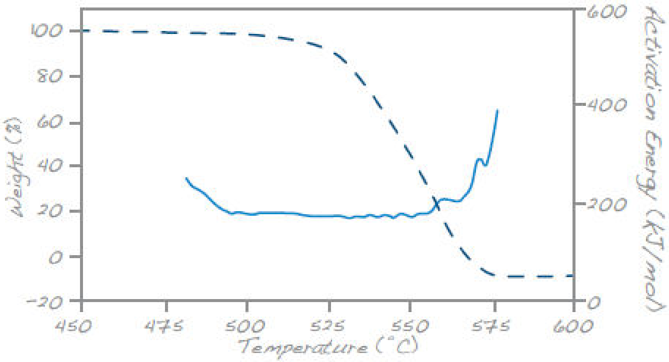
Heat Capacity



Activation Energy



Applications

SIMULTANEOUS THERMAL ANALYSIS

Polymer modified mortars

- ~ 25-123.3 °C: dehydration of pore water;
- ~ 123.3-345 °C: dehydration of calcium silicate hydrates;
- ~ 345-427 °C: weight loss due to polymer pyrolysis and dehydration of part of silicate hydrates;
- ~ 427-475 °C: dehydroxylation of calcium hydroxide; and
- ~ 475-711 °C: decarbonation of $CaCO_3$.

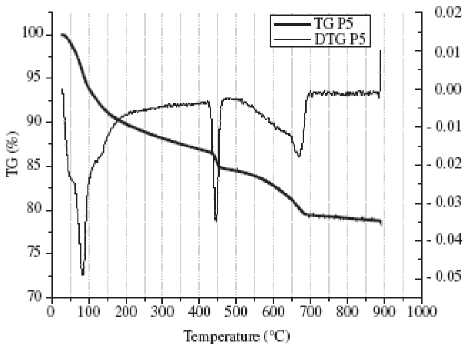


Figure 1. TG curve of the paste without polymer and 5% of silica fume P5.

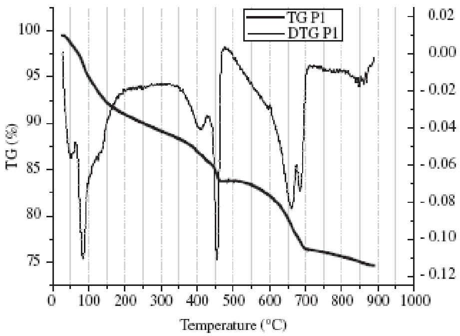


Figure 3. TG curve of the paste P1.

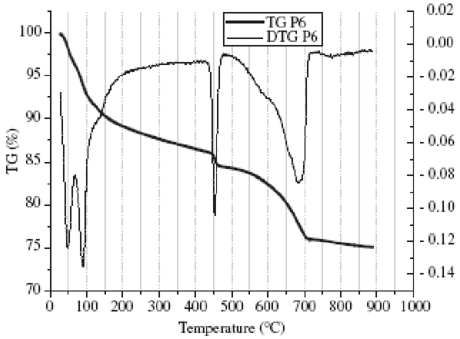


Figure 2. TG curve of the paste without polymer and 10% of silica fume P6.

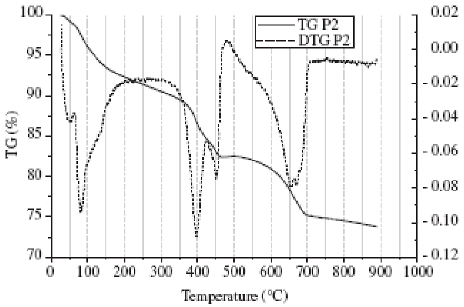
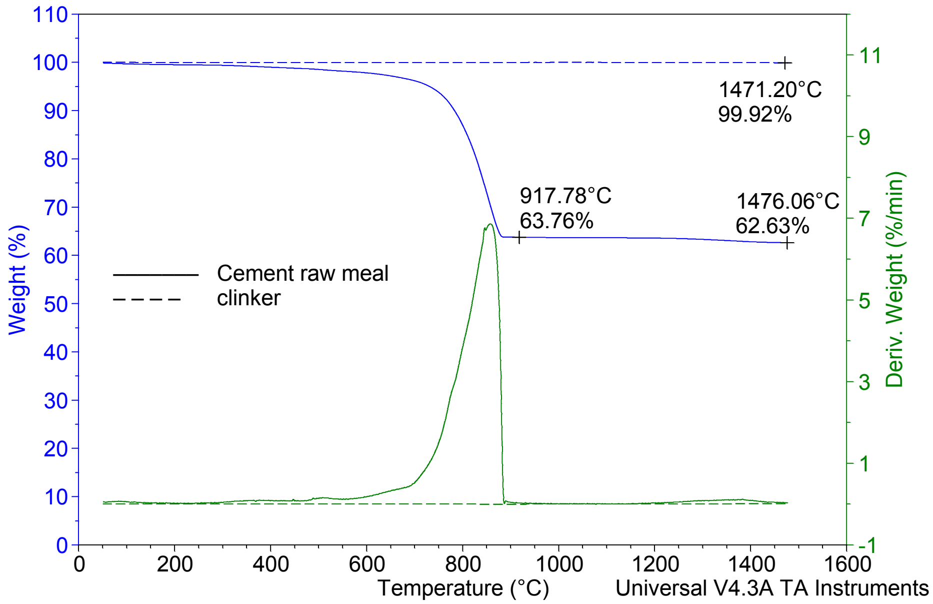


Figure 4. TG curve of the paste P2.

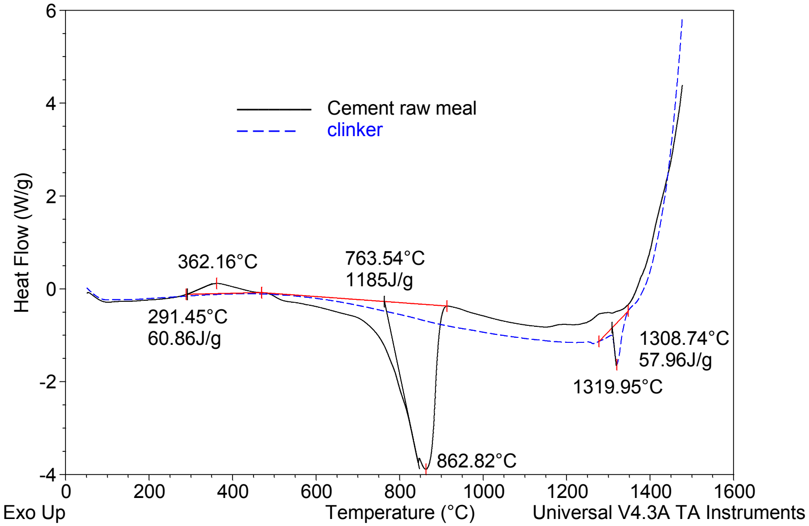
Materials Research, Vol. 9, No. 3, 321-326, 2006

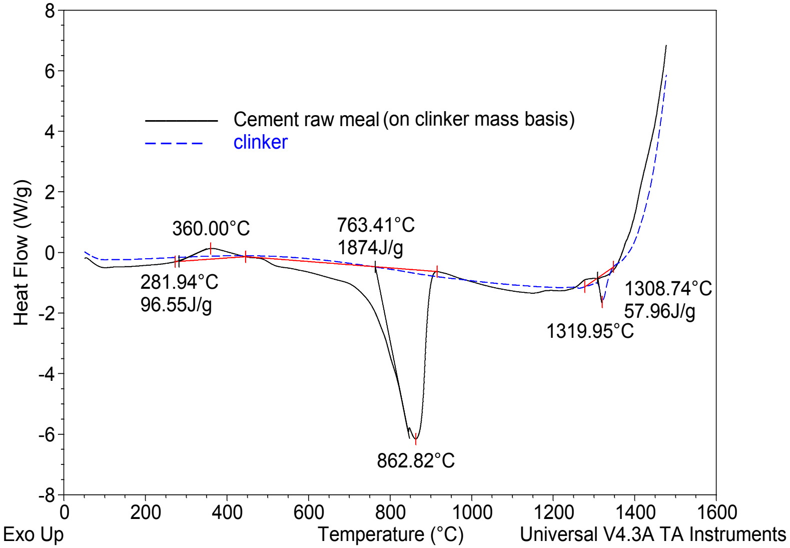
QUANTITATIVE THERMAL ANALYSIS APPLICATIONS IN PORTLAND CEMENT PRODUCTION

This application brief is intended to show how thermal analysis can be used to quickly obtain the clinker yield of a certain raw meal composition, as well as the heat required for its industrial firing process.



Comparison of dry raw meal (RM) and the clinker (CK) obtained at the end of its burning up to 1480°C from experiment performed at 20°C/min in air.





- Thermogravimetric (TG) and derivative thermogravimetric analysis (DTG) enables one to follow mass changes and decomposing rates during raw meal firing in cement kilns, as well as to calculate the clinker yield during cement production.
- Simultaneous DSC allows the simultaneous analysis of thermal effects of the transformations that occur during cement production and permits the calculation of respective transformation enthalpies.
- The energy requirement to decompose the main constituents of the raw meal, can be directly determined from the corresponding decomposition DSC peak area, which is expressed by default, on initial mass basis (raw meal mass basis).
- From DSC curves of the clinker obtained at the end of the raw meal thermal analysis, the temperature range of the partial liquid phase can be determined, as well as respective heat of fusion.

Gypsum addition to reduce the rate of setting

$$CaSO_4{\cdot}2H_2O \longrightarrow CaSO_4{\cdot}0.5H_2O \longrightarrow CaSO_4$$

Figure 1: CEMENT ANALYSIS - UNSEALED PAN

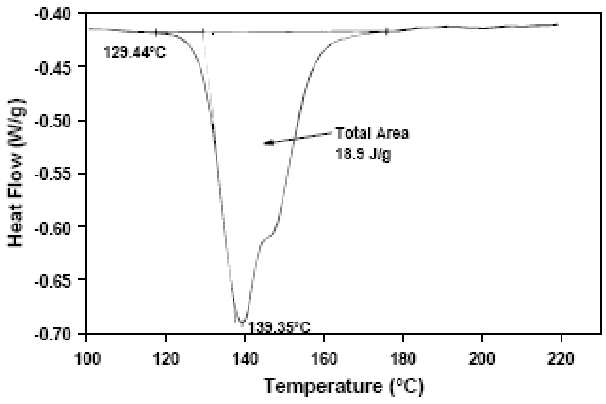
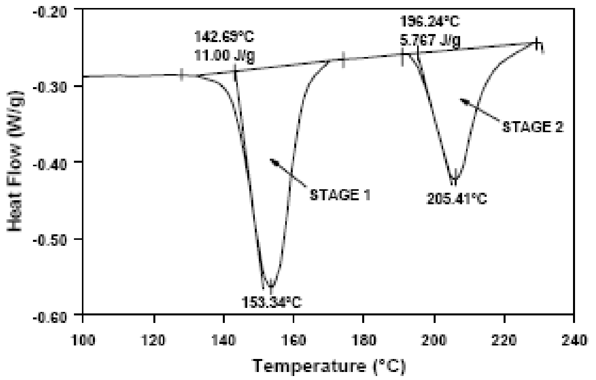


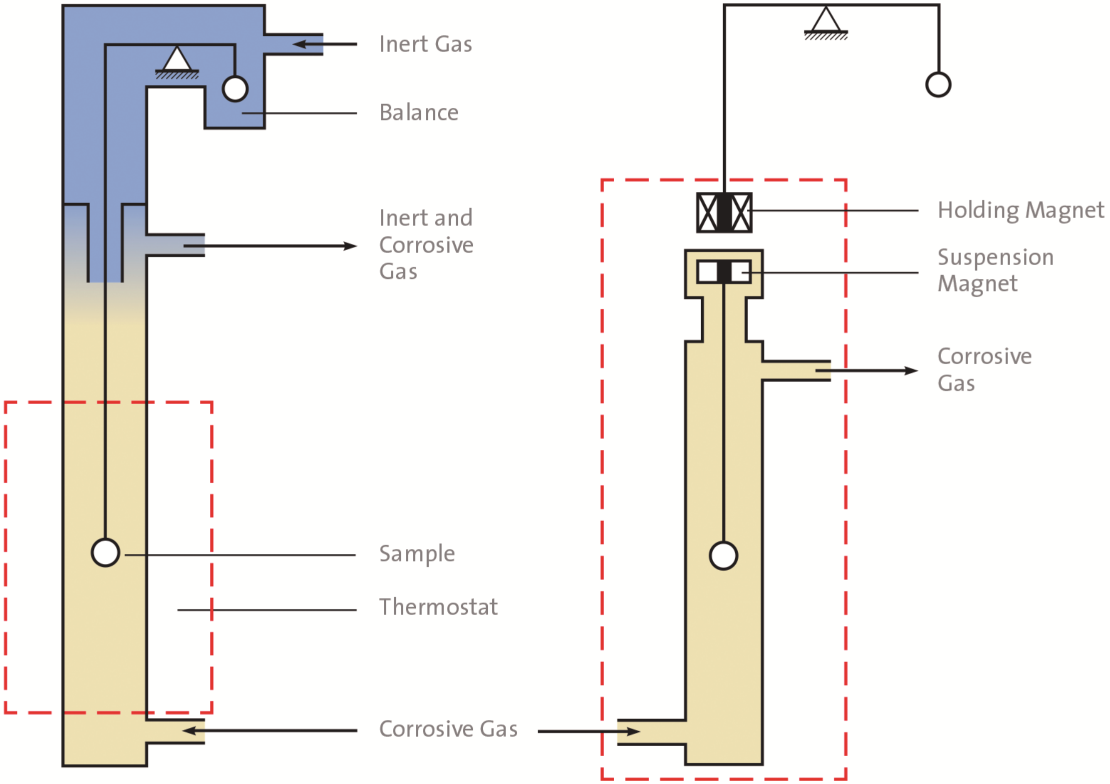
Figure 2: CEMENT ANALYSIS - HERMETIC PAN



- An essential process in the manufacture of Portland cement is the addition of around 5% gypsum (CaSO4.2H2O) to control (reduce) the rate of setting. During this milling process the thermal energy generated may cause partial dehydration of the gypsum to hemihydrate (CaSO4.0.5H2O) which adversely affects (increases) the rate of setting as well as the long-term properties of the set cement. Hence, it is of importance to monitor the amounts of both of these hydrates in the final cement.

Technology: MSB Gravimetric Measurements

Conventional vs. MSB Measurements
in Controlled Atmosphere



Conventional Measurements

MSB Measurements

Complete separation of MSB and reactor (environmental control) enables:

- Reactor temperature control from -196 °C to 1550 °C*
- Vacuum down to 0.01 mbar*
- Pressures to 700 bar*
- Corrosive reaction atmospheres
- Measurements with vapor to high dew points (humidity).
- Static reaction atmosphere measurements (no purge gas).
- Automatic re-tare function for unmatched long-term stability measurements

* Specification is model dependent

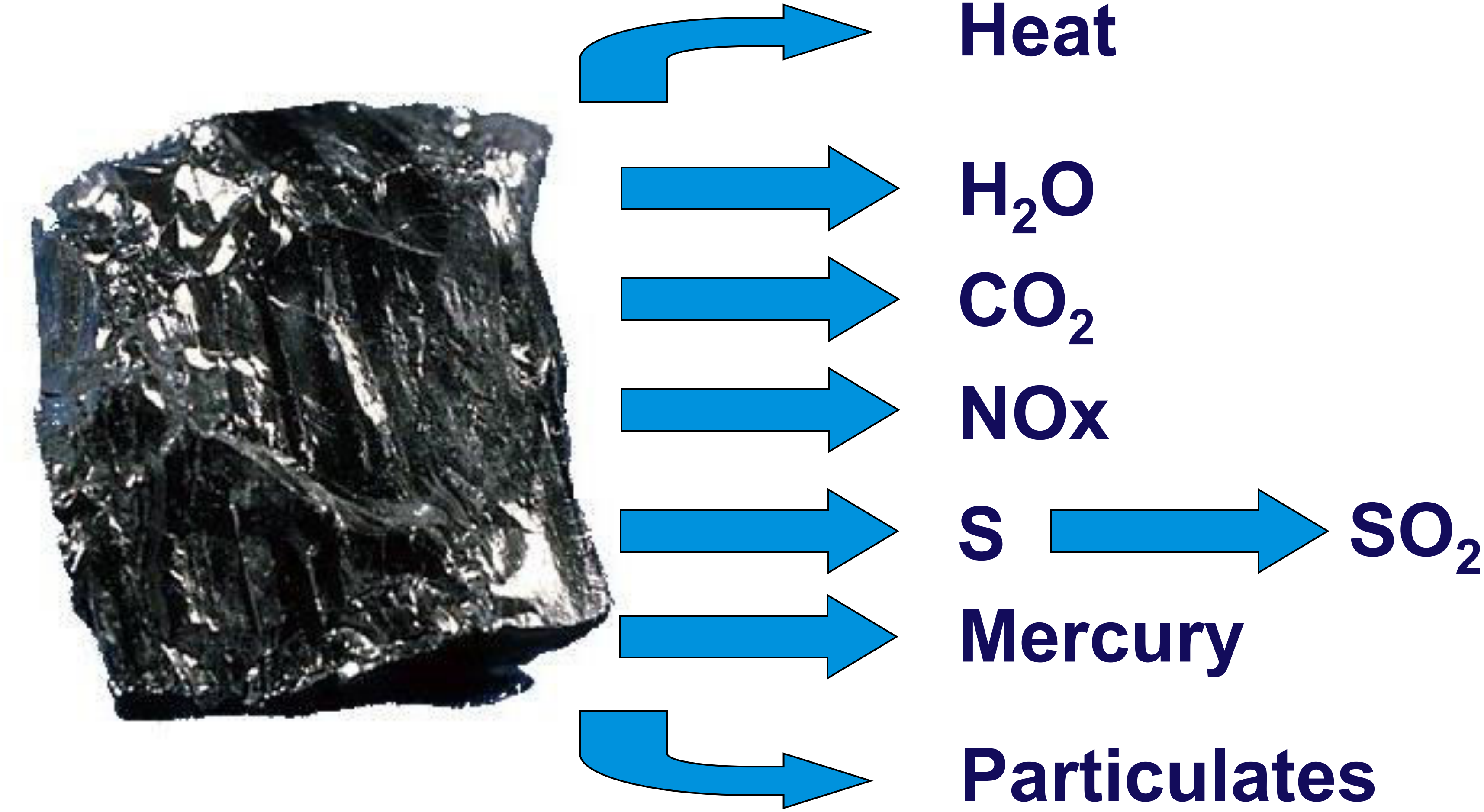
IsoSORP SA – Sorption Analyzers with MSB

Gravimetric analyzers for measurement of adsorption, absorption, and solubility of pure gases, gas mixtures, pure vapors, and gas & vapor mixtures.

Applications

HIGH PRESSURE SORPTION ANALYSIS

Burning Coal Produces…



Heat

H_2O

CO_2

NOx

S → SO_2

Mercury

Particulates

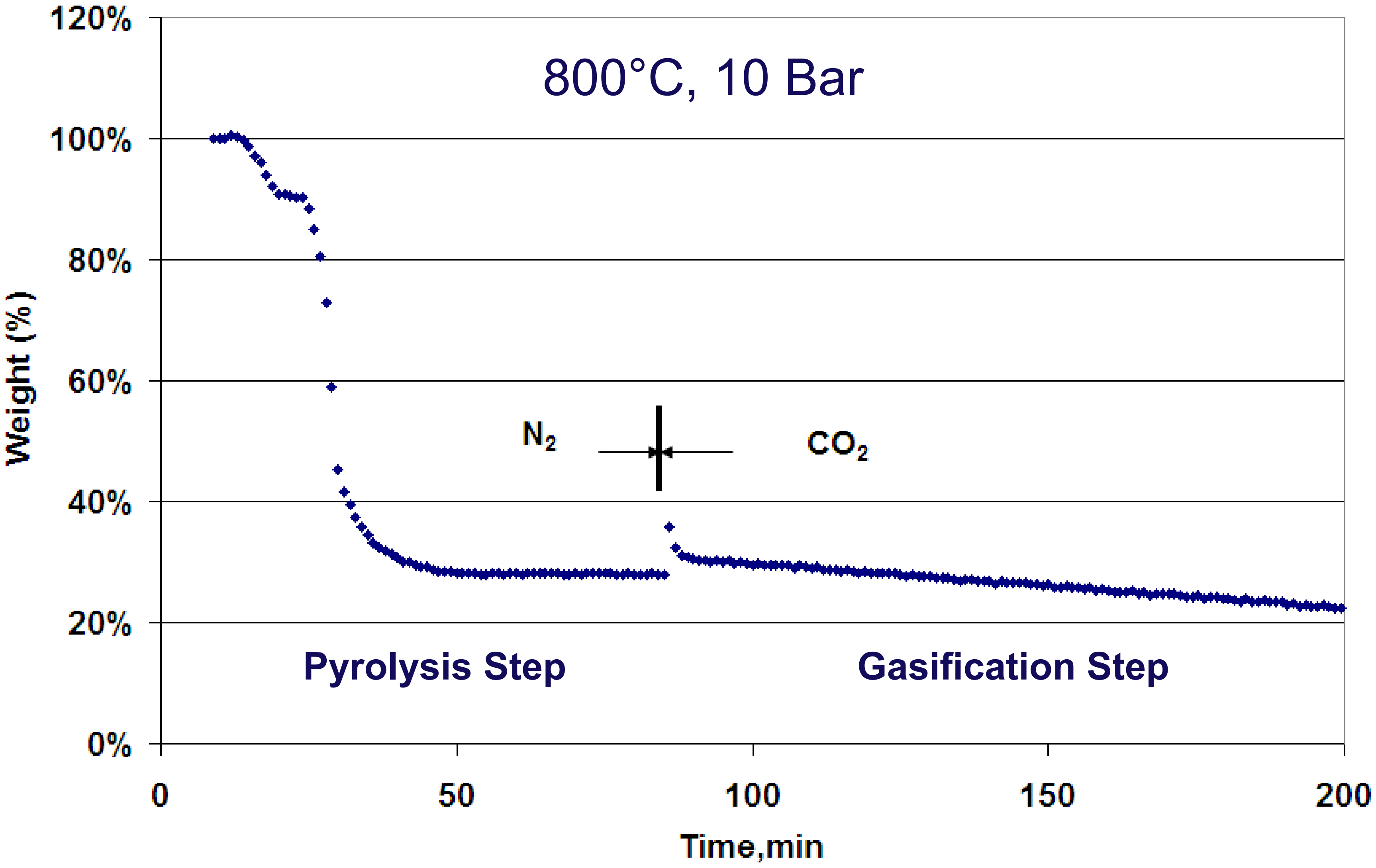
Clean Coal Technologies

- Wash coal prior to burning.
- Low NOx burners.
- CO_2 sequestration after burning.
- Gasification.
- Gasification + CO_2 sequestration.

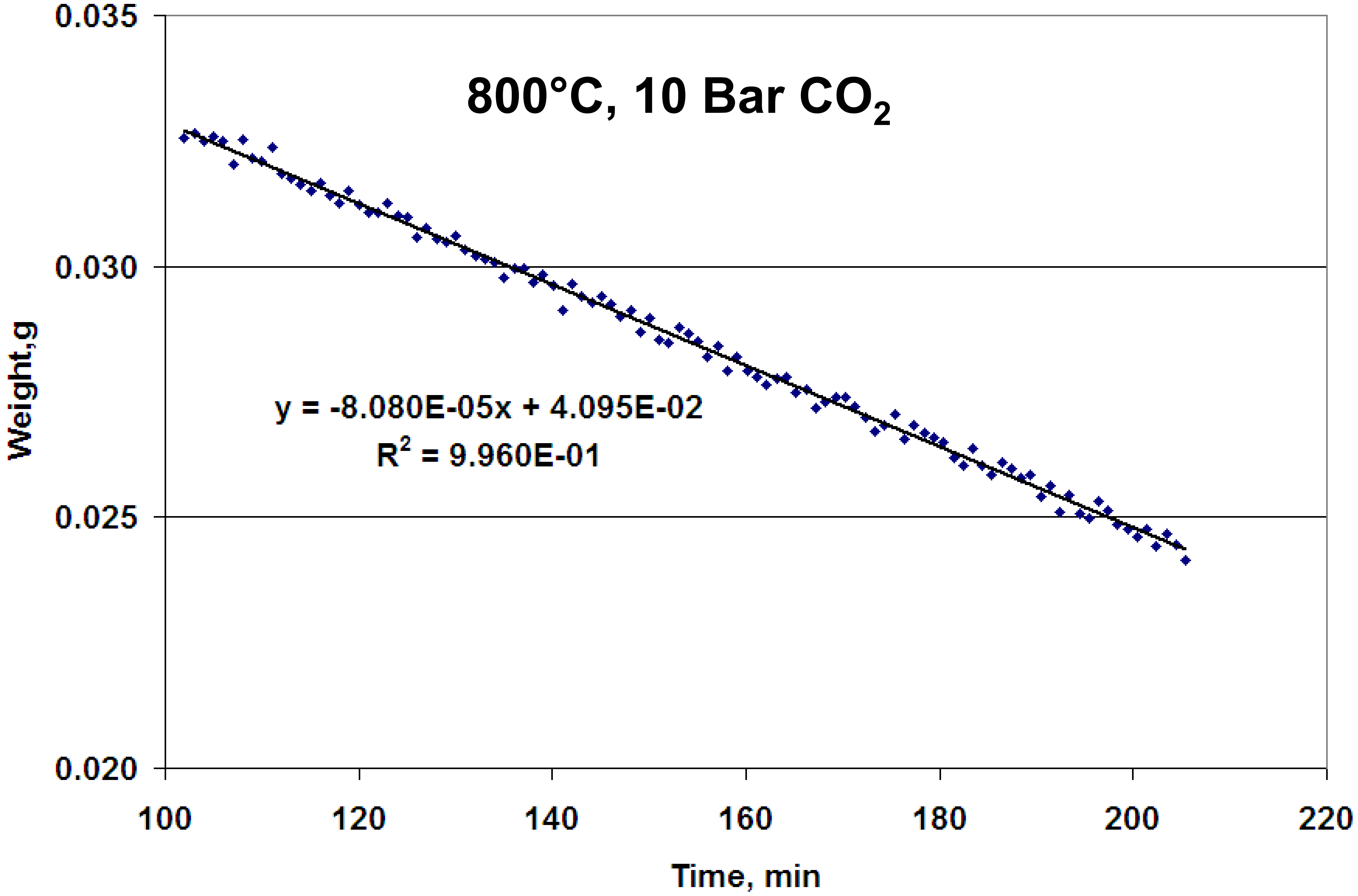
Gasification

- Process whereby coal or biomass material is used to produce a combination of H_2 and CO (a mixture termed Synthetic Gas or Syngas).
- Coal or biomass is first pyrolyzed to reduce the material to a carbonaceous char.
- The char is then heated in the presence of steam to produce the syngas. Pressure typically increases the conversion rate and percent conversion..

Biomass Gasification by CO_2



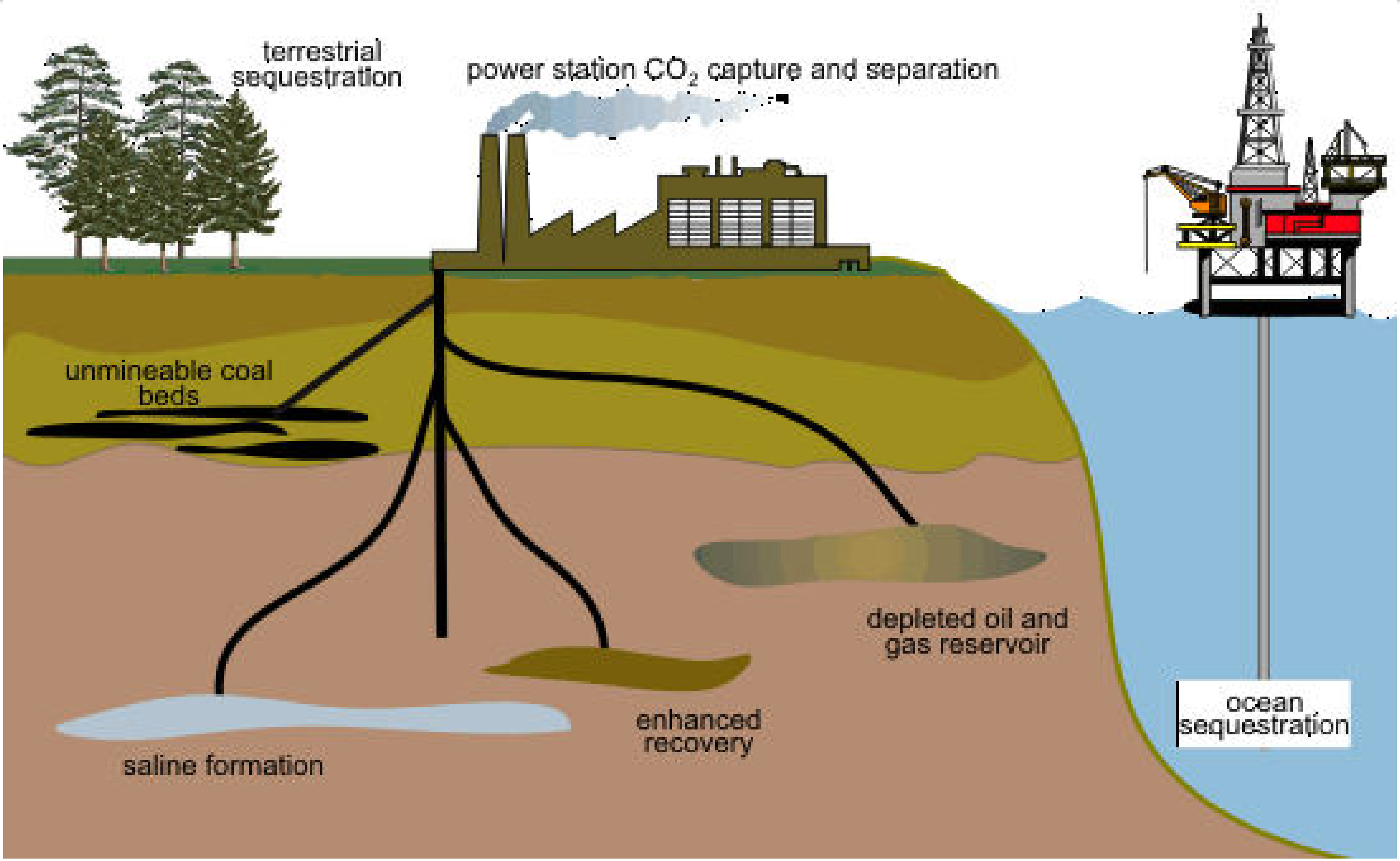
Biomass Gasification Rate



Carbon Dioxide Sequestration

- CO_2 needs to be removed from the syngas (and in the regular burning of coal).
- Options include absorbing the CO_2 into a solid for later desorbing and collection of the gas.
- Gas can then be bottled or pumped into geological structures, like the ocean floor or abandoned petroleum wells.
- China has begun to use captured CO_2 to provide carbonation for beverages.

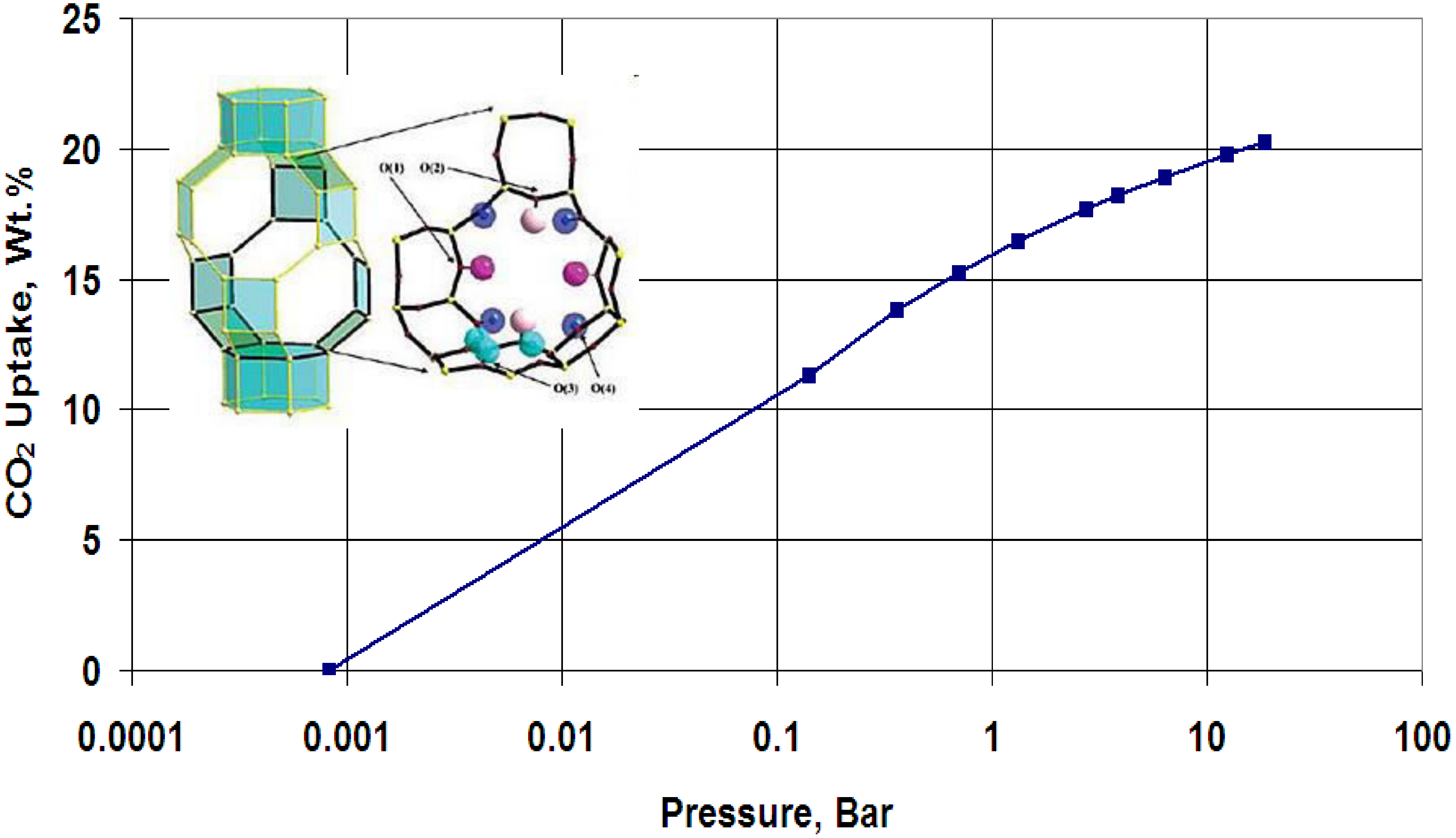
Carbon Dioxide Sequestration



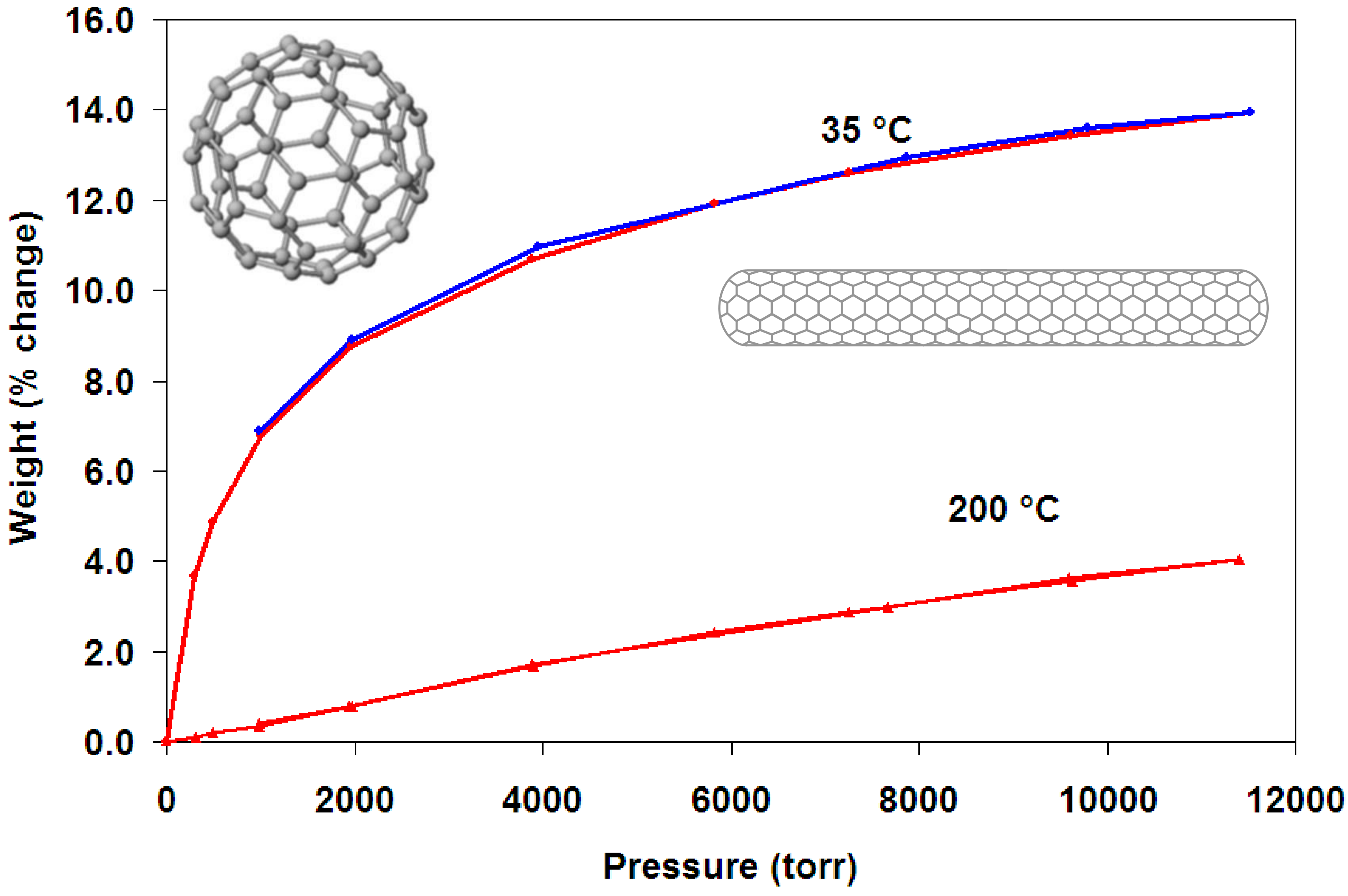
Adsorption Processes

- Knowledge of the adsorption process on a solid adsorbant is fundamental to:
  - Separation processes.
  - Purification of gases.
  - CO_2 sequestration.
  - Hydrogen storage.
  - Adsorption chillers.

CO_2 Sequestration on Raw Chabazite (60°C)



CO_2 Sequestration on Nanocarbon

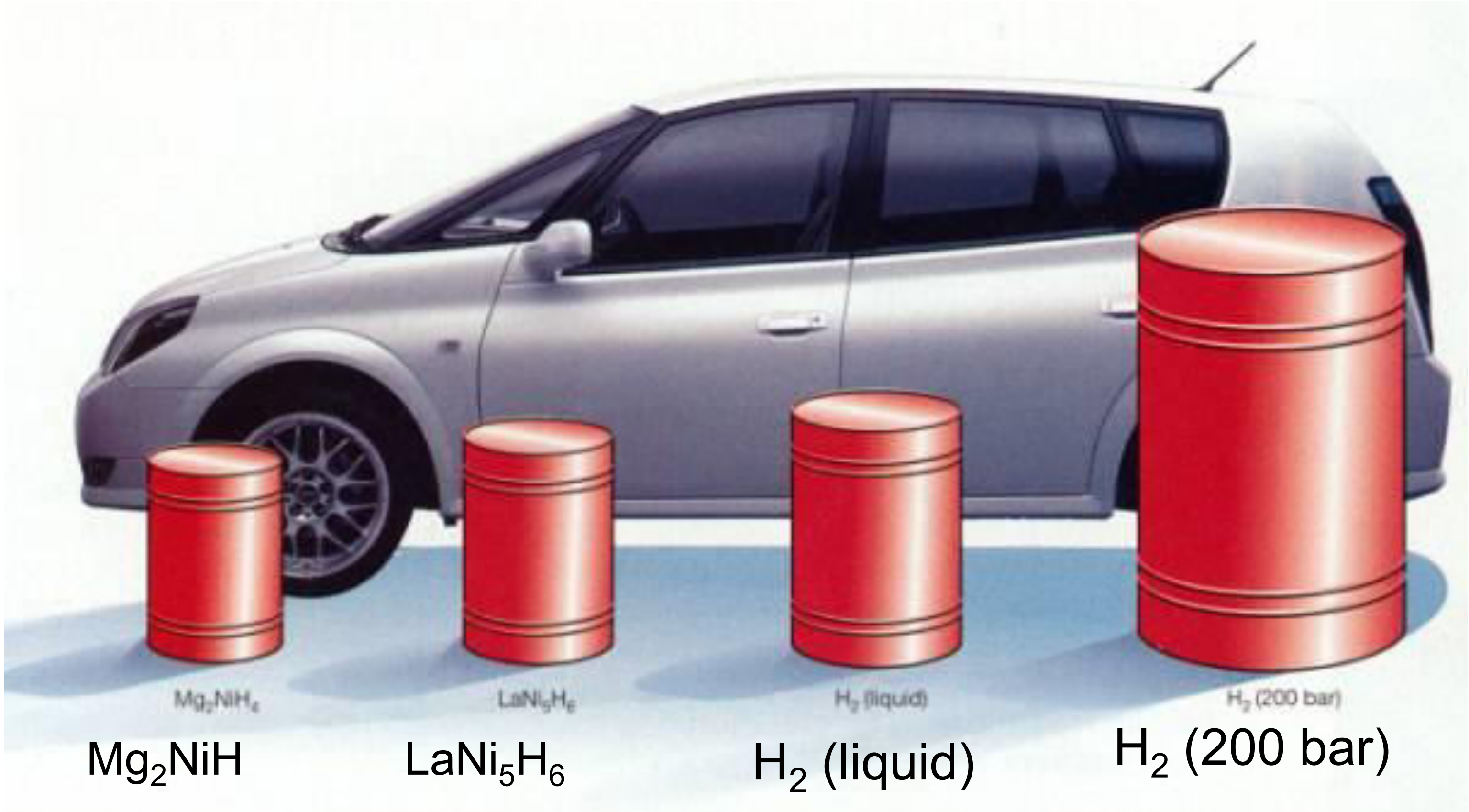


Fuel Cells

- Much research surrounds the development of hydrogen storage systems, especially for automobiles.
- Storing hydrogen in a solid is conceptually attractive because densities could be greater than gas or liquid containers and there is no need for compressed gas or cryogenic tanks to be on the auto.
- Problems though exist with storage densities of currently available materials and / or temperatures for desorbing the hydrogen.

Hydrogen Storage

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O\ (l) + \text{energy}$$



Mg_2NiH
3.16 wt%

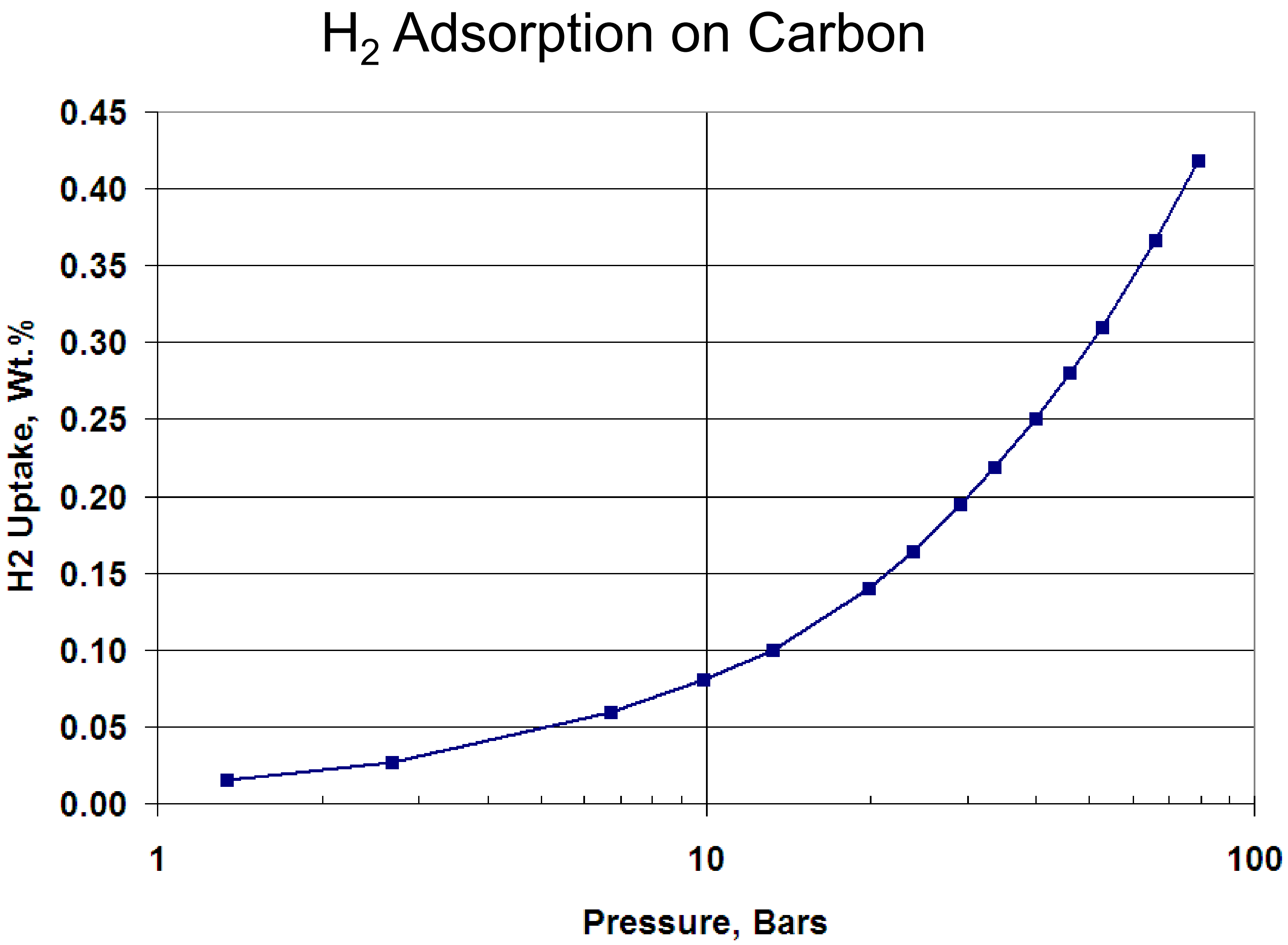
$LaNi_5H_6$
1.37 wt%

H_2 (liquid)

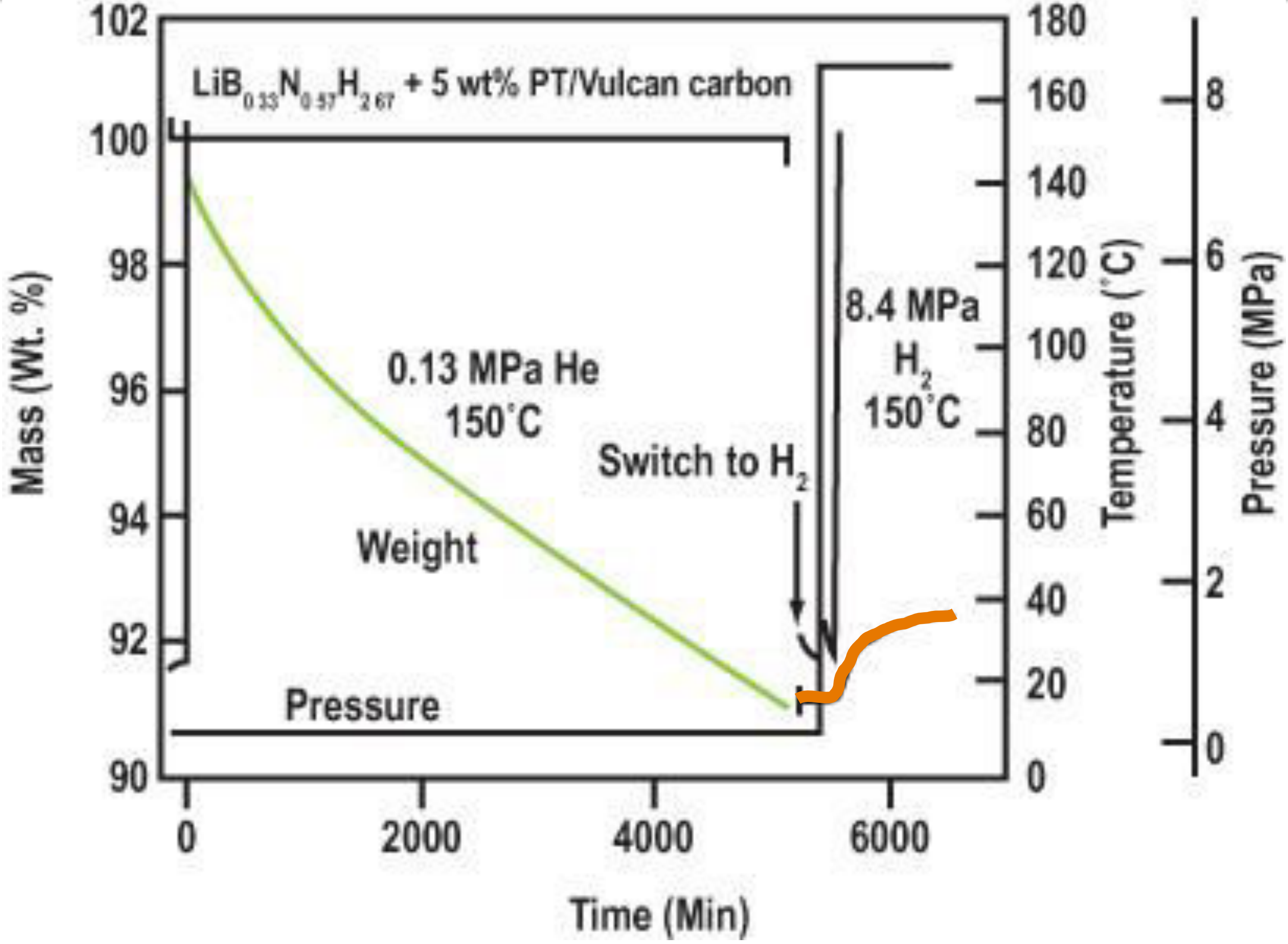
H_2 (200 bar)

Schlapbach & Züttel, Nature **414** (2001) 353

TGA-HP150 Data: Hydrogen Storage



Rehydrogenation of a $LiB_{0.33}N_{0.67}H_{2.67}$ Compound



Thank You

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