KEP Technologies

BUILDING MATERIALS

THERMAL ANALYSIS & CALORIMETRY SOLUTIONS

• CEMENT, PLASTER, CONCRETE, RAW MATERIALS •
• SETTINGS (HYDRATION) •
• THERMAL BEHAVIOR OF RAW MATERIALS •
• BUILDING MATERIAL PROPERTIES •

setaram
KEP TECHNOLOGIES

YOUR CHALLENGES

Cement, plaster and other building materials are essential in everyday life. Although some of them have been used for centuries to build enduring structures, their behavior is still not fully understood today. The constant search for improved building materials and for special cements for the consolidation of oil wells in the oil & gas industry leads to the development of new cementitious materials, formulations and additives.

Thermal analysis and calorimetry provide critical insights into the manufacturing of cement powders, the hydration of the powder, and the final product for building materials research and industry. Insights that can make the difference between construction success or failure.

KEP Technologies understands your challenges and offers a choice of solutions that provide experimental control, instrument versatility and quality results.

COMMON BUILDING MATERIALS - STUDIES & SOLUTIONS

This brochure presents some of our solutions in this field and we encourage you to contact us for more information.

The setting or hydration steps, rate (kinetics), heat release during the setting process, together with a comparison of various blends, formulations and various conditions (temperature, pressure) are typically measured by isothermal calorimetry.

Setting (hydration)

The reaction steps, phase transformations, heat content and heat transfer properties of the raw materials and their products (like clinker) during the different steps of the baking process need to be evaluated in order to better control the process parameters.

Thermal behavior of raw materials & processing/baking

The thermophysical and thermal stability characteristics of the final product are important for the application of the building material and are determined using a combination of thermal analysis and calorimetry techniques.

Building material properties

THE KEP TECHNOLOGIES ADVANTAGE

KEP Technologies is addressing it's offerings to the building materials market by making available the widest and most versatile choice of solutions. Now you can consult with one company, KEP Technologies, to address your challenges across the broadest number of building materials studies on the market.

Each solution embodies our “Reimagine Material Characterization” value proposition by delivering the three core customer benefits of **Experimental Control, Instrument Versatilty and Quality Results.**

We believe solutions that provide these benefits will deliver the highest value to our customers.

In addition to our core customer benefits, we are able to provide **customized solutions** by harnessing the engineering and project management of our highly skilled organization.

Modular design allows for upgraded and tailored functionality
Access to all previous non-proprietary custom requests
Open access to engineering development team

INSTRUMENT

CALVET PRO DSC

HIGHEST HEAT MEASUREMENT ACCURACY
Calvet 3D sensor based on thermocouples with Joule effect calibration.

EXTERNAL COUPLING CAPABILITY
Designed to increase your research options, including manometry, BET, gas analyzers, humidity controllers and gas panels.

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS to perform even the most demanding experiments with one instrument : high pressure (500bar) and high vacuum (10-4 mbar) studies, pressure measurement and control, packed bed reactor experiments.

SPECIFICATIONS

Temperature range (°C)	-120 to 830
Isothermal and temperature scanning (°C/min)	0.01 to 30
Pressure, non-controlled (bar [psi])	500 [7 250]
Pressure, measured and controlled (bar [psi])	350 [5 075] ; 400 [5 800]
Cell and crucible volumes (µL)	up to 320

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

THERMAL ANALYSIS OF MINERAL SALTS USED IN THE CEMENT INDUSTRY

INTRODUCTION

Cement is obtained from the baking of a mixture of clays and limestones in which silica is one of the main components. Mineral salts are numerous in the initial compound, and sometimes contain traces of nitrates. A controlled amount of gypsum can be added to the manufactured cement in order to retard its setting rate. The thermal behavior of the three different salts (silica, nitrate & gypsum) is investigated by DSC.

EXPERIMENT

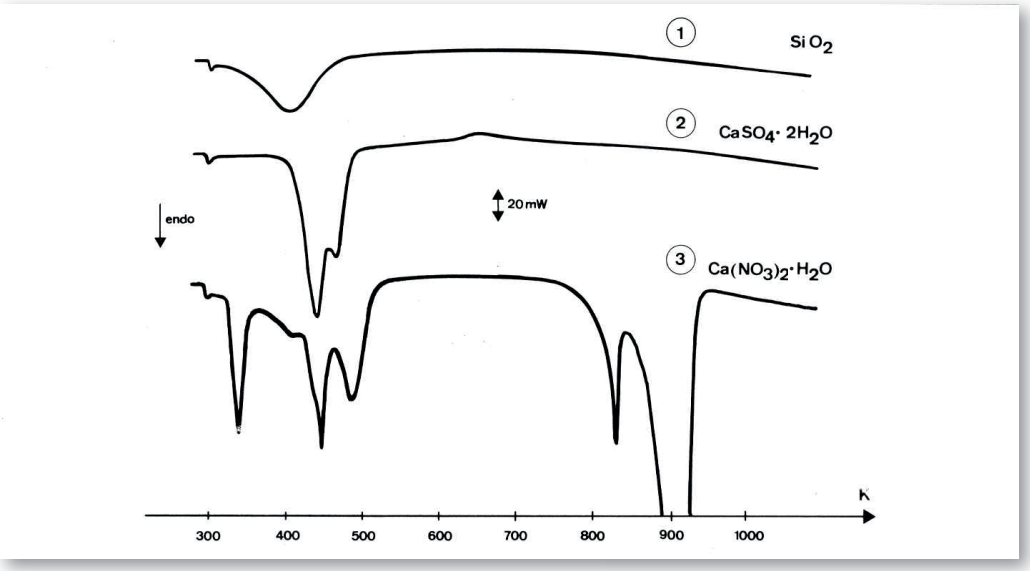
- Samples :
  - SiO_2 (49 mg)
  - $CaSO_4 \cdot 2H_2O$ (49mg)
  - $Ca(NO_3)_2 \cdot H_2O$ (59mg)
- Crucible : Platinum (open)
- Heating mode : 10K/min
- Atmosphere : Argon
- The CALVET PRO is used in the vertical mode

RESULTS AND CONCLUSION

Silica SiO_2 (gel)
After water vaporization from the gel, silica remains stable at high temperature.

Gypsum $CaSO_4 \cdot 2H_20$
Gypsum is dehydrated in two steps : 1.5 mole and 0.5 mole of water. At 600 K, a transformation into anhydrous calcium sulfate is detected.

Calcium nitrate $Ca(NO_3)_2 \cdot H_2O$
After the loss of a mole of water in several steps, melting begins at 750 K, followed by decomposition, which is highly endothermic and yields chalk.



HEAT CAPACITY OF CRUDE CEMENT AND CLINKER

INTRODUCTION

Heat capacity is a very important thermodynamic parameter, when determining the heat balance of a reaction. The specific heats of the different components, before and after the reaction, have to be known in order to define the correct heating of the system.
The heat capacity of crude cement and clinker is measured according to the stepwise method. An increment of temperature is scanned, and the calorimetric peak, corresponding to the sample heated is integrated, as shown below.

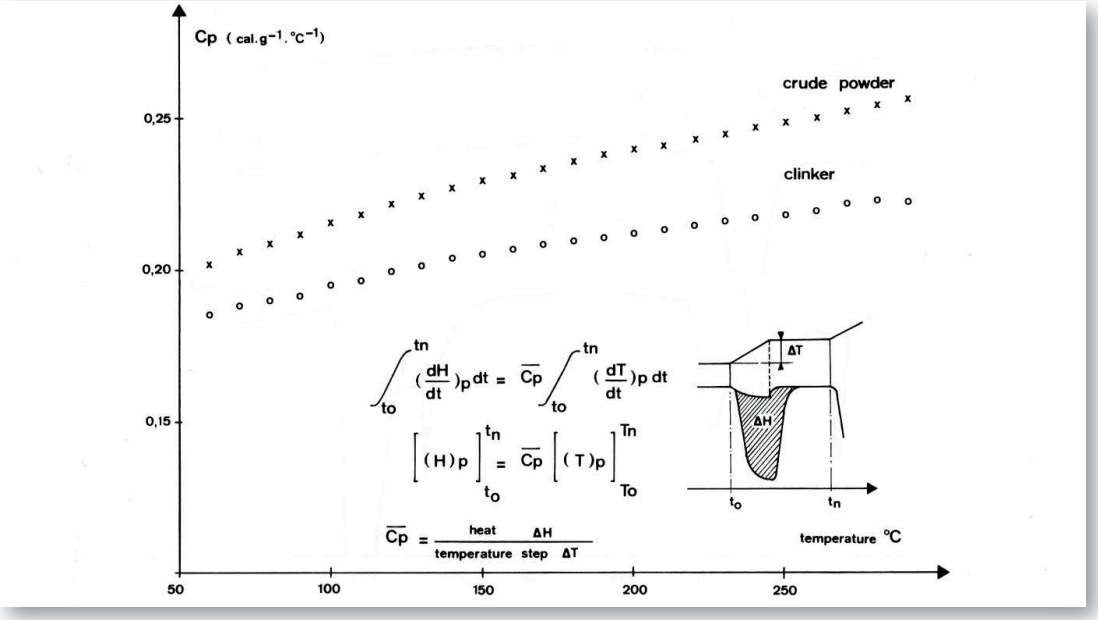
EXPERIMENT

- Samples :
  - Crude cement
  - Clinker
- Mass : 450 mg
- Crucible : Aluminum
- Heating mode : Step programming 2K/min
- Atmosphere : Argon

RESULTS AND CONCLUSION

Two tests are necessary to obtain a correct determination of Cp :
- one with the sample
- one without the sample

In both cases, the reference cell is empty.
The measurements show that the heat capacity of crude powder is higher than that of the clinker.
The difference for the temperature range investigated (50°C – 300°C) is about 0.025 $cal.g^{-1}\ °C^{-1}$



INSTRUMENT

THEMYS

ACCURATE AND SENSITIVE ULTRA-HIGH TEMPERATURE
heat flow measurement with Tri- Couple DTA technology

ULTRA-HIGH TEMPERATURE CAPABILITY
to 2400°C with a single furnace

MODULAR ADAPTIONS ALLOWING
TGA only, DTA only, TG-DTA, and TMA up to 2400°C, DSC only and TG-DSC up to 1750°C all in one instrument

HIGH ACCURACY & VERSATILITY
hang-down symmetrical beam balance, specifically designed for TGA applications

EXTERNAL COUPLING CAPABILITY
designed for evolved gas analyzers (FTIR, MS, GCMS, MS-FTIR,or FTIR-GCMS)

SPECIFICATIONS

Temperature range (°C)	room temperature to 1750 or to 2400
Isothermal and temperature scanning (°C/min)	0.01 to 100
Sample volume (µl)	up to 2500 in TGA
Optional protected DTA rods for enhanced corrosion resistance, tricouple DTA rods for enhanced sensitivity, protected tricouple for combined advantages	

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

BAKING OF CRUDE PORTLAND CEMENT

INTRODUCTION

After preparation of the raw materials (lime, clay, marl,…) in proportions dependent on the process selected, paste, powder or granules are introduced into the rotary kiln so that the mixture may be gradually heated to the clinkerization temperature, that is to say to the temperature at which partial melting occurs, about 1450°C.

Differential thermal analysis is used to simulate the conditions existing during cement manufacture and to characterize the physical and chemical processes which occur in the cement when it is heated to 1500°C.

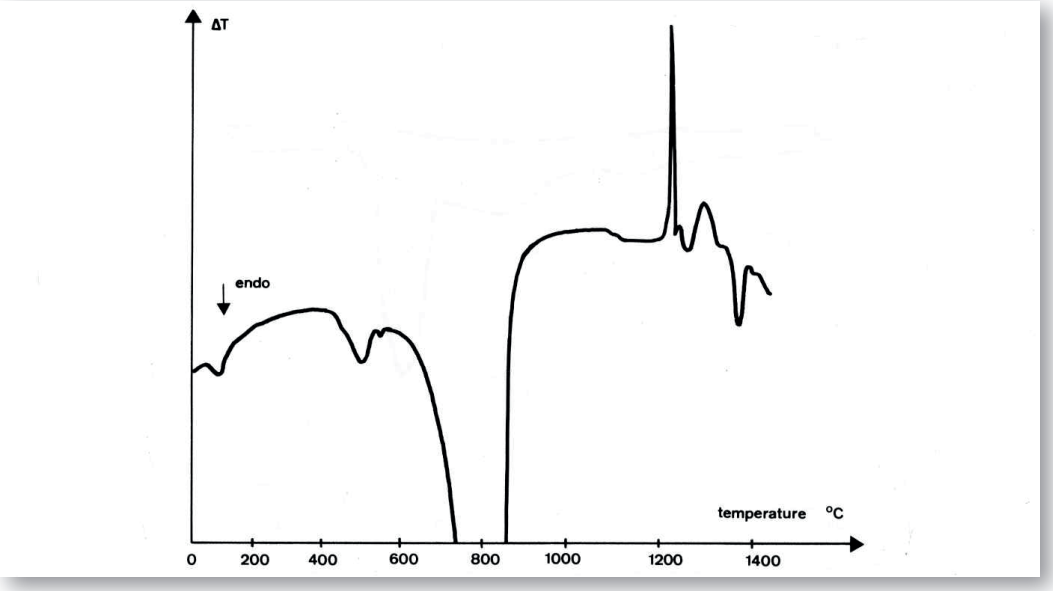
EXPERIMENT

- Samples : Portland cement (100 mg)
- Crucible : Platinum
- Heating mode : 7K/min
- Atmosphere : Argon

RESULTS AND CONCLUSION

The crude material exhibits several endothermic and exothermic transformations :

- 20°C – 200°C
dehydration and drying of the crude cement
- 200°C – 700°C
elution of water chemically bound within the clay materials (dehydroxylation)
- 700°C – 1100°C
decarbonation with emission of carbonic anhydrides
- 1100°C – 1450°C
clinkerization, corresponding to the formation of di and tricalcium silicates and calcium alumino ferrites



ANALYSIS OF CEMENT SAMPLES BY THERMOGRAVIMETRY COUPLED WITH FTIR SPECTROMETRY

INTRODUCTION

The aim of this analysis is to identify the evolved gases from a cement sample by thermogravimetry coupled with FTIR spectrometry.

EXPERIMENT

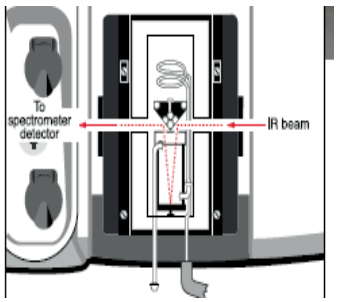
Experiments were conducted on a THEMYS with the outlet of the balance connected to a Nicolet 380 IR spectrometer by a heated connection line (maximum at 200°C).

The cement sample, previously reacted with HCl to remove its carbonate content, was analyzed in a platinum container under air flow at a scan rate of 20K/min from ambient temperature up to 1100°C.

The experimental conditions of the FTIR spectrometer were:

- Scan numbers: 32
- Resolution: 4cm^{-1}
- Spectral domain: 4000-400cm^{-1}

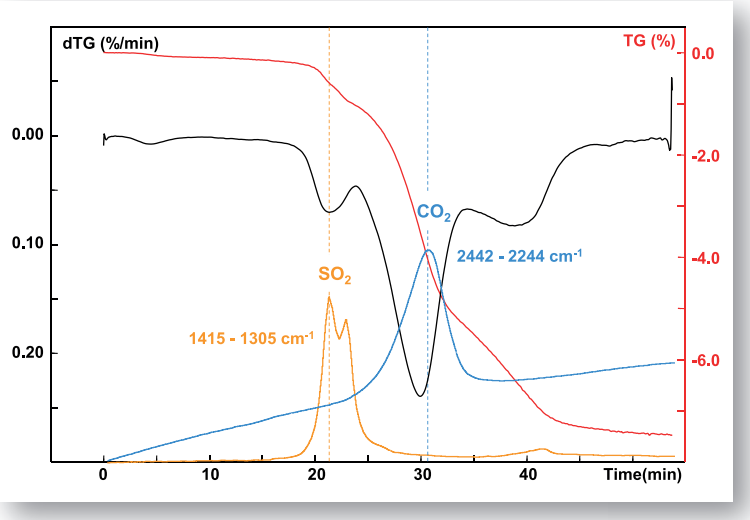
Cell gas accessory



RESULTS AND CONCLUSION

At 22 min, we observe a decrease of the mass, two exothermic peaks and an increase of the IR intensity. Thanks to a library of results we can associate this mass variation to the loss of SO_2.

In the same way, at 31 minutes, we note a large decrease of the mass, an exothermic peak and an increase of the IR intensity.
This mass variation corresponds to the loss of CO_2 and water.



INSTRUMENT

CALVET DC

IMPROVED HEAT CAPACITY AND HEAT MEASUREMENTS WITH THE CALVET DC

- heat flux DSC up to 1600°C – for accurate heat capacity, heat, and glass transition measurements
- drop calorimetry up to 1500°C – for accurate heat capacity, heat of dissolution and heat of formation measurements

VARIETY OF ATMOSPHERE CONDITIONS
possible with multiple carrier and reactive gas options

CONVENIENCE AND ECONOMY
with one instrument and furnace for TGA, TG-DSC, TGDTA, DSC, DTA, and TMA up to 1600°C

MODULAR ADAPTATION ALLOWING
TGA only, DTA only, TG-DTA up to 2000°C all in one instrument

SPECIFICATIONS

	CALVET DC	THEMYS LV
Temperature range (°C)	room temperature to 1600	room temperature to 2000
Isothermal and temperature scanning (°C/min)	up to 20	up to 20
Sample volume (µl)	up to 450 for heat flux DSC and 5700 for drop calorimetry	up to 18100 in TGA
Sample drop system	Manual or automated (optional)	

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

HEAT CONTENT OF CRUDE PORTLAND CEMENT

INTRODUCTION

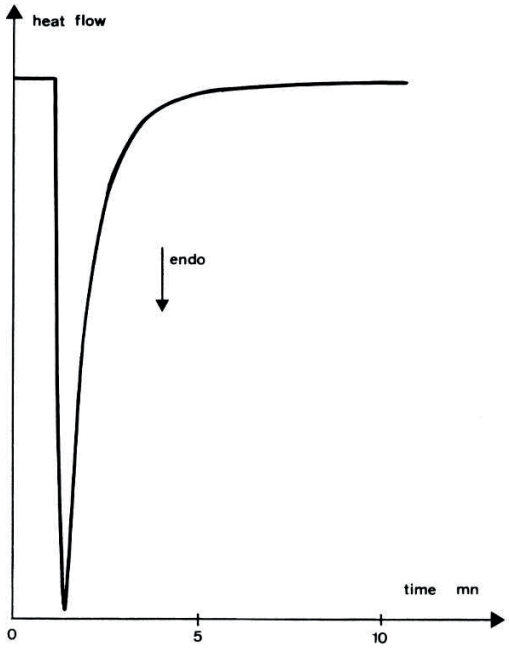
The issue of power consumption is becoming increasingly important in many industries, particularly those that use high temperature furnaces. Therefore, it is important to be able to establish total or partial heat balances for any given system.

The 1500°C calorimeter allows us to measure the heat which must be supplied to a system, for example to run clinkerization of crude Portland cement.

The sample, thermostated at ambient temperature, is dropped into the calorimeter which has been stabilized at 1430°C.

EXPERIMENT

- Sample : Portland cement
- Mass : 25.5 mg
- Crucible : Platinum
- Heating mode : isothermal 1430°C
- Calibration by dropping of platinum standards



RESULTS AND CONCLUSION

The recorded calorimetric peak is equivalent to the algebraic sum of the heat of the sample heated between 20°C and 1430°C, plus the heats associated with different thermal ranges.

The integration of the peak shows that 700 calories per gram of crude cement must be supplied to the system in order to transform the raw material into clinker.

APPLICATION OF THERMAL ANALYSIS TO THE CEMENT INDUSTRY

INTRODUCTION

The heat exchange during the clinkering reaction is measured by the drop technique in a multi-detector high temperature calorimeter.

EXPERIMENT

The multi-detector high temperature calorimeter includes a furnace with a carbon resistor. The temperature of the kiln is fixed and a few mg's of sample at room temperature is dropped into the kiln. A cell with 56 thermocouples records the heat exchanged by the sample to reach the defined temperature.

RESULTS AND CONCLUSION

In Fig. 1 the upper curve shows the results obtained for an industrial raw meal. The bottom curve shows the curve for the clinker: it corresponds to the heat which could be recovered from the cooler. In the curve corresponding to the burning of the material, we can see the endothermic part that corresponds to the decarbonation of the limestone and the exothermic part that corresponds to the formation of dicalcium silicate. These two reactions occur simultaneously but with a different rate. Although the peaks overlap with each other, the exothermic peak due to the formation of dicalcium silicate can be seen very distinctly.

It is interesting to relate these experiments to the real industrial process. Several processes exist and we have chosen three of the more recent systems : long dry kiln, kiln with heat exchanger, and kiln with a precalciner. In Fig. 2 we have tried to represent the reactions occurring in different zones of the kiln and the cooler: preheating, calcination, transition, burning and cooling zones.

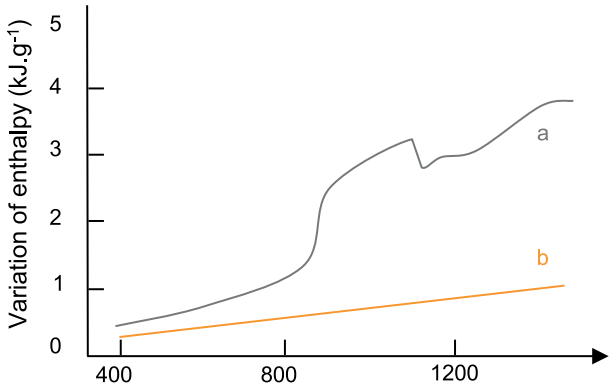


Figure 1 – 1 Variation of enthalpy vs. Temperature for: a) Portland cement raw mix, b) Portland cement clinker

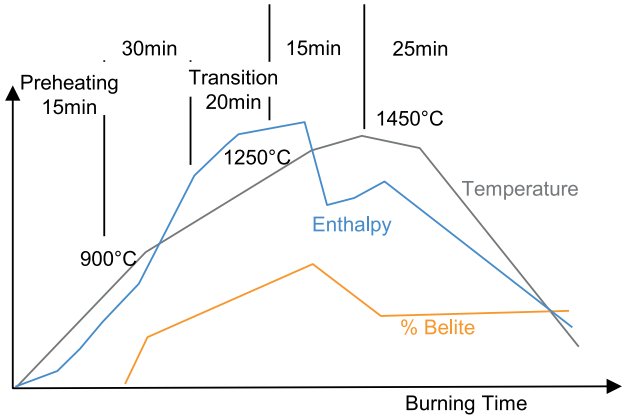


Figure 1 – Enthalpy of clinker formation in a long dry kiln. K = rotary Kiln, C = cooler

ANALYSIS OF PLASTER WITH HIGH VOLUME TG

INTRODUCTION

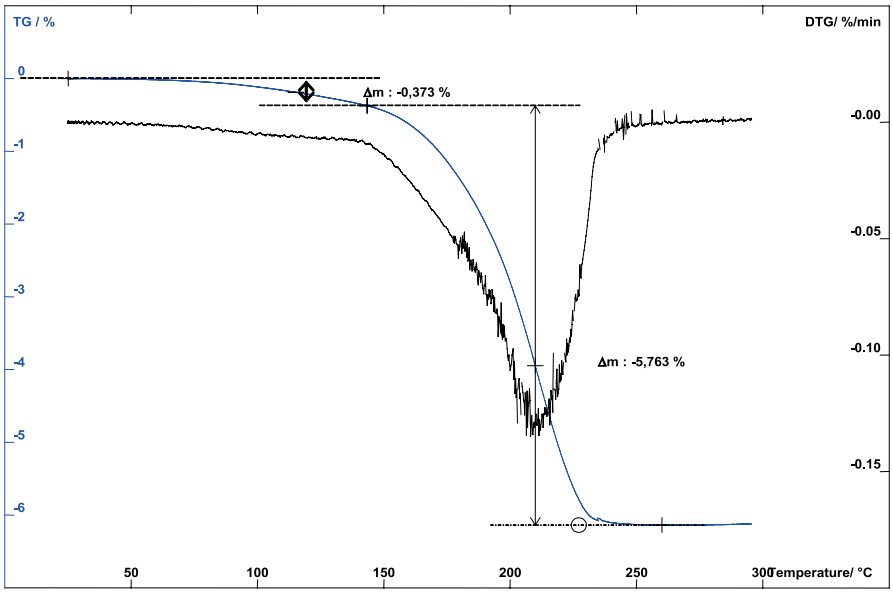
High volume thermogravimetry may be of great interest, because it makes heterogeneous sample analysis possible. It is especially interesting in the case of natural raw materials or ores, because with a larger sample size, the sampling is not so critical.
Using a large volume of sample is also a way to obtain measurements with better accuracy.
With the THEMYS LV, it is possible to use a crucible with a volume of 18 mL. If a solid sample is used its maximum dimensions can be : ø = 22 mm, h = 50 mm.

EXPERIMENT

- A sample of plaster is analyzed in TG mode only with the CALVET DC
- Sample mass : 13.35 g
- The temperature is programmed from ambient to 300°C at 1K/min
- Atmosphere : air

RESULTS AND CONCLUSION

The figure shows that we can separate the mass loss in two steps :
- Between ambient and 145°C : a mass loss of 0.373 % is measured due to the dehydration of gypsum.
- Between 145°C and 250°C : a mass loss of 5.763 % is measured due to the dehydration of plaster.



SETLINE DSC

EASY TO USE WITH ROBUST SENSOR TECHNOLOGY
ensuring quality, consistent and reliable data

AVAILABLE WITH HIGH PRESSURE CRUCIBLES
up to 500 bar at 600°C

REASONABLY PRICED INSTRUMENT & SENSOR
for easy, cost effective replacement

LOWER COST OF OWNERSHIP
through simplified maintenance and a Replacement Parts Guarantee

TECHNICAL & APPLICATION SUPPORT
for fast expert help with any questions

CALISTO 2.0 EXCLUSIVE SOFTWARE
for intuitive and easy data handling

SPECIFICATIONS

Temperature range (°C)	-170 to 700
Programmable heating rate (°C/min)	0.01 to 100
Enthalpy accuracy / precision* (%)	+/- 0.8 / 2.5
Temperature accuracy / precision* (°C)	+/- 0.30 / 0.50
DSC measurement range (mW)	+/- 6 000
Atmosphere	Inert gas, air, High-pressure crucibles up to 500 bar at 600°C

** Based on indium melting tests*

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

DEHYDRATION OF GYPSUM

INTRODUCTION

Knowing the thermal behavior of raw materials is interesting as it allows one to understand their behavior during baking. Moreover, one may use these data to determine the materials content in the final product. For instance, gypsum is used for preparing plaster products. It is also found in small amounts in cements. The residual presence of gypsum causes quicker setting in cement. It is thus important to control the gypsum content in cement powders.

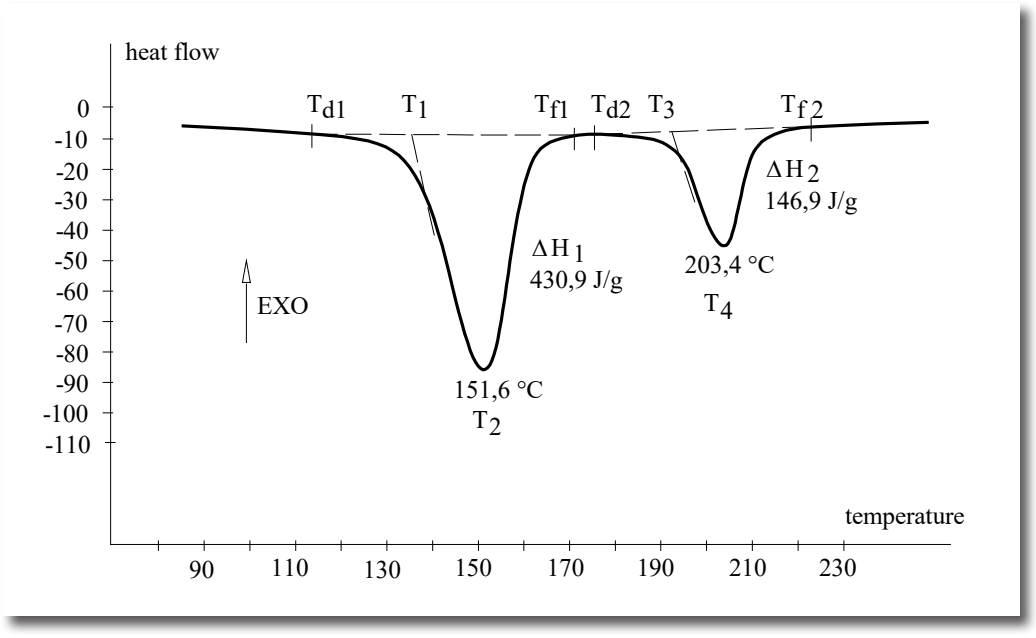
EXPERIMENT

- Sample mass : 25 mg.
- Crucible : aluminium (120 µl) with a semi-tight cover
- Carrier gas : argon.
- The temperature is programmed from 20°C up to 250°C at 5 K/min.

RESULTS AND CONCLUSION

The dehydration of gypsum ($CaSO_4 \cdot 2H_2O$ = dihydrate) presents two steps : after the loss of 3/2 H_2O it produces $CaSO_4 \cdot ½H_2O$ which is plaster. At high temperature, another loss of $½H_2O$ occurs, which produces anhydrite.
The DSC signal of gypsum dehydration shows two distinct endothermic effects corresponding to these two steps:
The dehydration of gypsum into plaster between 120°C and 170°C (ΔH1 = 430.9 J/g)
The dehydration of the plaster formed into anhydrite between 180°C and 225°C (ΔH2 = 430.9 J/g).

After running a test with cement under the same conditions and determining ΔH1 of the cement, it becomes possible to calculate the gypsum content of the tested cement.



DSC ANALYSIS OF A PLASTER CONTAINING PHASE CHANGE MATERIALS

INTRODUCTION

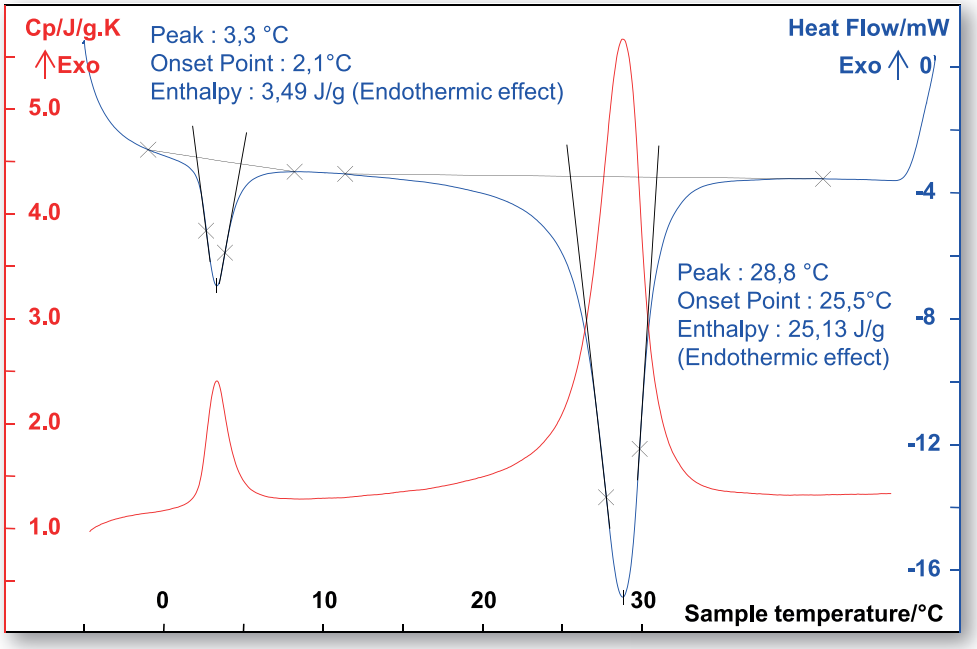
Phase change materials (PCMs) are substances with high heats of fusion which can store or release large amounts of energy before melting or solidifying. Therefore, they have been employed in thermal energy storage, building insulation and off peak power utilization for example.
Thus, many analyses are perfomed to determine the variation of enthalpy of the materials using the integral of the Cp in DSC.

EXPERIMENT

A sample of plaster containing PCM appeared like a very compact white powder.
Approximately 50 mg of sample was analyzed in order to determine the Cp.
Experiments were conducted on a DSC 131 in aluminum crucibles (100µL) at a heating rate of 3K/min between -5°C and 45°C under nitrogen. A blank was run using the same conditions.

RESULTS AND CONCLUSION

Two endotherms are observed on the DSC curve at 2.1 and 25.5°C. The first peak likely corresponds to the fusion of the water contained in the sample. The second shows the phase change of the PCM.



INSTRUMENT

CALVET

HIGHEST HEAT MEASUREMENT ACCURACY
Calvet 3D sensor based on thermocouples with Joule effect calibration

MODIFIABLE TEMPERATURE CONDITIONS
for increased flexibility and replication of real life conditions

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS
to perform even the most demanding experiments using one instrument :
- high pressure (500bar) and high vacuum
- pressure measurement and control
- mixing/stirring experiments

EXTERNAL COUPLING CAPABILITY
Designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels

SPECIFICATIONS

Temperature range (°C)	ambient to 300
Isothermal and temperature scanning (°C/min)	0.001 to 2
Pressure, measured and controlled (bar [psi])	350 [5,075] ; 600 [8,700]; 1 000 [14,600]
Cell and crucible volumes (ml)	up to 12.5

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

HIGH PRESSURE CALORIMETRY APPLIED TO THE STUDY OF CEMENT HYDRATION

EXPERIMENT

Cementing is one of the most important procedures during oil or gas well construction. It is meant to create a cement cover in the annulus between the steel casing and the wellbore. The slurry is mixed on the surface at ambient temperature and then gradually increases in temperature and pressure as it is pumped down the well. Setaram microcalorimeters equipped with controlled high pressure cells connected to an appropriate HP pump are able to simulate such conditions.

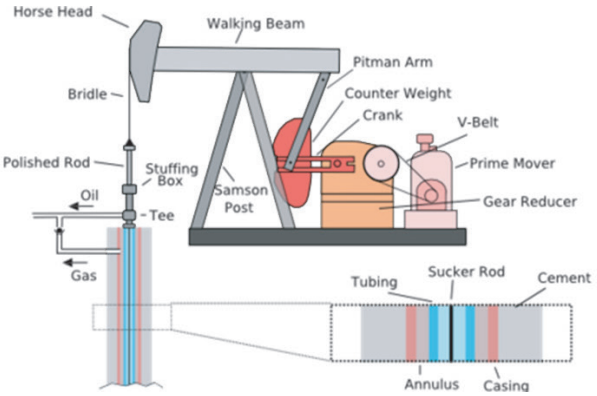


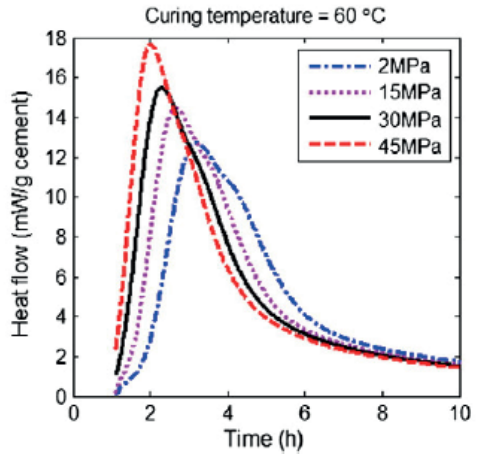
Figure 3 – Principle of an oilwell (Source: Wikipedia)

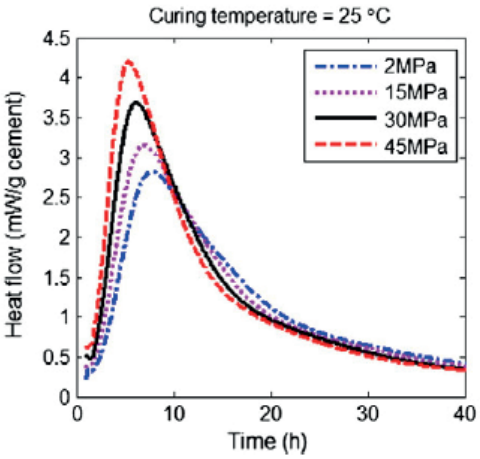
Pang et al. applied [2] to this field a CALVET calorimeter with 600 bar resistant cells. They tested class H and Class G cement with a mass of 2.8g at temperatures of 25, 40 and 60°C. The tested pressures, applied with a HP syringe pump were 20, 150, 300 and 450 bar.

RESULTS AND CONCLUSION

The effect of pressure on the Class H cement (w/c=0.38) at 25 °C and 60 °C is that with increasing pressure, the heat release rate also increases during the acceleration period.

Replicate tests for this method showed maximum differences of 7 minutes (0.12 hours) in the determination of the induction period and differences of 0.11 mW/g cement in the maximum heat release rate of hydration for the cement.





HYDRATION : CALCIUM SULFATES (PLASTER & ANHYDRITE III) IN WATER

INTRODUCTION

Four forms of calcium sulfate are known : dihydrate : $CaSO_4 \cdot 2H_20$ (gypsum), hemihydrate : $CaSO_4 \cdot ½\ H_20$ (plaster) and two anhydrites $CaSO_4$: natural and insoluble anhydrite and soluble anhydrite III (obtained by heating plaster up to 200°C). Plaster and anhydrite III, which are soluble in water, are used in the building industry, because of their setting properties. The reversal mixing vessel is particularly well adapted for the investigation of plaster setting. Water and plaster are initially separated in the vessel, then mixed.

EXPERIMENT

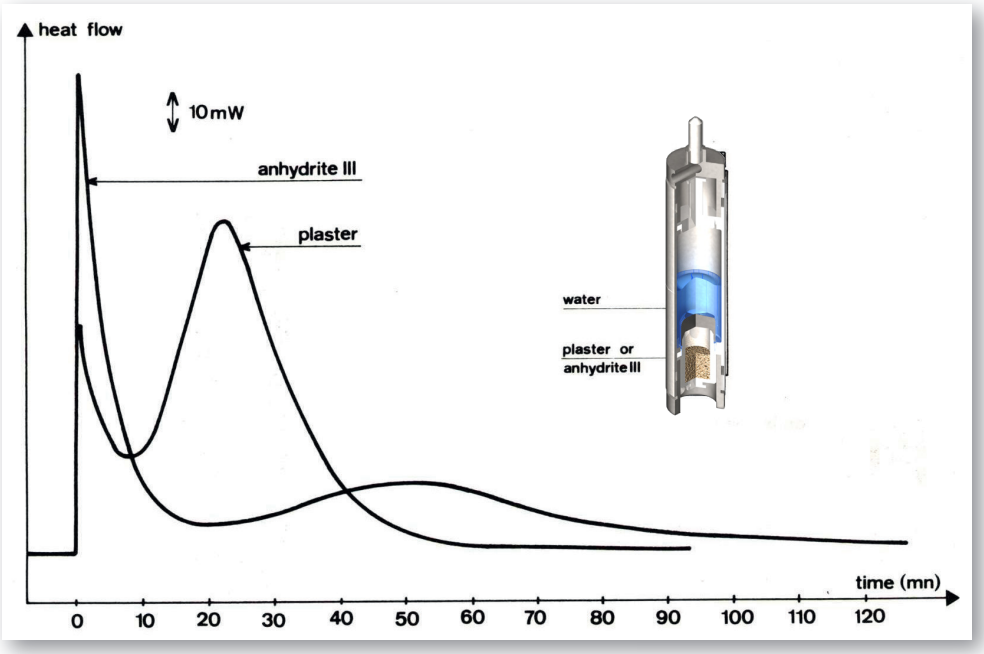
- Samples :
  Plaster (625 mg) or
  Anhydrite III (625 mg)
  Water (500 mg)
- Vessel : reversal mixing vessel
- Heating mode : isothermal 28°C

RESULTS AND CONCLUSION

The sample and water are initially separated by a lid in the mixing vessel. The mixing of the two compounds is carried out by reversing the calorimeter.
Two stages are seen on the recorded thermograms:

- dissolution of the sample in water
- setting of the mixture (hydration)

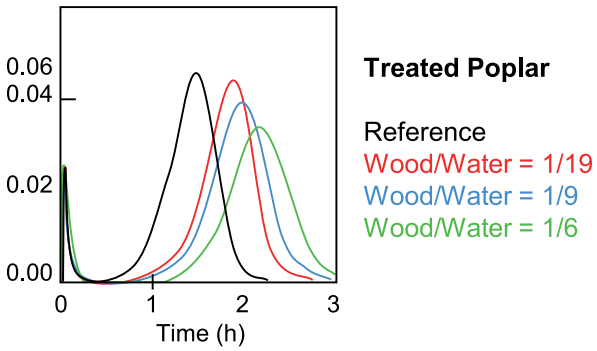
The setting can be characterized by the half crystallization time (at the top of hydration peak).
In this case the setting of plaster (t1/2 = 25 min) is faster than that of anhydrite (t1/2 = 50min).



THE INFLUENCE OF AQUEOUS WOOD EXTRACTS ON THE HYDRATION KINETICS OF PLASTER

INTRODUCTION

For several decades, many investigations have been done on the reinforcement of mineral binders (cement, concrete or plaster) using organic agents such as sisal, Kraft pulp, or cellulose fibers instead of the usual mineral reinforcing agents such as glass or asbestos fibers.



The influence of the poplar/water ratio on the hydration kinetics of plaster

EXPERIMENT

Wood extracts were prepared with various water / wood ratios in order to observe the influence of concentration. Ground wood (ten grams) was placed in ultra pure water for 1h under magnetic stirring. The mixture was then filtered using a Büchner funnel and refrigerated until the experiments took place.

A CALVET calorimeter was used with an accessory to stir the plaster and wood extract mixture. The mixture (aqueous extracts / plaster ratio 1:1) was stirred in the CALVET for 2 min after coming into contact. The experiment was performed at 25°C.

RESULTS AND CONCLUSION

Two exothermic phenomena were observed. The first corresponds to the dissolution of plaster in the liquid immediately after contact and stirring. Then, the curve returns to the baseline: during a certain time no reaction is observed. Gypsum nucleation is suspected to take place at this stage of reaction.

The second exothermic phenomenon represents the hydration reaction itself: the increase of heat flow shows, at the same time, gypsum crystal growth and plaster dissolution. After the total depletion of plaster, the heat flow decreases. Only further crystal growth occurs during the last part of the curve.
Advantages of composites plaster/wood :

- this product is healthier than cement reinforced by asbestos fibers
- it is less expensive
- it is lighter
- it makes it possible to use cellulose materials of rejects such as wood chips

The results show clearly that wood has a delaying effect on the hydration of hemihydrate.
We can also note that the peak time, which corresponds to the total depletion of plaster, increases with the wood/water ratio: the concentration of extracts influences the time of hydration.

INSTRUMENT

MICROCALVET

HIGHEST HEAT MEASUREMENT ACCURACY
Calvet 3D sensor based on Peltier elements with Joule effect calibration.

MODIFIABLE TEMPERATURE CONDITIONS
for increased flexibility and replication of real life conditions

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS
to perform even the most demanding experiments using one instrument :
• high pressure (1000bar) and high vacuum, pressure measurement and control
• mixing experiment

EXTERNAL COUPLING CAPABILITY
Designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels

SPECIFICATIONS

Temperature range (°C)	-45 to 120
Isothermal and temperature scanning (°C/min)	0.001 to 2
Pressure, measured and controlled (bar [psi])	400 [5,800] 1 000 [14,600]
Cell and crucible volumes (ml)	up to 1

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

ISOTHERMAL MIXING CALORIMETRY APPLIED TO THE STUDY OF CEMENT HYDRATION

EXPERIMENT

Ordinary Portland Cement is mainly composed of tricalcium silicate (C3S) dicalcium silicate (C2S), and tricalcium aluminate (C3A). It may also have low-level gypsum content. When mixed with water, after a fast partial dissolution, both C3S and C2S react with water to form calcium silicate hydrate and calcium hydroxide. These effects can be observed during an in-situ mixing calorimetry experiment as shown in figures 1 and 2.

RESULTS AND CONCLUSION

We can notice that immediately after the mixing operation, a fast and highly exothermic effect is recorded (i). According to Biernacki [1], this exotherm can be attributed to the dissolution of the tricalcium silicate (C3S) part of the cement powder. Because its kinetics are so fast, this event cannot be accurately detected and interpreted with ex-situ mixing techniques. Longer term data (hydration and hardening) are presented in figure 2.

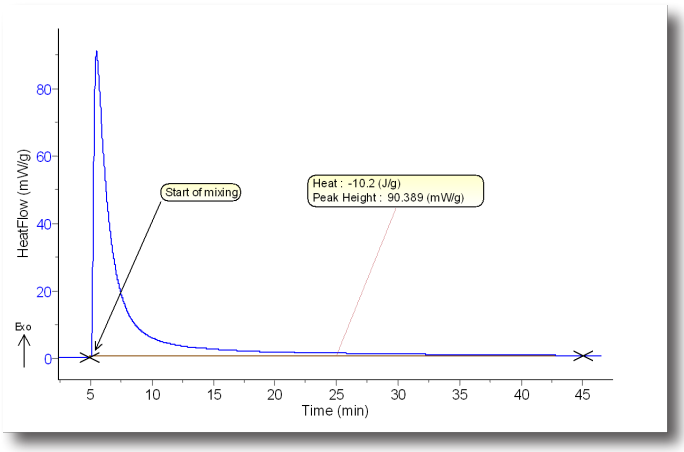


Figure 1 – In-situ mixing experiment (CEM 52.5M cement) - first hour

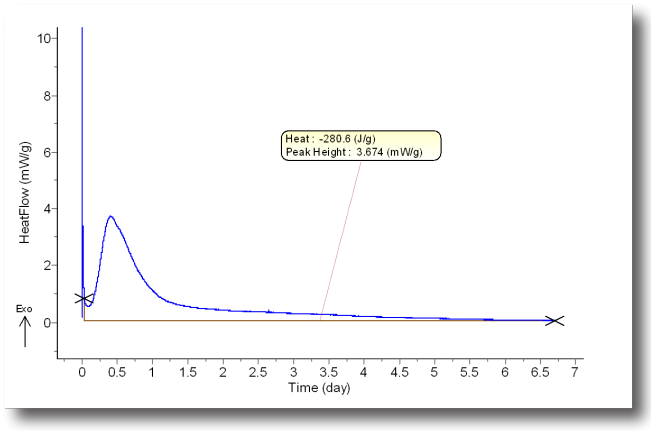


Figure 2 – Mixing experiment (CEM 52.5M cement) - up to 7 days

VS • Specifications are given as indications only and are not contractual • 12/25

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