

# Measurements of the Influence of Storage Time and Storage Temperature on Properties of Raw Inorganic Binders and Dry Mortars

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## Abstract

Inorganic binders and dry mortars were stored in room climate and in a freezer over a four-year period. The rate of reaction and flow properties (only dry mortar) were tested to study the influence of storage time and storage temperature on the materials. Material properties were found to change in time and material stored at room temperature showed significantly higher changes than material stored at low temperature.

## 1. Introduction

Testing of material properties is a frequent matter in material science. Many raw materials, such as cement and calcium sulphates change their properties when stored. As they mainly are natural materials, the properties of newly produced products also change over time. This makes it hard to evaluate repeated tests or to extend measurement series at later stages as the materials used have changed their properties during storage and that newly manufactured materials may have different properties.

Changes in material properties over time are caused by chemical or physical processes [1] or by interaction with the ambient environment such as humidity from air. As the rates of most processes increase with an increase in temperature, storing material in a freezer instead of at room temperature would be expected to slow down these processes.

The isothermal heat production from a cement specimen that is mixed with a certain amount of water will have a specific pattern at a given temperature. This can be used as a fingerprint of the material as it is the result of all chemical reactions that proceed in the material. If the properties of a raw material change significantly, this will most probably also influence the heat production of the material.

The aim of the present investigation is to study whether there will be any significant differences in properties of raw materials when stored at different temperatures over a long time period. For this purpose, isothermal calorimetry was used to monitor heat production as a function of time. Some tests of flow properties were also made.

## 2. Materials

Three raw materials and three commercial self-levelling flooring compounds (SLC) were tested:

- Portland cement (PC) w/c 0,4
- Calcium aluminate cement (CAC) w/c 0,38
- Beta-hemihydrate calcium sulphate (beta-HH) w/b 0,35
- Normal drying SLC A, w/b $\approx$ 1,0
- Rapid drying SLC B, w/b $\approx$ 0,7
- Industrial SLC C, w/b $\approx$ 0,6

The SLC contain a mixture of PC, CAC and calcium sulphate as binders and fine aggregates, fillers and additives. A general description of such materials is given by Harbron in [2] and materials A, B and C are further described by Anderberg and Wadsö in [3].

## 3. Method

All materials were stored in glass jars sealed with metal screw caps with rubber seals during the whole period and were not exposed to light while being stored. The first measurements were performed 4-5 months after the material had been manufactured. Part of the material had been stored at room temperature and part of it in a freezer at  $-25$  °C. No difference could be seen between materials stored at different temperatures at this stage. Measurements after 4-5 months on material stored at room temperature are therefore used as reference values in the present study. New measurements of all materials, stored both at room temperature and in a freezer at  $-25$  °C were performed after about two and four years.

The isothermal calorimeters used (TAM Air, Thermometric AB, Järfälla, Sweden) consist of eight isothermal heat conduction calorimeters in a thermostat. Each calorimeter holds a 20 ml ampoule with the sample and a similar reference ampoule. 200 g of dry powder of each material was mixed with water outside the calorimeter for two minutes and about 10 g (5 ml) were poured into each ampoule, after which the ampoule was sealed, weighed, and charged into the calorimeter. This process took about 4 minutes. Each measurement continued for three days and double specimens were used for each material.

There will always be an initial disturbance during about 15 minutes when a sample is charged into the calorimeter due to that the sample does not have the same temperature as the calorimeter. This will happen even if the sample is carefully thermostated before the measurement. It is possible to remove a large part of this disturbance with the Tian equation, Eq. 1, where  $P$  (W/g) is the thermal power after

correction,  $P_0$  (W/g) is the thermal power prior to correction and  $\tau$  (s) is the time constant.

$$P = P_0 + \tau \frac{dP_0}{dt} \quad (1)$$

In cement calorimetry it is usually not necessary to do this correction except for fast setting systems and in studies of initial reactions. In this study the Tian correction was only used for beta-hemihydrate hydration.

The most sensitive property of SLC is the flow and most products are manufactured to be within certain flow test limits. In addition to calorimetric measurements, the flow of the SLCs was also tested after four years and compared with recommended target values. A 68 mm diameter, 35 mm high ring and a glass plate were used. The products were mixed and directly poured into the ring. Ten minutes after starting mixing, the ring was slowly lifted during three seconds and material still on the ring were allowed to drip off for ten seconds. The diameter was measured after three minutes in two perpendicular directions.

#### 4. Results

The calorimetric results are presented as graphs showing the thermal power as a function of time for the first hours after mixing and the thermal power as a function of the heat. The heat is the integral of the thermal power. The graphs presenting the thermal power as a function of time show the measured calorimetric values as from time 0, start of mixing. The heat produced is calculated from the start of the main reaction, which is set to be when the rate of reaction starts to increase again after the dormant period. Note that the thermal power is related to the reaction rate and the heat to the extent of reaction (degree of hydration), so these graphs are essentially showing the rate of reaction as a function of the extent of reaction. For clarity are only four measurements shown in the graphs below, reference measurements after four months, measurements after 20 and 48 months of material stored at room temperature and measurements after 48 months of material stored in a freezer.

The results for the Portland cement, Figs 1 and 2, show a clear decrease in rate of reaction with storage time as well as a slightly increased dormant period when stored at room temperature. Storing in a freezer for 48 months gave similar results as storing in room climate for 20 months.

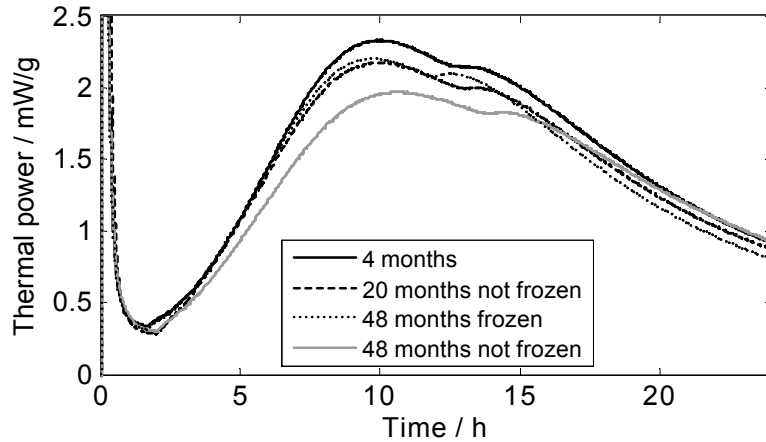


Figure 1. Portland cement, thermal power as a function time.

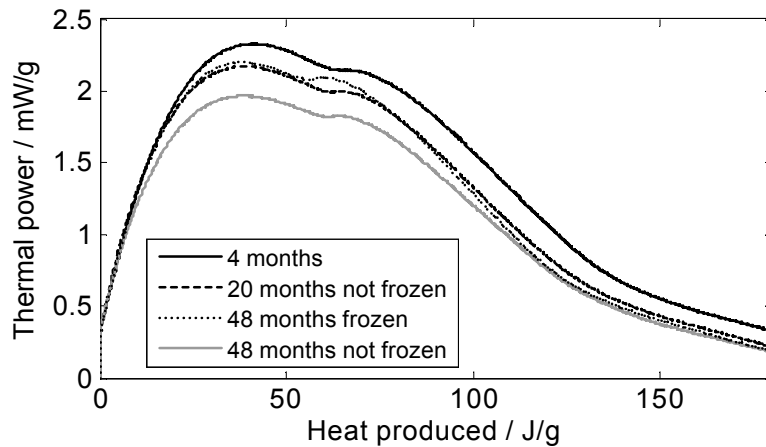


Figure 2. Portland cement, thermal power as a function of the extent of reaction, heat.

The measurements performed on aluminat cement, Figs. 3 and 4, show a different behaviour compared to Portland cement. The dormant period decreases in time when stored at room temperature. The decrease in dormant period when stored at low temperature was very small. However, when comparing the rate of reaction as a function of the extent of reaction there was a significant difference between the measurement at four months and the other measurements while there was little difference between materials stored at room temperature and at a lower temperature.

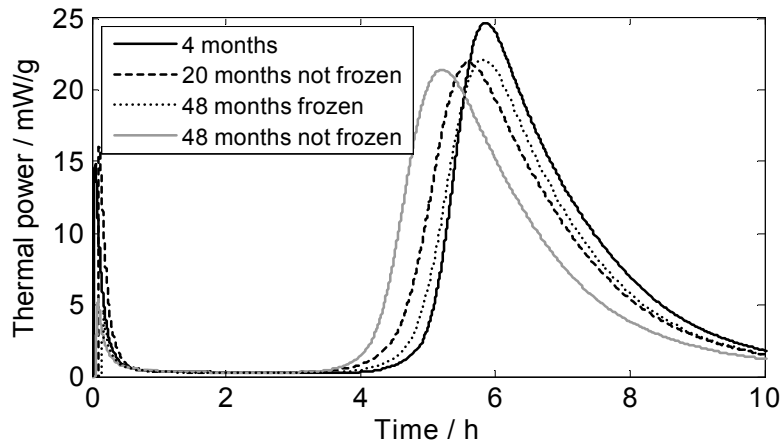


Figure 3. Aluminate cement, thermal power as a function of time.

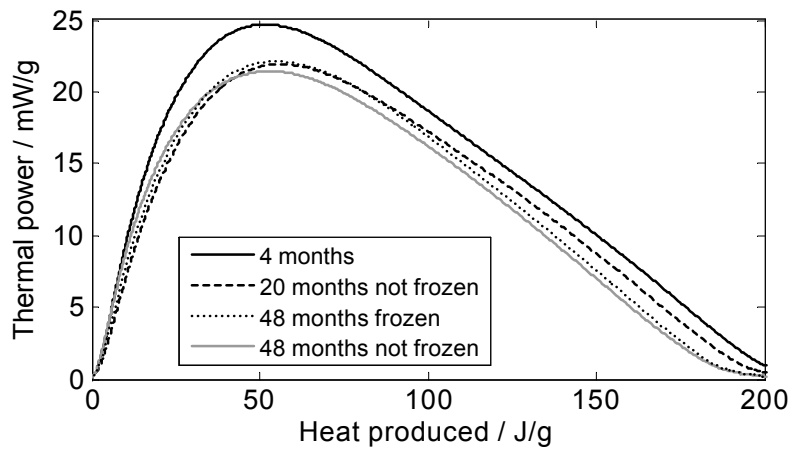


Figure 4. Aluminate cement, thermal power as a function of the extent of reaction, heat.

For beta-HH, Fig. 5, the main reaction started after less than 20 minutes after mixing. These results have therefore been corrected with the Tian correction, Eq. 1. As no clear point for starting the integration calculating of the heat could be found, the thermal power as function of heat is not shown. The results did not show any clear trends.

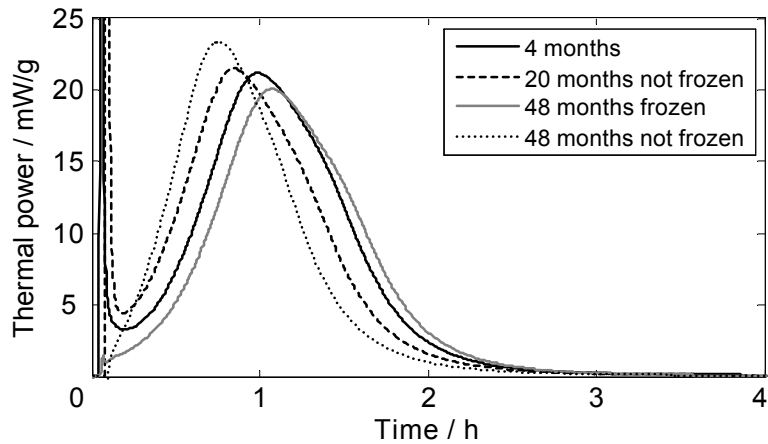


Figure 5. Beta-HH, thermal power as a function of time.

Measurements performed on the three SLCs are presented in Figs. 6-11. The graphs principally show a consistent pattern for all three materials when stored at room temperature. The dormant period is prolonged and the rate of reaction is lower when the storage time is increased. Material stored at a lower temperature show nearly similar dormant periods as reference measurements and only slightly lower reaction rates as functions of the extent of reaction.

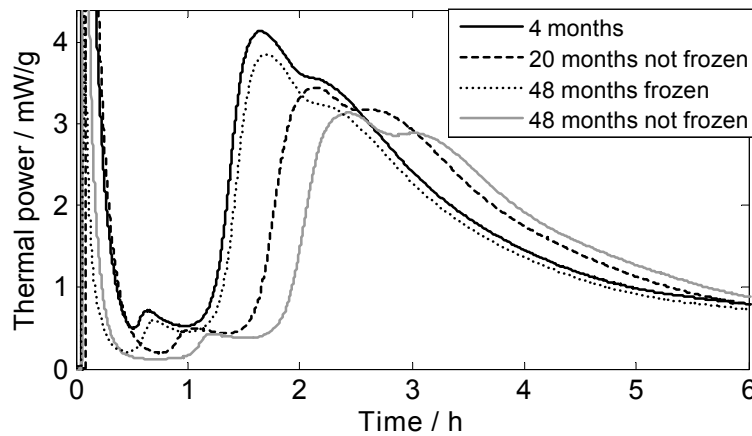


Figure 6. SLC A, thermal power as a function of time.

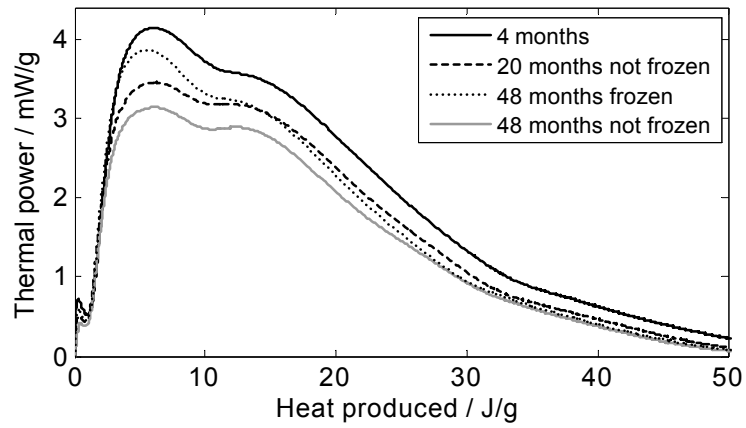


Figure 7. SLC A, thermal power as a function of extent of reaction, heat.

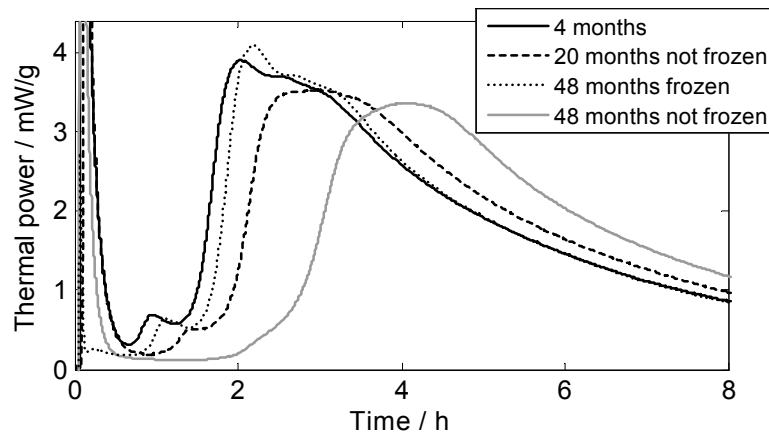


Figure 8. SLC B, thermal power as a function of time.

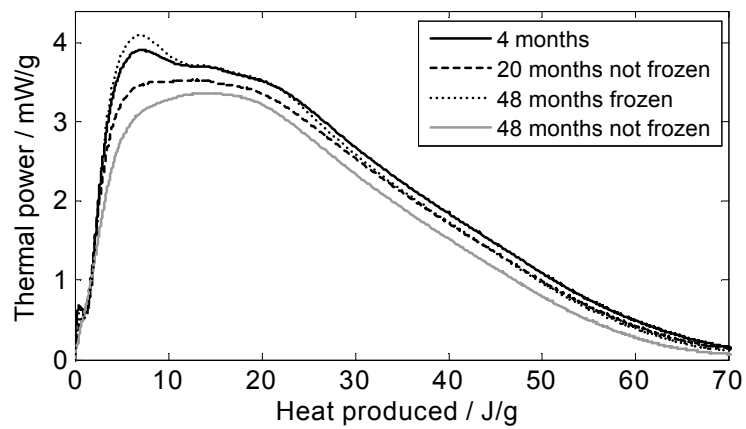


Figure 9. SLC B, thermal power as a function of extent of reaction, heat.

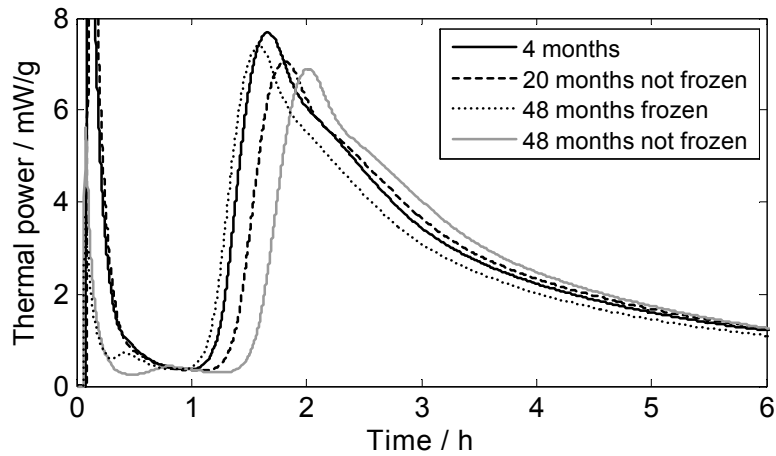


Figure 10. SLC C, thermal power as a function of time.

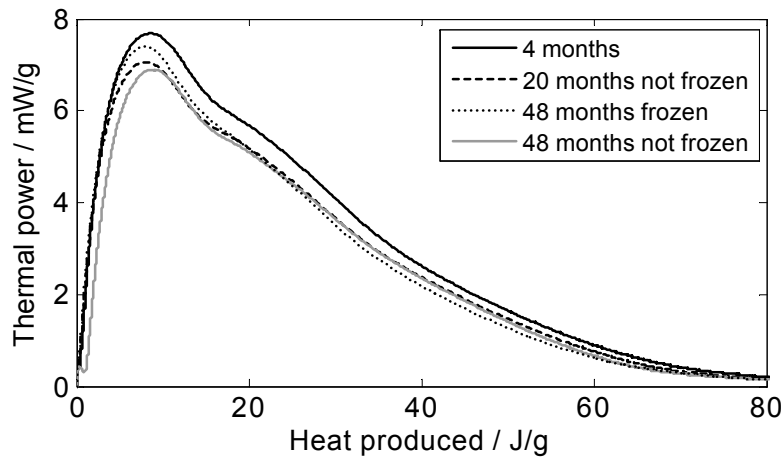


Figure 11. SLC C, thermal power as a function of extent of reaction, heat.

The flow measurements show a consistent difference between materials stored at room temperature and material stored in a freezer. Target and measured diameters are given in Table 1. Generally a deviation of  $\pm 10$  mm from the target value is accepted. Material stored in a freezer falls inside these intervals while material stored in a room climate do not. No separation was observed in the measurements.

Table 1. Measured diameters and target values of flow tests in mm

	SLC A	SLC B	SLC C
Room	210	233	226
Freezer	227	245	244
Target value	235	250	240



## 5. Discussion

The results for the three SLCs show that the complex dry mortars can be stored for up to four years in a freezer without changing their properties significantly. This is useful for manufacturers and others that perform long-term studies on such materials. Storing at low temperature was not as beneficial for the raw materials.

It is clear from the present measurements that materials stored at low temperature show less change in the calorimetric result and in the flow test. An interesting issue is whether the heat produced at complete hydration will differ depending on storage time or if the reaction rate only is slower in older materials. The present measurements do not give an answer on this.

The rate of reaction is dependent on the mixing procedure [4]. Using mixing methods with different mixing intensity will therefore give different calorimetric results. One reason is that in some materials, particles tend to adhere to each other during storage [1]. Using a method with higher mixing intensity will more likely break up the adhered particles. It is possible that the seen results are partly caused by the formation of particle aggregates and this effect may be partly reversible by using a higher mixing intensity than in the present study.

## 6. Conclusion

Storing dry cement based material at low temperatures can be a good alternative when performing measurements over a long time period. The measurements show that the influence of time on the properties material decreases at lower temperatures.

## Acknowledgements

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