TAM AIR
ISOTHERMAL CALORIMETRY

New Castle, DE USA

Lindon, UT USA

Hüllhorst, Germany

Wetzlar, Germany

Shanghai, China

Beijing, China

Tokyo, Japan

Seoul, South Korea

Taipei, Taiwan

Bangalore, India

Sydney, Australia

Guangzhou, China

Eschborn, Germany

Brussels, Belgium

Etten-Leur, Netherlands

Paris, France

Elstree, United Kingdom

Barcelona, Spain

Milano, Italy

Warsaw, Poland

Prague, Czech Republic

Sollentuna, Sweden

Copenhagen, Denmark

Chicago, IL USA

São Paulo, Brazil

Mexico City, Mexico

Montreal, Canada



TAM AIR isothermal calorimetry

Monitoring the thermal activity or heat flow of chemical, physical and biological processes provides information which cannot be generated with other techniques. Isothermal calorimetry is a powerful technique for studying heat production or consumption and is non-destructive and non-invasive to the sample. The TAM Air offers unmatched sensitivity and long-term temperature stability with flexible sample requirements.

The TAM Air is the ideal tool for large scale calorimetric experiments, capable of measuring several samples simultaneously under isothermal conditions. This system is especially well-suited to processes that evolve or consume heat over the course of days and weeks such as cement and concrete hydration, food spoilage, microbial activity and more.

A Powerful Tool for the Study of Cement and Concrete Hydration Processes

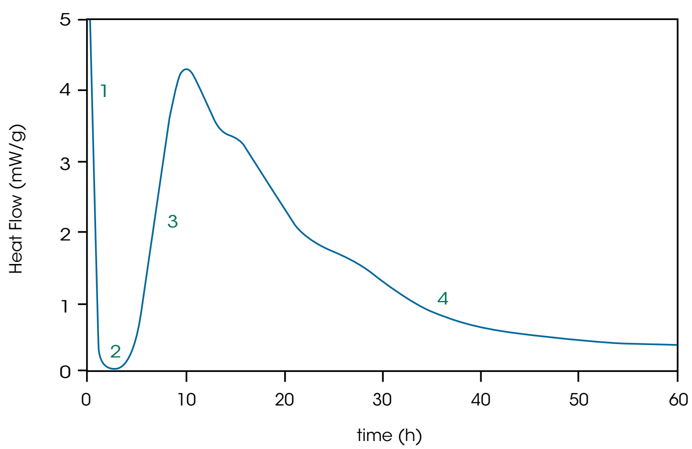
Determining the heat of hydration of cement and concrete is important and traditionally the heat of hydration has been determined by measuring the heat of solution (ASTM C186). More recently, isothermal calorimetry tests using TAM Air are favored because they accurately and reliably measure the heat of hydration (ASTM C1702) and predict the setting behavior of various cement mixtures. The samples tested in the TAM Air are often paste samples, where the cement hydration process can continuously be followed over time; it is also of importance to test not only the cement but also the final mixture of mortar or concrete. This allows for detection of incompatibility between the materials. The mixing effect on the same cement in a paste and in a concrete mixture will also be different as the aggregates will add to the shear forces.

Reliable, Robust, Versatile

The 8-Channel Standard Volume TAM Air is ideal for homogenous paste samples while the 3-Channel Large Volume calorimeter can accommodate the more heterogenous concrete samples as well. The shape of the heat flow curve will reflect the cement hydration process and the different phases of the complex process can be determined.

The addition of admixtures will change the shape of the heat flow curve and the admixture effect can be quantified. The integrated heat flow over time will give the extent of hydration. Using isothermal calorimetry, the heat of hydration is measured with TAM Air by monitoring the heat flow from the specimen while both the specimen and the surrounding environment are maintained at the same temperature. With this ability to accurately maintain a stable temperature over long periods of time, the TAM Air has become the instrument of choice for studying not only the reaction kinetics of pure cement pastes, but also the temperature-dependence of these reactions. The TAM Air is a reliable, robust tool for quality control analyses in cement plants, understanding and optimizing innovative cement admixtures during product development, and general research within the cement R&D laboratory.

Instrument of Choice for Standardized Testing on Cement and Concrete



Phase 1: Rapid initial process – Dissolution of ions and initial hydration

Phase 2: Dormant period – Associated with a low heat evolution and slow dissolution of silicates

Phase 3: Acceleration period – Silicate hydration

Phase 4: Retardation period – Sulphate depletion and slowing down of the silicate hydration process

Performance Specifications

	3-Channel Large Volume Calorimeter	8-Channel Standard Volume Calorimeter
Thermostat Specifications		
Calorimeter Positions	3	8
Operating Temperature Range	5 °C to 90 °C	5 °C to 90 °C
Thermostat Type	Air	Air
Thermostat Stability	± 0.02 °C	± 0.02 °C
Maximum Sample Size	125 mL	20 mL
Calorimeter Specifications		
Limit of Detection	8 µW	4 µW
Short Term Noise	<± 8 µW	<± 2.5 µW
Precision	± 40 µW	± 20 µW
Baseline over 24 hours		
Drift	< 80 µW*	< 40 µW*
Deviation	<± 20 µW	<± 10 µW
Error	<± 45 µW	<± 23 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

Isothermal Calorimetry

Calorimetry requires little or no sample pretreatment; solids, liquids and gases can all be analyzed. When heat is produced in a sample, isothermal calorimetry measures the heat flow. The sample is placed in an ampoule that is in contact with a heat flow sensor that is also in contact with a heat sink. When heat is produced or consumed by any process, a temperature gradient across the sensor is developed. This will generate a voltage, which is measured. The voltage is proportional to the heat flow across the sensor and to the rate of the process taking place in the sample ampoule. This signal is recorded continuously and in real time.

For each sample there is a reference that is on a parallel heat flow sensor. During the time that the heat flow is monitored, any temperature fluctuations entering the instrument will influence both the sample and the reference sensors equally. This architecture allows a very accurate determination of heat that is produced or consumed by the sample alone while other non-sample heat disturbances are efficiently factored out.

High Performance Temperature Control and Stability

The TAM Air is an air-based thermostat, utilizing a heat sink to conduct the heat away from the sample and effectively minimize outside temperature disturbances. The calorimeter channels are held together in a single removable block. This block is contained in a thermostat that uses circulating air and an advanced temperature regulating system to keep the temperature very stable within ±0.02 K. The high accuracy and stability of the thermostat makes the calorimeter well-suited for heat flow measurements over extended periods of time, e.g. weeks. TAM Air Assistant™, a powerful, flexible and easy-to-use software package, is used for instrument control, experimental setup, data analysis and reporting of results.

The Isothermal Calorimetry Advantage

Isothermal calorimetry, as practiced using the TAM Air, has several advantages over other calorimetric techniques for heat of hydration measurement. Unlike the legacy solution method, isothermal tests using the TAM Air are extremely safe, provide continuous real-time data, and require little intervention by the operator.

Isothermal experiments using the TAM Air also have distinct advantages over adiabatic and semi-adiabatic measurements. These non-isothermal techniques are subject to temperature changes brought about by the heat of reaction which may be unrealistic. Maintaining isothermal control greatly improves the ability to differentiate between reaction temperatures, increases the resolution between hydration events, and allows for accurate modeling of reaction kinetics.

Calorimeters

The TAM Air calorimeter block is available in two versions, both employing twin-type calorimeters. The 3-Channel Large Volume Calorimeter block has three twin-type calorimeters that can accommodate 3 samples of up to 125 mL volume. The 8-Channel Standard Volume Calorimeter can accommodate eight samples of up to 20 mL volume. In both calorimeter blocks, all the samples can be measured simultaneously and independently of each other. The only characteristic of each experiment in common is the thermostat temperature. The calorimeter blocks are interchangeable in the TAM Air thermostat and enable a high level of flexibility depending on the sample size and physical format.

8-Channel Standard Volume Calorimeter

The TAM Air 8-Channel Standard Volume Calorimeter consists of an eight-channel twin-type calorimeter block and data logging system. The calorimeters are designed for 20 mL glass or plastic ampoules or the 20 mL Admix ampoules. This sample volume is ideal for measuring more homogeneous materials such as unfilled cement through its hydration process, foods, biological materials, and thermosets in curing.

3-Channel Large Volume Calorimeter

The TAM Air 3-Channel Large Volume Calorimeter consists of a three-channel twin-type calorimeter block and data logging system. The calorimeters are designed for 125 mL glass or stainless steel ampoules. This large volume calorimeter design is especially important for heterogeneous samples and those that contain large particles, such as concrete with aggregate and soil samples.

TAM Air Ampoules

The sample handling system for TAM Air includes static 20 mL and 125 mL ampoules, as well as a 20 mL Admix ampoule system. The ampoules available for use in the 8-Channel Calorimeter block accommodate sample sizes up to 20 mL volumes. Both glass and plastic (HDPE) closed ampoules are available. These ampoules enable maximum flexibility for sample management and sensitivity. The 3-Channel Large Volume Calorimeter block accommodates sample sizes of up to 125 mL. These 125 mL ampoules are available in both glass and stainless steel.

20 mL HDPE

20 mL Glass

125 mL Glass

125 mL Stainless Steel

Admix Ampoule

The Admix Ampoule is a 20 mL accessory available for the 8-Channel Standard Volume Calorimeter. It is used for initiating reactions inside the calorimeter, and can be used for monitoring a reaction from the initial injection. The Admix Ampoule can be configured with or without a motor for stirring. For samples such as mixtures of cement and water, manual stirring is recommended. For liquid systems, a motor may be used for stirring. The Admix Ampoule can only be used with 20 mL disposable glass ampoules.

Admix Ampoule with manual stirring

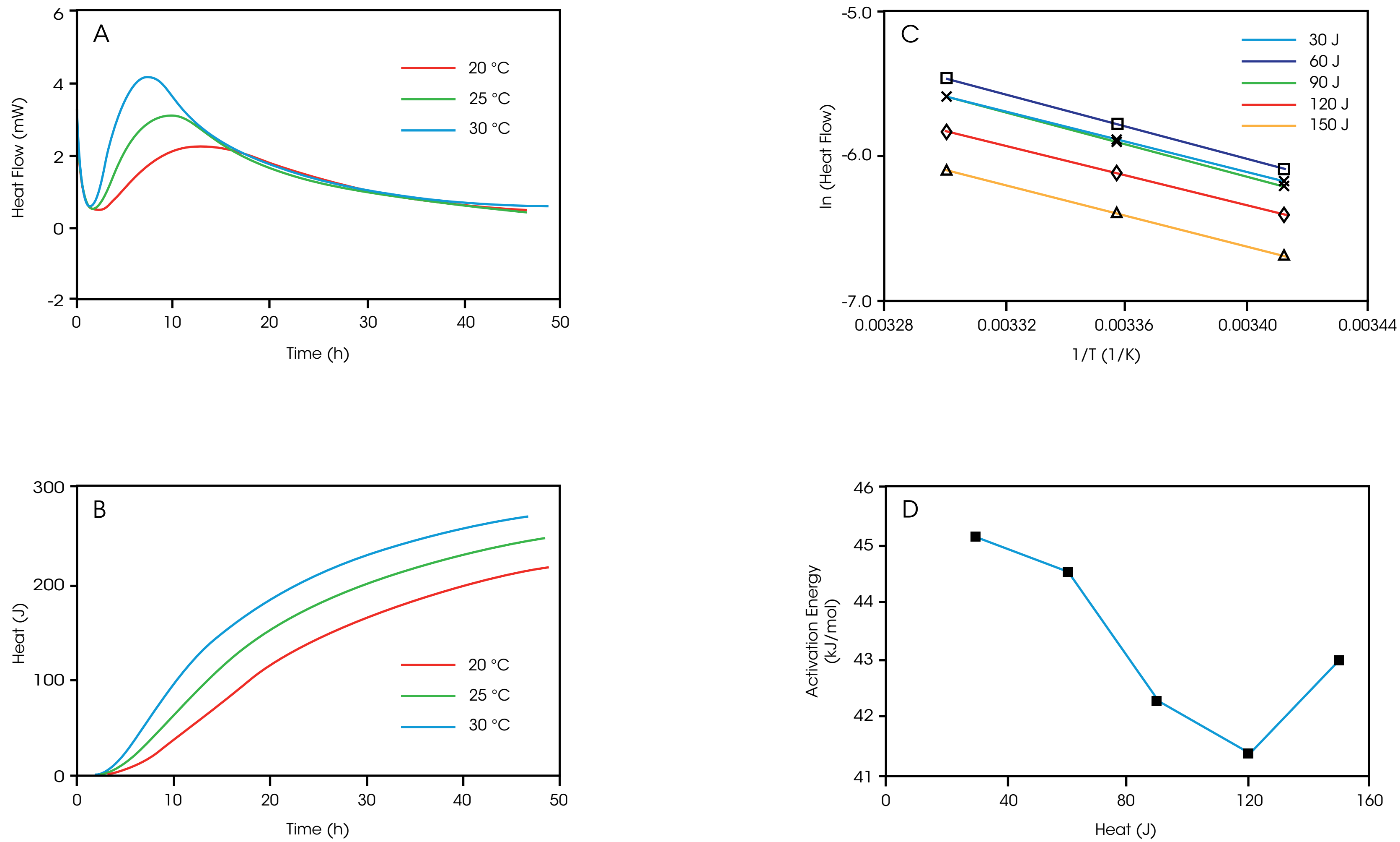
Admix Ampoule with stirring motor

Complexity of Cement Hydration Process

The cement hydration process is temperature-dependent and mechanistically complex. Controlled studies at multiple temperatures provide setting profiles at each condition as well as insight into the multiple chemical reactions and their individual temperature dependencies.

The directly measured output of a TAM Air measurement is the heat flow profile over time. A direct reflection of the rate of reaction, this is shown for three temperatures of the same system in Figure A. The integral of this heat flow over time, the Total Heat, is a measure of the extent of reaction, and is also shown in Figure B.

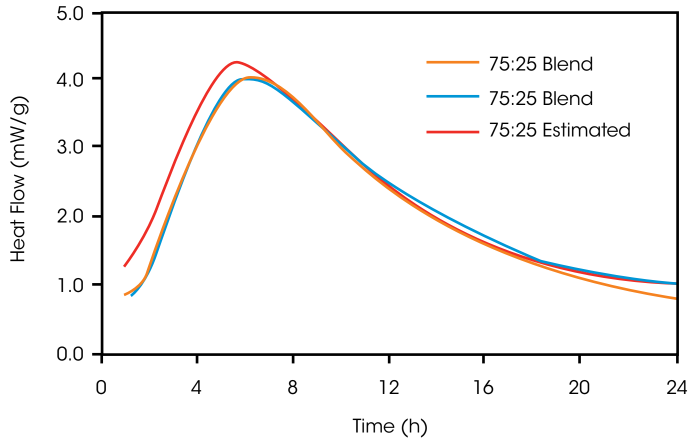
An Arrhenius plot of the reaction rate (heat flow) at several defined extents of reaction (total heat) allows for the calculation of the apparent activation energy at each stage of the process. A reaction with a single mechanism would show a constant activation energy throughout the process. As shown in Figure D, the cement hydration process is complex, going through several sub processes realised by the multiple activation energies.

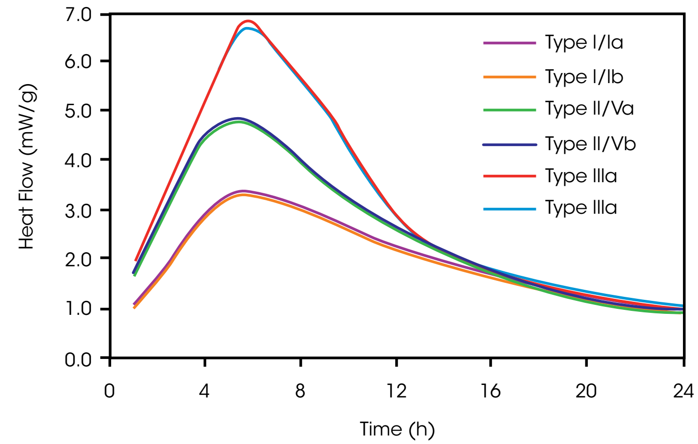

A
Heat Flow (mW)
Time (h)
20 °C
25 °C
30 °C
6
4
2
0
-2
0
10
20
30
40
50
B
Heat (J)
Time (h)
300
200
100
0
C
ln (Heat Flow)
1/T (1/K)
30 J
60 J
90 J
120 J
150 J
-5.0
-6.0
-7.0
0.00328
0.00332
0.00336
0.00340
0.00344
D
Activation Energy
(kJ/mol)
Heat (J)
46
45
44
43
42
41
0
40
80
120
160

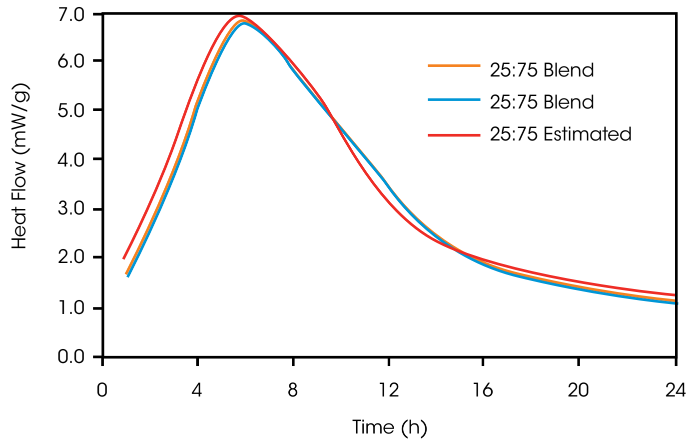
Cement Blending

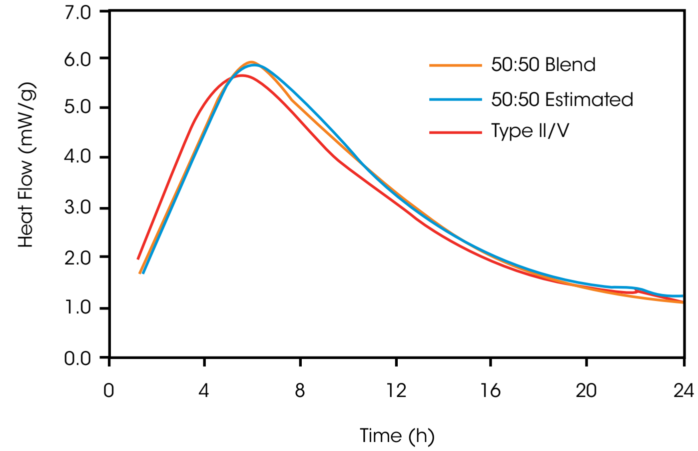
This figure provides plots of the heat release rate (heat flow) for the first 24 h of hydration for six cement pastes examined by isothermal calorimetry (3 pure and 3 blends). In general, results for the two replicate specimens for each cement paste fall directly on top of one another. For the three initial cements, the heat release during the first 24 h increases with increasing cement fineness, as would be expected due to the increased (in contact with water) surface area. Interestingly, for these six cements based on a single clinker, the peak in heat release rate always occurs at about 6 h, while by 24 h, the heat release rate has diminished to a value close to 1 mW/g cement.

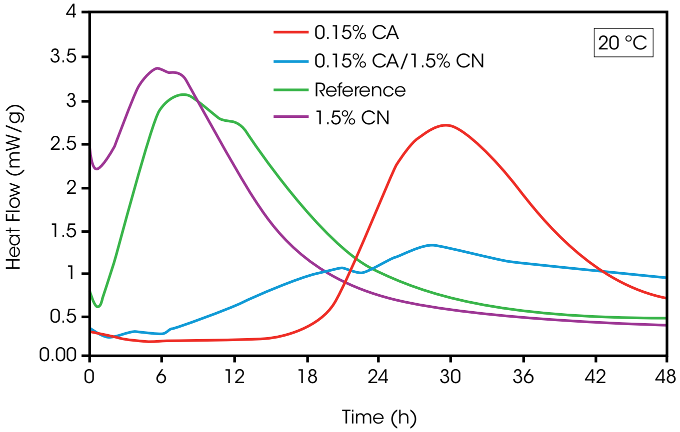
The heat flows measured during the first 24 h for the three blended cements are predicted quite well by applying the simple law of mixtures. The results imply that for the w/c = 0.4 cement pastes examined in this study, the particles are likely hydrating independently of one another during the first 24 h, such that the degree of hydration of blends of the fine and coarse cements can be quite accurately computed simply as a weighted average of their (measured) individual hydration rates. [1]

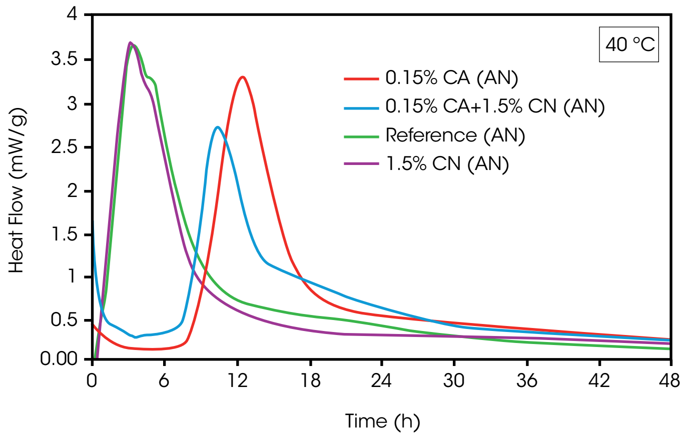

75:25 Blend
75:25 Blend
75:25 Estimated
Heat Flow (mW/g)
Time (h)
5.0
4.0
3.0
2.0
1.0
0.0
0
4
8
12
16
20
24


Type I/Ia
Type I/Ib
Type II/Va
Type II/Vb
Type IIIa
Type IIIa
Heat Flow (mW/g)
Time (h)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
4
8
12
16
20
24


25:75 Blend
25:75 Blend
25:75 Estimated
Heat Flow (mW/g)
Time (h)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
4
8
12
16
20
24


50:50 Blend
50:50 Estimated
Type II/V
Heat Flow (mW/g)
Time (h)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
4
8
12
16
20
24

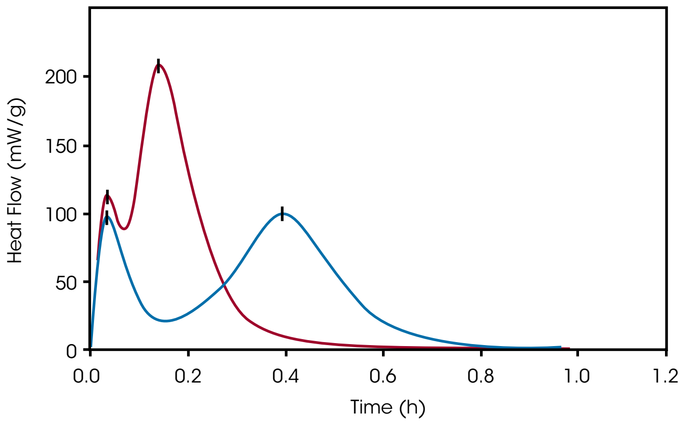


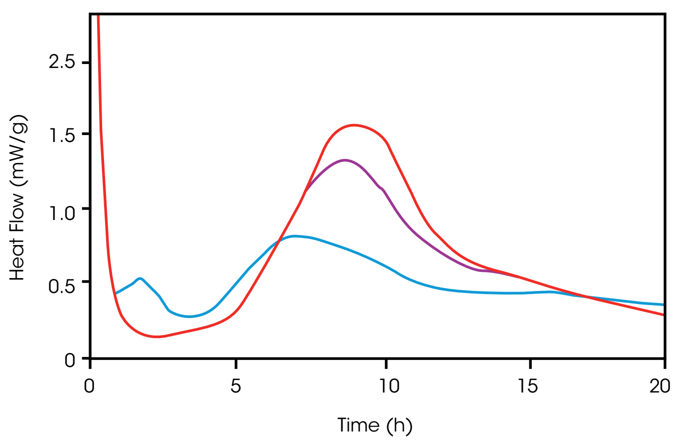


Cement Paste Setting Time

The synergy of citric acid (CA) and calcium nitrate (CN) is clearly seen from the rate of hydration heat. CA is essentially a setting retarder relative to the reference, although the heat of hydration is slightly reduced and CN is clearly a setting accelerator. Together they behave as a hardening retarder lowering the rate of hydration heat and distributing it over a longer time.

The rate of hydration heat for the same mixtures at 40 °C shows that the function as hardening retarder is reduced at higher temperature. This data along with the cumulative heat data indicate that the admixture combination may not function in the semi-adiabatic case of massive concrete. [2]



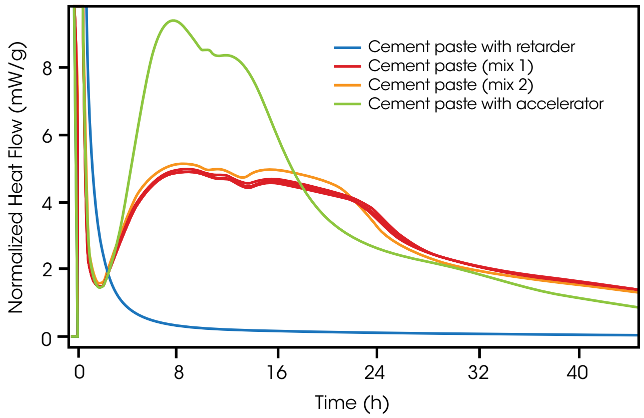


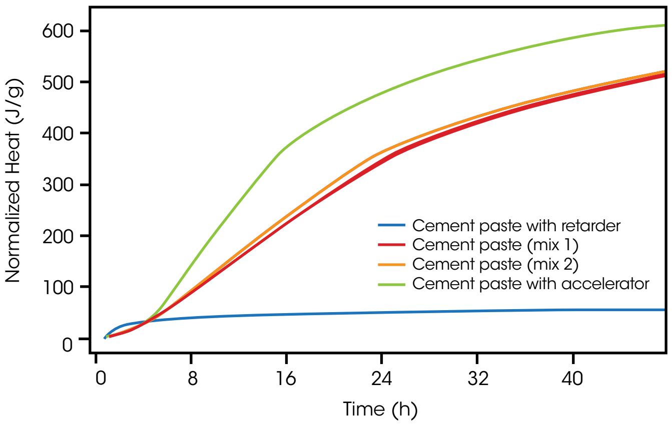
Hydration of Calcium Sulfate Hemihydrate

Identical samples of 2 g of calcium sulfate hemihydrate powder were mixed with a hydrating agent at a liquid to solid ratio of 1:2 using an admix ampoule in the TAM Air. The blue curve represents data for a sample hydrated with deionized water. The red curve is for a sample hydrated with a 5% sodium chloride solution. It is demonstrated that sodium chloride accelerates the calcium sulfate hydration reaction.

Setting Time of Cement

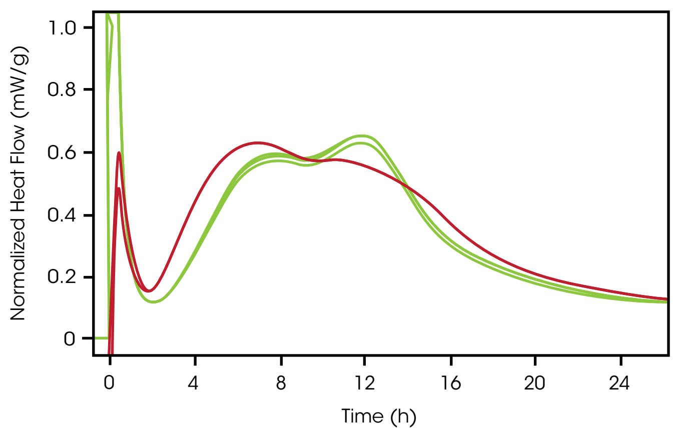
The TAM Air calorimeter has been shown to be excellent for diagnosis of problems related to setting time and premature stiffening of cement. The blue curve in the figure to the right represents an industrial cement produced with too little soluble calcium sulfate. This cement suffers from early stiffening because of the aluminate reactions at 1–1.5 h hydration. It also suffers from low early strength, because the aluminate hydrates formed retard the strength-giving silicate hydration indicated by the unusually small silicate peak at 5-10 h. When 0.5% (purple curve) and 1.0% (red curve) of calcium sulfate hemi-hydrate was added to the cement the undesired early peak disappeared, and the strength-giving silicate peak regained its normal shape. The results indicate that premature stiffening is caused by a lack of soluble calcium sulfate.

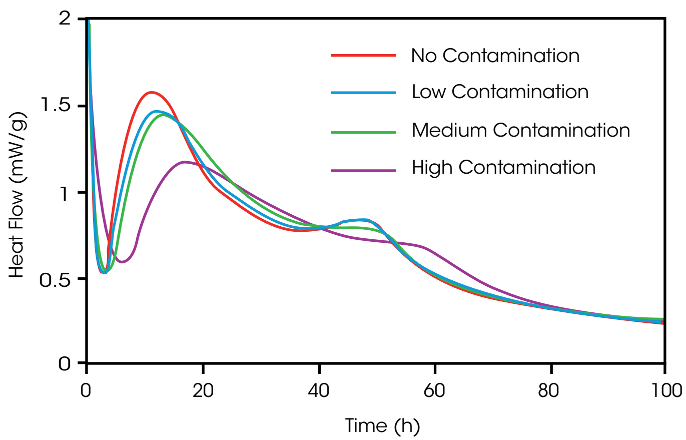




Cement Paste Variations

In this example three cement pastes (w/c 0.45) were measured at 25 °C in the 3-Channel Large Volume Calorimeter for the TAM Air. The paste is measured as a fresh specimen (red), an identical formula mixed and measured a week later (orange), with an admixture accelerator (green), and with a retarder (blue). The accelerator can be seen to accelerate the silicate reaction while the retarder accelerates the initial aluminate reaction but greatly retards the silicate reaction. The total heat evolved is a measure of the overall extent of reaction. In this representation it is especially easy to see the initial acceleration of the aluminate reaction caused by the retarder, but the silicate reaction which drives setting is delayed beyond the time scale of this study.



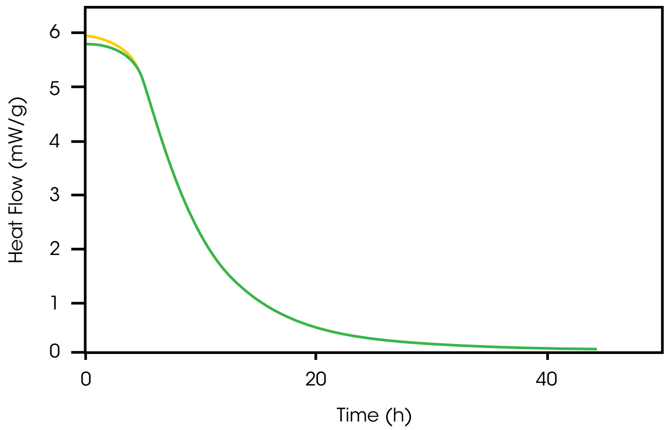


Hydration Process of Concrete

The hydration process of two different concrete (w/c 0.55) samples with (green curves) and without superplasticizer (red) were measured using the TAM Air 3-channel Large Volume Calorimeter. The samples were prepared to contain 50 % small aggregates (0-8 mm) and 33 % large aggregates (8-16 mm). The concrete in this example is a shotcrete and the superplasticizer is used to first be able to pneumatically apply the concrete onto a surface and have it stick to this surface even if it is on a vertical wall or a roof. The high capacity of the 3-channel Large Volume Calorimeter allows for these filled samples to be measured under their exact use conditions.

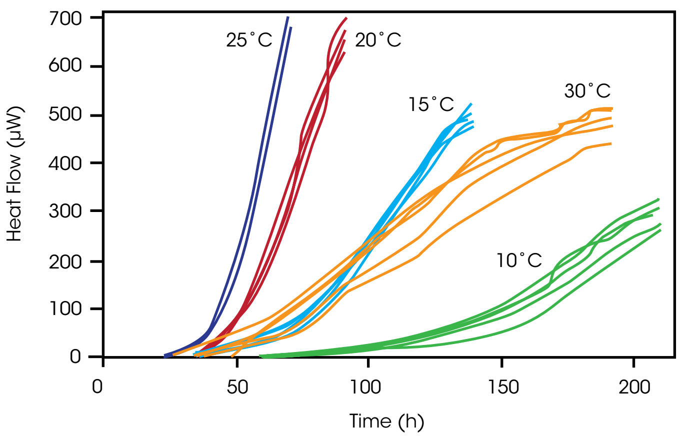
Cement Thermal Profiles with Contaminants

Cement setting thermal profiles can be influenced by contaminants. The graph shows the steady decrease in thermal power as the contamination of the cement mortar by a mixture of soil and sawdust increases (0; 0.9; 2.5 and 5.9% of w/c = 0.6 cement mortar).



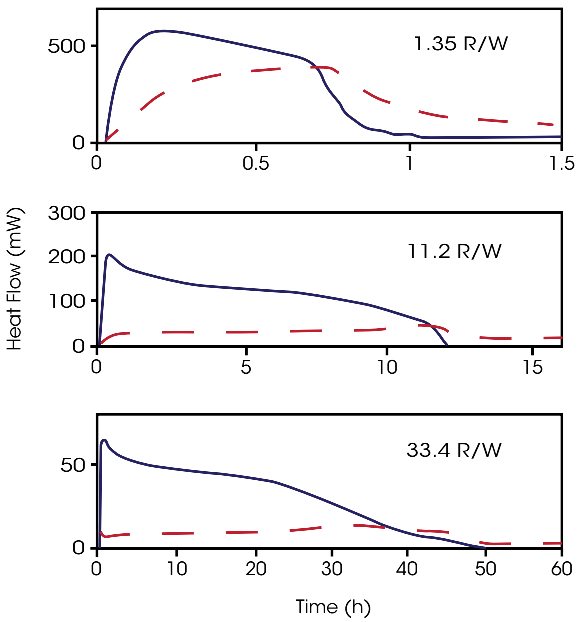
Epoxy Curing

Here we see the heat flow as a function of time. It can be seen that the spread of results is low and that after an initial reaction period of five hours the heat production rate decrease is similar to an exponential decay. After 45 h the thermal power is approx. 0.06 mW/g, i.e. 600 μW for a 10 g sample. As the detection limit for TAM Air is better than 4 μW it would still be possible to follow the reaction for an even longer time than was done here. [3]



Fungal Growth

At each temperature multiple inoculated specimens were measured. This figure shows the results at the five temperatures. It is seen that the results for each temperature agrees rather well with each other. Calorimetric measurements can be a valuable addition to the measurement techniques for predictive microbiology. [4]



TAM Air Battery Testing

The properties of batteries during discharge with three different resistance loads are shown. Single channels in TAM Air were charged with 1.5 V alkaline batteries, size AAA. Three resistors of different values were placed in an adjacent channel for connection to the batteries. The solid line represents the useful energy in the battery which is the heat production measured in the resistor, while the dotted line is the heat production from the battery itself, i.e. the internal losses.

The batteries were fully discharged during the course of the evaluation in the TAM Air. The lowest resistances cause a rapid drain of the battery (e.g. as in a flashlight) whereas the highest resistances cause a very low rate of discharge (e.g. as in an alarm clock). [5]

notes

[1] Bentz, D.P. Blending Different Fineness Cements to Engineer the Properties of Cement-Based Materials. Mag. Concrete Res.
[2] Justness, H., Wuyts, F. and D. Van Gemert. Hardening Retarders for Massive Concrete. Thesis. Catholic University of Leuven. 2007.
[3] Wadsö, L. Curing of Epoxy Adhesive Studied by TAM Air. TA Instruments Application Note 2007.
[4] Lars Wadsö and Yujing Li. A test of models for fungal growth based on metabolic heat rate measurements. 2000.
[5] Lars Wadsö. Investigations into Dry Cell Battery Discharge Rates using TAM Air. 2000. TA Instruments, AN 314-03.

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