Thermal Behaviour of Materials Based on Calcium Sulfo-aluminate Cement

J. Péra[1], J. Ambroise[1]
[1]*Institut National des Sciences Appliquées de Lyon, Villeurbanne, France*

Abstract :

This paper deals with the thermal behaviour (up to 1,250°C) of different materials based on calcium sulfo-aluminate cement: cement pastes, standard mortars and lightweight mortars. The behaviour of calcium sulfo-aluminate cement pastes containing varying amounts of phosphogypsum (0 to 40%) and two types of calcium aluminate clinker was first investigated. The best behaviour was shown by the pure clinker and the cement containing 20% phosphogypsum. Then, standard mortars containing siliceous sand, and either pure clinker or cement containing 20% phosphogypsum were heated up to 1250°C. They remained intact. Finally, lightweight materials using calcium sulfo-aluminate cement and either perlite or vermiculite were investigated. All samples containing vermiculite remained intact up to 1250°C.

1. Introduction

Calcium sulfoaluminate cements have been primarily developed in China in the 1970's [1-5]. The main component of the clinker, yeelimite, can be synthesized at temperatures 200-300°C lower than those required by the formation of normal portland cement. Moreover, a lower amount of limestone in the raw mix is needed, and this leads to a reduction of both thermal input for the calcination process and emission of CO_2. The corresponding clinkers are relatively soft and require less grinding energy than Portland clinkers. Calcium sulfoaluminate cement is obtained by mixing calcium sulfoaluminate clinker with large amounts of calcium sulfate as gypsum or anhydrite (up to 40%). The source of calcium sulfate can be chemical gypsum such as phosphogypsum. Consequently these binders can give a substantial contribution to the saving of natural resources, energy and environment.

Designed by the CBMA (China Building Materials Academy), calcium sulfoaluminate cements were intended for the manufacture of self-stress concrete pipes, due to their expansive properties. Then, they were applied in such as other fields: quick setting concrete, fibre-reinforced composites, and concrete with high sulfate resistance [6-9]. In China, their production is significant (1 million tonnes/year), even if very low when compared to that of Portland cement (575 million tones/year). In USA, sulfoaluminate clinker is added to portland cement to produce shrinkage-compensating cement (ASTM Type K), but the available quantities remain low. In Europe, Australia, India and Japan, laboratory investigations have been undertaken on such cement [10-12]; however its industrial production is limited.

This paper presents the results of an investigation on the thermal behaviour (up to 1250°C) of different materials based on calcium sulfoaluminate cement: cement pastes, standard mortars and lightweight mortars.

2. Materials and microstructural investigation techniques

Calcium sulfoaluminate (CSA) cements were obtained by mixing CSA clinker with phosphogypsum in varying amounts. The microstructural evolution of the hydrated systems was investigated by means of X-Ray Diffraction (XRD) analysis of Fourier Transformed Infra-red (FTIR) spectrometry.

Two types of CSA clinker were used: CK1, obtained in an industrial rotary kiln, and CK2, produced in a pilot tunnel kiln. CK1 was produced in China. CK2 was produced by burning the following mixture at 1350°C:

- phosphogypsum: 12.1%,
- limestone: 26.7%,
- clay: 25.5%,
- bauxite: 35.7%.

The mineralogical composition of CSA clinkers is given in Table 1. CK1 contained more yeelimite than CK2, due to the nature of the raw mixtures used in each process. Bauxite used to get CK1 was free of iron oxide.

When calcium sulfoaluminate cement (CSA) hydrates, ettringite ($C_6A\Sigma_3H_{32}$) is formed according to the following reactions:

$C_4A_3\Sigma + 2C\Sigma H_2 + 34H \Rightarrow C_6A\Sigma_3H_{32} + 2AH_3$, in absence of calcium hydroxide,

$C_4A_3\Sigma + 8C\Sigma H_2 + 6CH + 74H \Rightarrow 3C_6A\Sigma_3H_{32}$, in presence of calcium hydroxide.

with: $C = CaO$; $S = SiO_2$; $A = Al_2O_3$; $\Sigma = SO_3$; $H = H_2O$.

In this work, CSA cements were both paste and mortar hydrated at room temperature and then submitted to high temperature, up to 1250°C.

Table 1 -- Composition of CSA clinkers (w_t %).

Component	CK1	CK2
Yeelimite ($C_4A_3\Sigma$)	66	60.9
Belite (C_2S)	15.6	17.4
Perovskite (CT)	9.9	7.9
Mayenite ($C_{12}A_7$)	7.1	
Ferro-aluminate (C_4AF)		7.9

3. Thermal behaviour of cement pastes

Both CK1 and CK2 clinkers were used for preparing the CSA cements to be paste-hydrated. The phosphogypsum amount in the CSA cement was equal to 0, 20, 30 and 40%.

Each cement was hydrated at W/C = 0.30, and cast in Plexiglas mini-cylinders (ϕ = 20 mm, h = 40 mm). The samples were demoulded at 7 days of age and cured in plastic bags at 20°C until 28 days. Then, they were placed in an electrical furnace and submitted to different temperatures (750, 1000, and 1250°C) for 2 hours. The compressive strength and the mass loss were measured after each thermal treatment.

The influence of temperature on the compressive strength of cement pastes is presented in Fig.1. The behaviour of the two types of clinker is similar:

- an important strength loss between 20°C and 750°C: about 70%,
- a slight decrease between 750°C and 1250°C, and even a small increase at 1250°C when pure clinker is used,
- a better behaviour shown by the pure clinker and the cement containing 20% phosphogypsum.

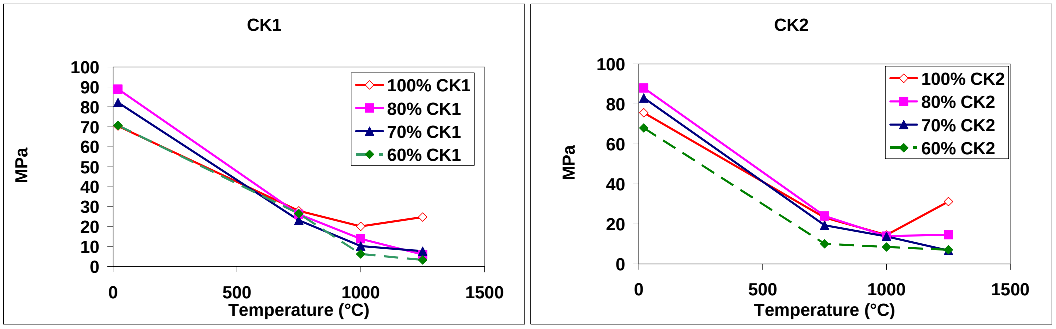

Figure 1 — Compressive strength of pastes versus temperature.

The mass loss is shown in Fig.2. Similar phenomena are observed for the two types of clinker:

- an important mass loss between 20°C and 750°C: 23 to 30%,
- a mass stabilization between 750°C and 1250°C,
- a mass loss increasing with the increase of phosphogypsum content.

A similar mass loss was found by Park et al. [3]: 28% at 750-1000°C. This is attributed to the decomposition of ettringite: ettringite contains 32 moles of combined water leaving the structure as temperature increases.

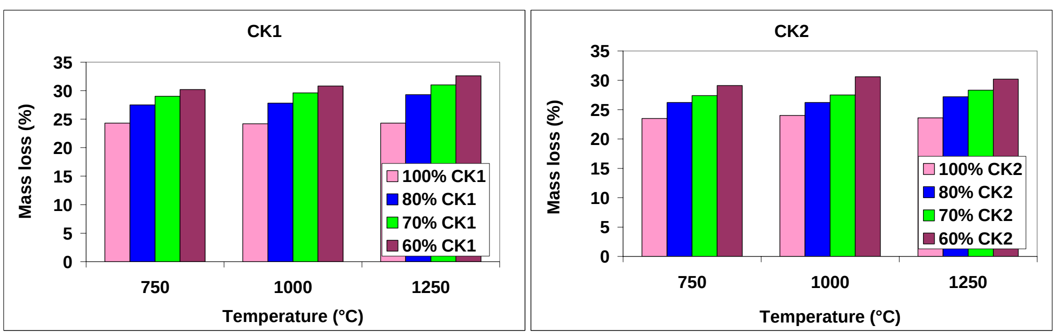

Figure 2 — Mass loss of pastes versus temperature.

XRD investigations undertaken on pastes containing pure clinker revealed the presence of ettringite as main hydration product at 20°C (Fig. 3). Anhydrous yeelimite and belite were still present. After thermal treatment at 1000°C and 1250°C, ettringite decomposed, so that yeelimite concentration increased.

In the pastes containing 20% phosphogypsum, the same phenomena appeared and anhydrite ($CaSO_4$) was identified when the temperature reached 1000°C (Fig. 4). These results were confirmed by FTIR investigations: the starting material was obtained after thermal treatment at 1250°C.

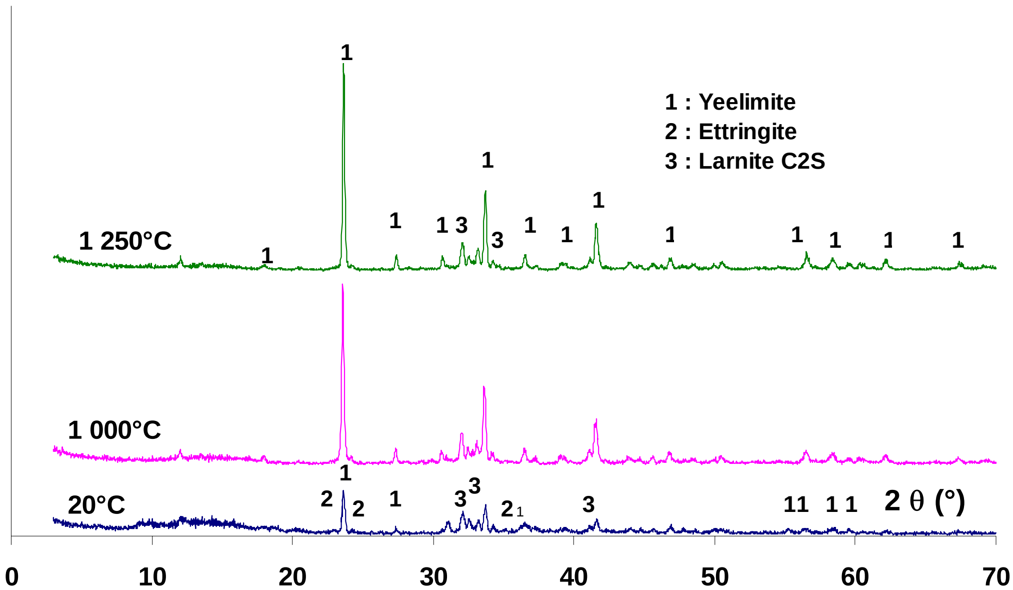

Figure 3 — XRD patterns as a function of temperature: 100% CK2.

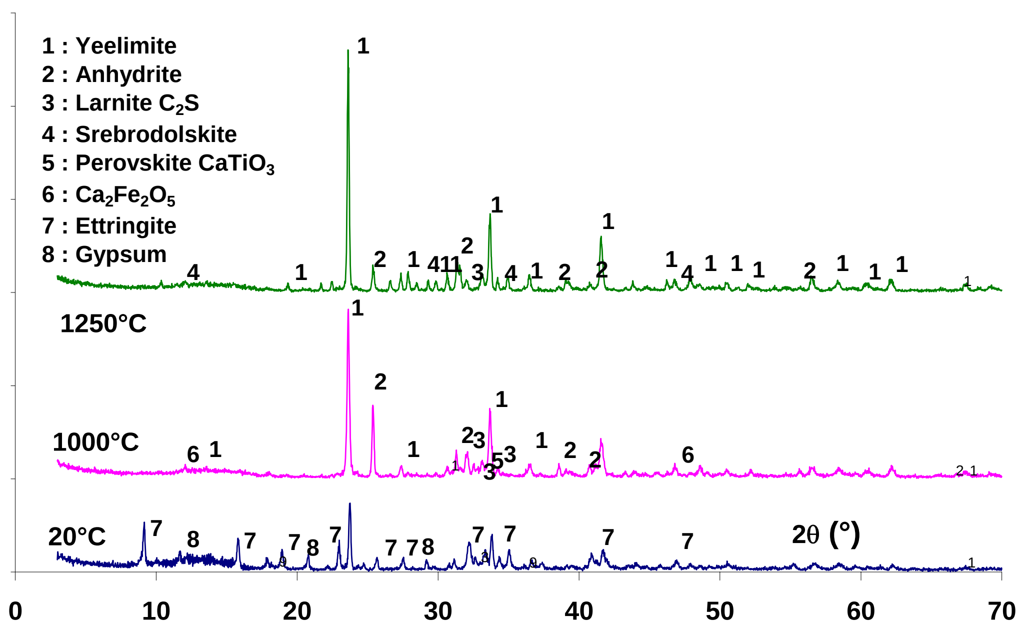

Figure 4 — XRD patterns as a function of temperature: 80% CK2.

4. Thermal behaviour of standard mortars

Four types of CSA cement were used: 100% CK1, and 80% CK1 – 20% phosphogypsum, 100% CK2 and 80% CK2 – 20% phosphogypsum. Prismatic samples (40 mm x 40 mm x 160 mm) of standard mortar (Cement/Sand = 1/3; Water/Cement = 0.5) were prepared. They were demoulded after 24 hours and kept in plastic bags at 20°C until 28 days of age. Then, they were heated to 1000°C and 1250°C. Mortars remained intact up to 1250°C. The mass loss is presented in Fig. 5, and the evolution of compressive strength is shown in Fig. 6. A higher mass loss was observed with CK1. A higher strength was recorded with CK2. The higher amount of iron oxide in CK2 can explain these results: at high temperature, it acts as a melting agent and contributes to the transformation of the mortar into a ceramic body.

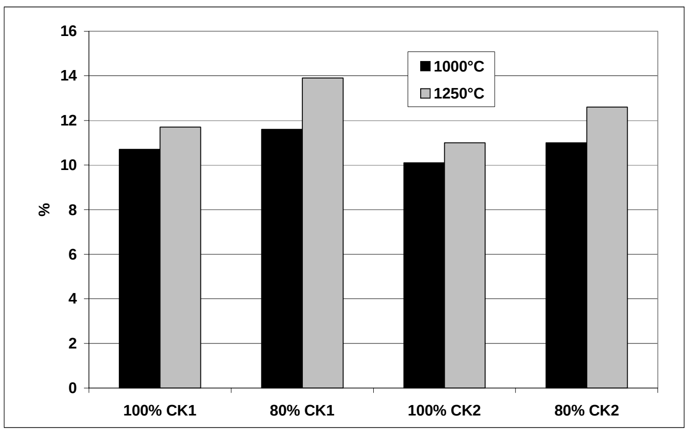

Figure 5 — Mass loss of standard mortars.

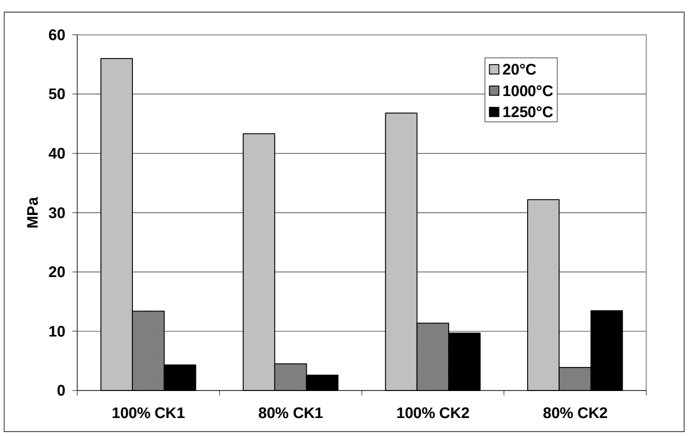

Figure 6 — Evolution of the compressive strength of standard mortars.

5. Thermal behaviour of lightweight mortars

A lightweight mortar able to support temperatures up to 1250°C was designed using:
a) either 100% CK1 clinker or 80% CK1 clinker + 20% phosphogypsum as CSA cement,
b) either perlite or vermiculite as lightweight aggregate,
c) a system of admixtures able to entrain air and perfectly embed aggregates, in order to get some insulating properties.

The composition of the binder was the following (w_t %):
- CK1 clinker: 72.5 or 58;
- phosphogypsum: 0 or 14,5;
- normal Portland cement (NPC – CEMI 52.5): 18;
- calcium hydroxide: 9.5.

NPC was used as an accelerator of CSA cement, while calcium hydroxide emulsified the binder, thus allowing a higher lightweight aggregate content.

The system of admixtures was composed of:
- a thickening agent (mixture of polyvinyl alcohol and starch): 3.56% of the binder;
- an accelerator (lithium carbonate): 0.003% of the binder;
- hollow micro-balls of glass which enhanced the workability of the product : 2.6% of the binder

Mixture proportions of lightweight mortars were:
- binder: 570 kg/m^3
- lightweight aggregate: 430 kg/m^3
- admixtures: 35.1 kg/m^3
- water: 1650 L/m^3.

The dry specific gravity was in the range 0.37 (perlite) - 0.45 (vermiculite).

5.1. Perlite-based materials

Prismatic samples (40 mm x 40 mm x 160 mm) and thin plates (150 mm x 150 mm x 30 mm) were made. Thin plates were cast on a tiling before being introduced in the furnace. They were equipped with two thermocouples: one at the interface between the tiling and the plate, the other at the top of the plate, in order to record the degree of insulation brought by the mortar. The temperature effects are indicated in Tables 2 and 3. The specimens were destroyed at 1240°C.

Table 2 — Influence of temperature on lightweight mortar containing perlite. 100% CK1. Prismatic samples.

Temperature (°C)	**Phenomena**
850	Distortion of the sample ; one crack at the upper face
1000	Large crack at the lower face
1120	New cracks
1230	Volume decrease
1240	Destruction of the sample

Table 3 — Influence of temperature on lightweight mortar containing perlite. 80% CK1. Prismatic samples.

Temperature (°C)	**Phenomena**
900	No problem
1000	Distortion of the sample
1240	Destruction of the sample

These results point out the influence of the nature of aggregates on the fire resistance of mortars: standard mortars containing siliceous aggregates remains intact at 1250°C, while perlite, whose melting temperature is 1100°C, leads to vulnerable materials. Nevertheless, this kind of mortar showed good insulating properties at 1000°C, as illustrated in Fig. 7. When the plate cast on the tiling was maintained at 1000°C for one hour, the temperature at the interface between the mortar and the tiling remained constant at 470°C.

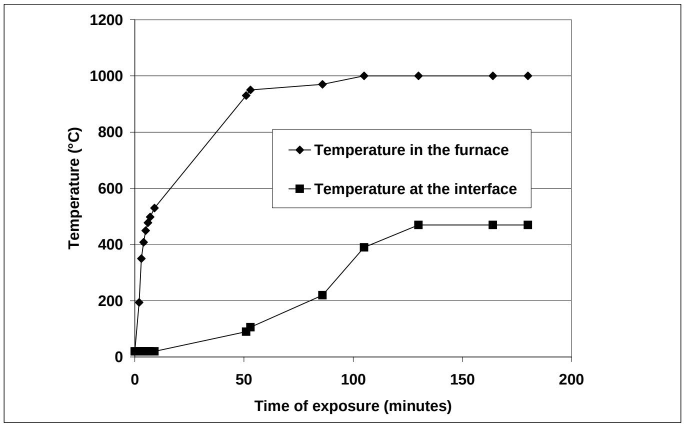

Figure 7 — Insulating properties of lightweight mortar based on perlite (100% CK1).

5.2. Vermiculite-based materials

Two types of prismatic samples were cast: 40 mm x 40 mm x 160 mm, and 70 mm x 70 mm x 140 mm. In these last specimens, thermocouples were placed at the upper side of the sample and in the heart of the sample, as shown in Fig. 8.

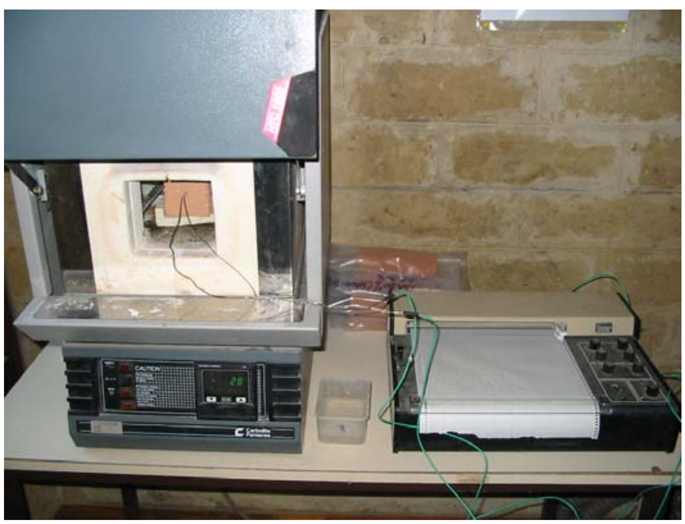

Figure 8 — Position of thermocouples.

All samples remained intact up to 1250°C. Compressive strength is indicated in Fig. 9. Mortars containing 80% CK1 presented the best residual strength.

The thermal behavior of both mortars was similar (Figs. 10 and 11):
- up to 400°C in the furnace, there was not any temperature increase in the sample,
- over 400°C in the furnace, the temperature reached 100°C in the sample and remained constant for 30 minutes,
- when the temperature in the furnace reached 650°C, there was a drastic temperature increase in the sample.

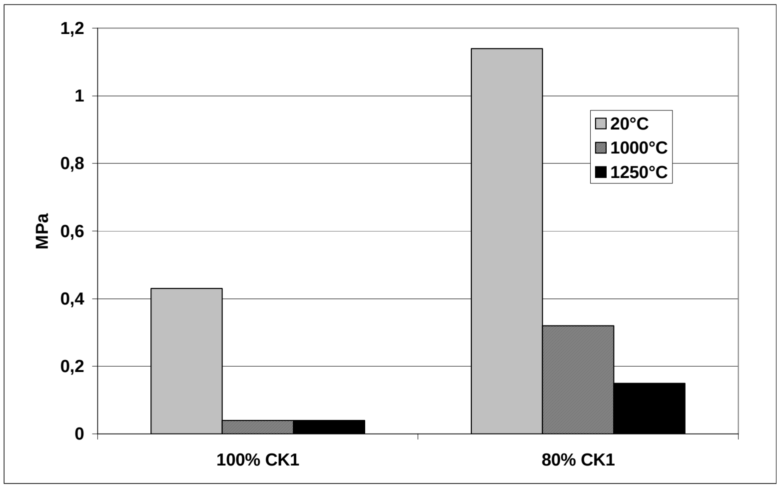

Figure 9 — Compressive strength of mortars containing vermiculite.

This can be explained as follows: the temperature remained constant in the sample when water vaporized and contributed to the thermal insulation of the mortar. When all water was lost, this protecting effect disappeared and the temperature increased in the sample. This was confirmed by FTIR spectrometry: all water disappeared over 750°C.

The presence of gypsum decreased the insulating property of mortar: the time required by the sample to get the same temperature as the furnace was 10 minutes for the mortar containing 20% gypsum, while it was 24 minutes without gypsum. Mortars containing vermiculite presented lower insulating properties than those of mortars incorporating perlite.

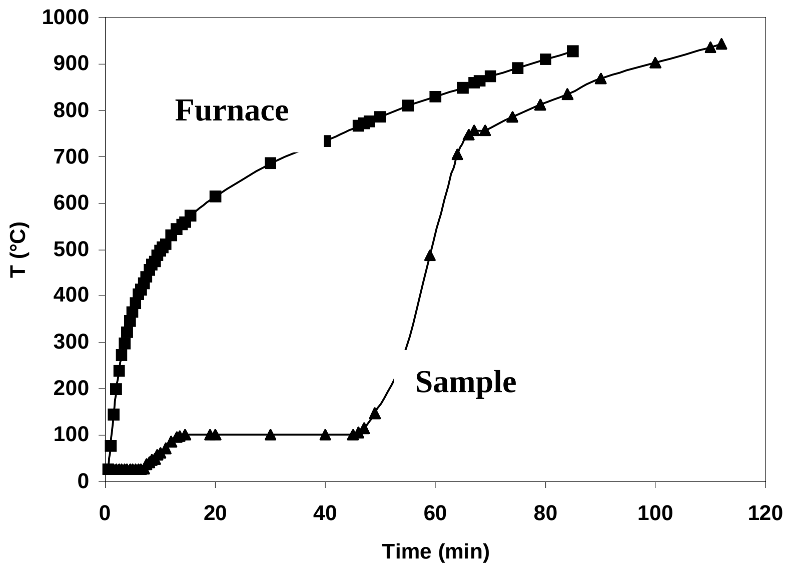

Figure 10 — Insulating properties of lightweight mortar based on vermiculite. 100% CK1.

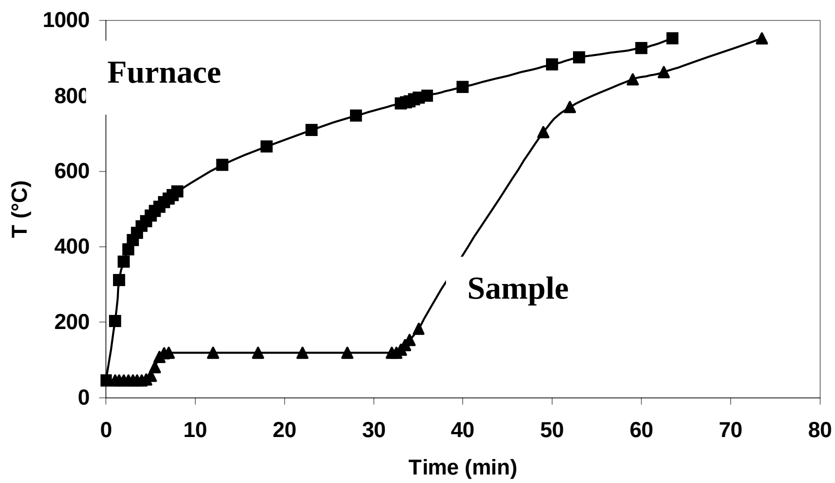

Figure 11 — Insulating properties of lightweight mortar based on vermiculite. 80% CK1.

6. Conclusions

Based on the above results, the following conclusions can be made:

1. The behaviour of calcium sulfoaluminate cement pastes up to 1250°C is remarkable: the specimens are not destroyed and the starting

material (yeelimite) sets up again from ingredients which are decomposed from ettringite.

2. Standard mortars containing siliceous sand remain intact up to 1250°C, without any spalling as observed in mortars cast with normal portland cement.

3. It is possible to design fire-resistant lightweight materials using calcium sulfoaluminate cement and vermiculite. The use of perlite has to be avoided due a low smelting point (1100°C). Such material exhibits interesting insulating properties.

7. References

[1] J.A. Deng, W.M. Ge, M.Z. Su, L.X. Ying, Sulfoaluminate cement series. Proceedings of the 7th International Congress on the Chemistry of Cement, Ed. SEPTIMA, Paris, 1980, Vol.4, 381-386.

[2] M.Z. Su, Y. Wang, L. Zhang, D. Li, Preliminary study on the durability of sulfo/ferro-aluminate cements. Proceedings of the 10th International Congress on the Chemistry of Cement, Gothenburg, Sweden, Ed. H. Justnes, 1997, Vol.4, 4 iv 029,12 pp.

[3] C.K. Park, B.K. Kim, S.Y. Hong, G.Y. Shin, Microstructural change of calcium sulfoaluminate cement paste due to temperature. Proceedings of the 10th International Congress on the Chemistry of Cement, Gothenburg, Sweden, Ed. H. Justnes, 1997, Vol.4, 4 iv 068, 6pp.

[4] L. Zhang, M.Z. Su, Y. Wang, Development of the use of sulfo and ferroaluminate cements in China. Advances in Concrete Research, 1999, Vol.11, n°1, 15-21.

[5] L. Zhang, F.P. Glasser; New concretes based on calcium sulfoaluminate cement. Proceedings of the International Conference "Modern Concrete Materials; Binders, Additions and Admixtures", Dundee , UK, 1999, 261-274.

[6] J. Beretka, N. Sherman, M. Maroccoli, A. Pompo, G.L. Valenti, Effect of composition on the hydration properties of rapid-hardening sulfoaluminate cements. Proceedings of the 10th International Congress on .the Chemistry of Cement, Gothenburg, Sweden, Ed. H. Justnes, 1997, Vol.2, 2 ii 029, 8pp.

[7] A.D.R. Brown, Application of calcium sulfoaluminate cements in the 21 th century. Proceedings of "Conrete 2000", Dundee, UK, 1993, Vol.2, 173-178.

[8] N. Sherman, J. Beretka, L. Santoro, G.L. Valenti, Long term behavior of hydraulic binders based on calcium sulfoaluminate and calcium sulfosilicate. Cement and Concrete Research, 1995, Vol.25, n°1, 113-126.

[9] W. Kurdowski, C.M. George, F.P., Sorrentino, Special cements. Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Brazil, 1986, Vol.1, 292-318

[10] G.A. Muudbhaktal, P.S. Parmeswaran, A.S. Heble, B.V.B. Pat, A.K. Chatterjee, Non alitic cement from calcium sulfoaluminate clinker. Optimisation for high-strength and low-temperature application. Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Brazil, 1986, Vol.4, 364-370
[11] P.K. Mehta, Investigations on energy-saving cements. World Cement Technology, 1980, May, 166-177.
[12] J. Beretka, L. Santoro, N. Sherman, G.L. Valenti, Synthesis and properties of low energy cements based on $4CaO.3Al_2O_3.SO_3$. Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, India, 1992, Vol.1, 292-318.