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Sintering of Natural Anhydrite–Glass Composite

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Abstract

In this paper, solid phase sintering of a natural anhydrite–glass composite from powders of these materials is described. The microstructure of the sintered material has been analysed by means of scanning electron microscopy and X-ray emission. Some properties of this new material have been determined. Specific applications for this new sintered material are suggested. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

Sintering of natural anhydrite (NA) has not been previously reported. This is not suppressive, because NA is not considered a 'technological material'. Nevertheless, NA could become an important building material, both in indoor and outdoor applications.

The NA raw material is mainly composed of $CaSO_4$, in its anhydrite II allotropic phase, with a minor content of the dihydrate or gypsum ($CaSO_4.2H_2O$). Both NA and gypsum are widely distributed in the earth's crust. It is well known that gypsum is very useful as a building material because it easily loses its hydration water, and when water is added again to this calcined powder, it reverts to the original dihydrate — the set and hardened gypsum product.

This setting property is not present in NA, and this is the very reason for the current lack of interest in NA as a building material. Nevertheless, anhydrite rocks can be easily crushed and milled, obtaining a fine powder which can be moulded and fired in many useful geometrical configurations for buildings and other applications.

2 Materials

Anhydrite II phase of $CaSO_4$ is stable from 40 to 1180°C, under normal pressure. Its density lies between 2·93 and 2·97 g cm^{-3}, the greater one of the different calcium sulfate phases. The water solubility at 20°C is low (0·27 g per 100 g of solution) and, due to the high density and close-packed crystal lattice (rhombic), it reacts very slowly with water.[1]

NA stone used in this research was supplied by EPYSA as medium-sized rocks of 15 cm maximum length, sharply edged and of grey colour [Fig. 1(a)]. This raw material is very pure, with energy dispersive X-ray (EDX) analysis of small NA grains revealing the chemical (oxides) composition of nearly 55 wt% SO_3 and 45 wt% of CaO. Figure 1(b) collects the X-ray diffraction spectra of NA powder. Two spectral diagrams are included, the first corresponding to NA powder at room temperature and the second to NA powder after heating at 1000°C for 1 h in air and cooled. Both diffractograms are remarkably similar, and related to the pattern of pure anhydrite (X-ray diffractometer: Philips PW182, Cu anode, $5° < \theta < 60°$). This analysis confirms that the NA powder is very pure crystalline $CaSO_4$.

Several blocks of anhydrite were cleaned, crushed and milled, by means of an electric pallet mill, with a sieve of 0·08 mm mesh size, through which NA powder was collected. This NA powder obtained shows mat white colour. By optical microscopy, two main sizes of equiaxed particles were identified: (1) a small one, from 1 to 5 μm, and (2) a larger one, about 60 μm mean diameter. NA powder was dried in an oven at 105°C for a long time (at least 3 days), and stored in a room at controlled relative humidity conditions (RH < 5%).

Glass powder was obtained from ordinary glass (softening temperature: 730°C), crushed and ground in the same pallet mill and sieve just described. It was dried and stored under similar conditions as NA powder. Table 1 shows the chemical composition (oxides) of this glass powder.

Two sets of green specimens were prepared for sintering: set A from pure anhydrite powder, and set B from a mixture composed of 80 wt% of pure anhydrite powder and 20 wt% of glass powder.

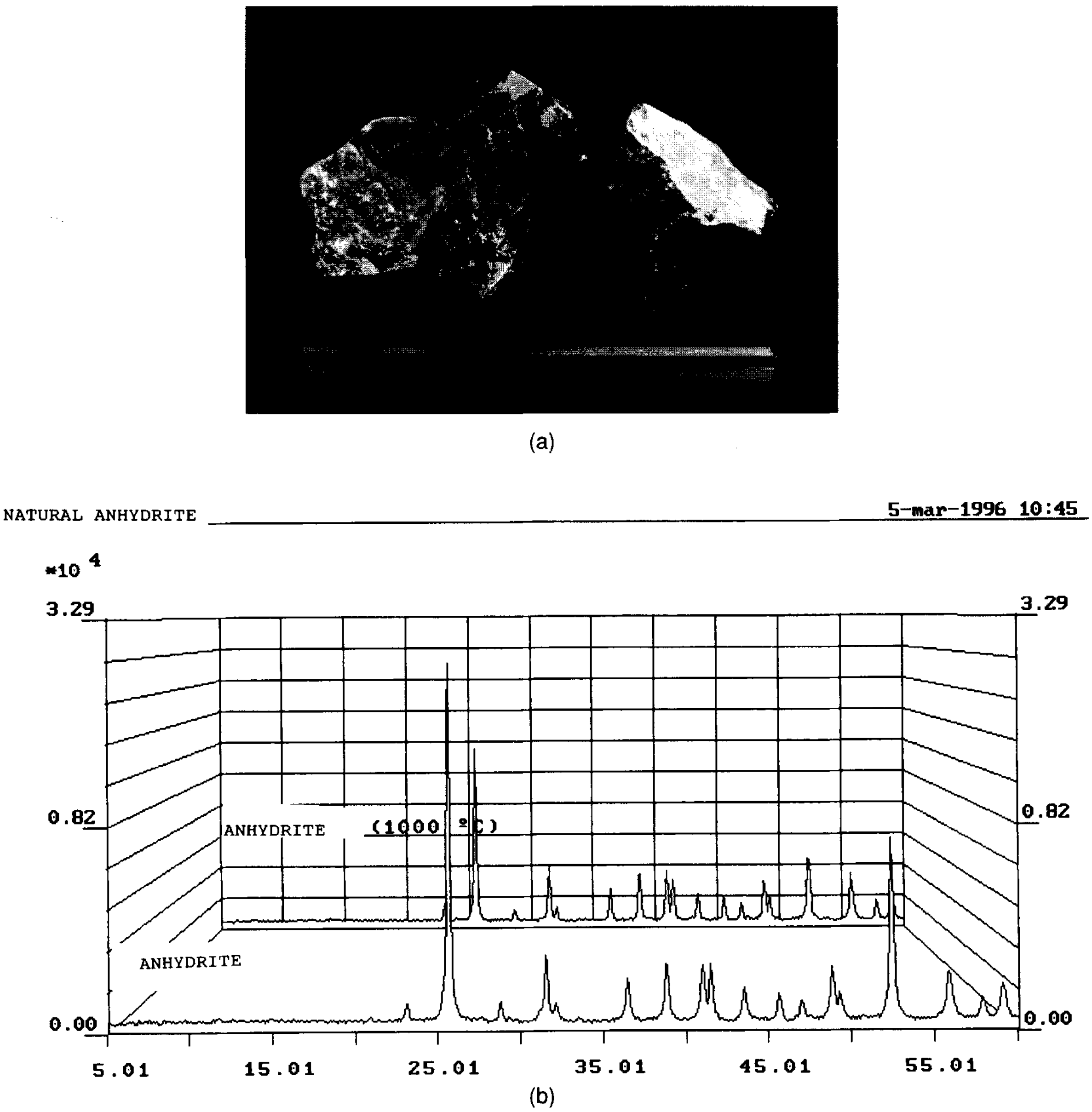

Fig. 1. (a) Natural anhydrite stones, supplied by EPYSA. (b) X-ray diffractograms of NA powder at room temperature (face) and after heating at 1000°C and cooled in air (back).

Table 1. Chemical composition (oxides) of glass powder

Component	*wt%*
SiO_2	72·0
Al_2O_3	1·6
MgO	3·0
Na_2O	12·5
K_2O	2·0
CaO	8·9

3 Experimental

The green specimens were sintered in air by means of two different techniques: (1) uniaxial hot pressing[2] and (2) compaction in a closed die after vibration and sintered in a furnace. In each case, 900°C was chosen as the sintering temperature.

3.1 Uniaxial hot pressing

A cylindrical closed die made of Inconel (Fig. 2) was used. With inner diameter 13 mm, the length of the green specimen within the die was 20 mm. Temperature was controlled by means of a thermocouple attached into the die. A hollow cylindrical electric furnace was specially designed and constructed, attaining a maximum temperature of 1200°C.

Only class or set A green specimens (5 g each) were fired, during 15 min under uniaxial hot pressing, without obtaining in any case a sintered product. The compression stress was increased from 150 to 220 MPa without better performance.

3.2 Sintering in furnace

A different dismountable die made of high strength steel alloy was designed and constructed

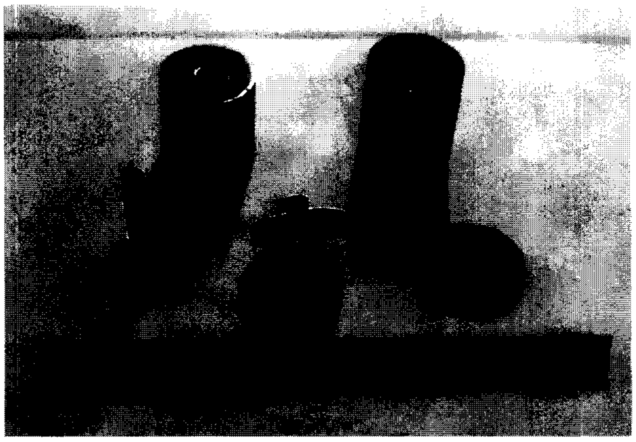

Fig. 2. Cylindrical closed die of Inconel, for hot uniaxial pressing of natural anhydrite powders.

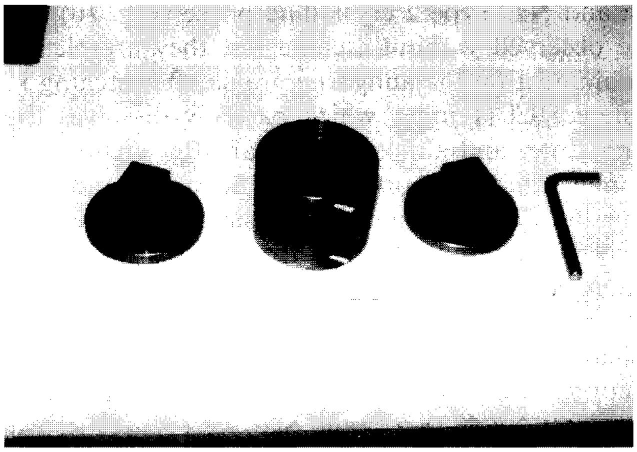

Fig. 3. Dismountable die of high strength steel, for green compaction of prismatic specimens at room temperature.

(Fig. 3), to obtain square-based prismatic green specimens (surface: 10 cm^2).

3.2.1 Set A

A lot of set A green specimens, composed of 25 g of NA powders, were conformed and compacted, after vibration of 180 cycles (Fig. 4), by compression in this die at 200 MPa. Afterwards, they were extracted from the die and fired in a furnace at 900°C for different times, namely 24, 42, 48 and 72 h.

3.2.2 Set B

The green specimens of set B were manufactured by mixing NA powder (80 wt%) and glass powder (20 wt%) above described, to obtain 25 g of the mixture for each specimen. Once the powders were mixed, each green specimen was compacted in the die, first by vibration (180 cycles) and then by dry pressing at 200 MPa at room temperature. Subsequently, each specimen was extracted from the die, fired in the furnace for 8 h at 900°C in normal air conditions, and cooled in the open furnace.

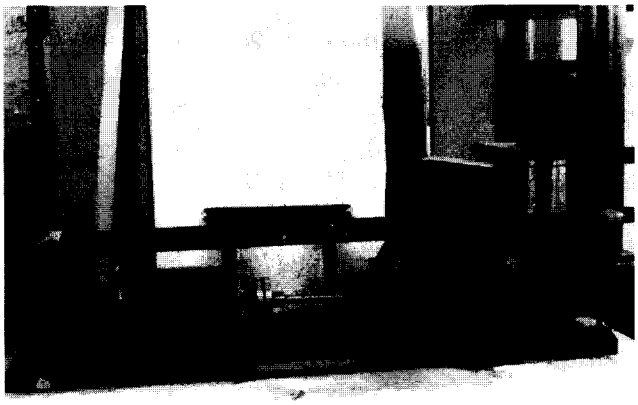

Fig. 4. Electrical vibrator ICON, for compaction of green specimens before pressing and firing.

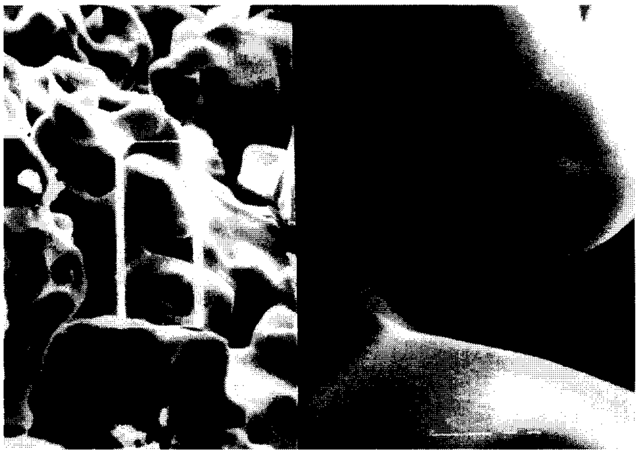

Fig. 5. Sintered pure natural anhydrite (×1500 and ×7500), showing the solid skeleton and neck growth between grains. The porosity is very high.

4 Results and Discussion

The first batch of small cylindrical specimens did not sinter but were only hot and pressure densified, showing characteristics of green compacting.

The second batch specimens fired, namely set A, showed some characteristics of sintered materials, but the sintering time increase (from 24 to 72 h) did not enhance the material properties nor the microstructural densification; the final density of the sintered specimens was 1·9 g cm^{-3} (65% of theoretical). The Shore C hardness of set A specimens was measured to be between 80 and 95, greater than those of water conglomerate plaster (mean Shore C hardness ≈ 65); its compressive strength was > 20 MPa and shear strength $\approx 1{\cdot}5$ MPa. Scanning electron microscopy showed set A sintered specimens to exhibit a solid skeleton, with neck growth between neighbouring grains, due to surface diffusion by an Ostwald ripening mechanism: small grains are absorbed by the big ones (Fig. 5). The porosity was very high, and the bonding between grains was weak.

Set B sintered specimens showed different and improved properties than the other two. Shore C hardness was out of scale, compression strength was > 50 MPa, shear strength ≈ 5 MPa and density was 2·30 g cm^{-3} (≈80% of theoretical). Scanning electron microscopy analysis of set B sintered specimens (Fig. 6) shows that anhydrite grains are not sharply edged but smooth, and bonded together by means of both neck growth (Fig. 7) and an interphase composed mainly of Ca, Si, S, and small quantities of K, Na and Mg (Fig. 8). The porosity is very low.

Three different techniques have been applied to observe by EDX the interphase between anhydrite grains: (1) without etching; (2) etching by dilute 1 : 9 HCl, 1 min and (3) etching by dilute 1 : 9 HCl, 2 min. Three different crystalline phases and a mixed one can be identified, besides the anhydrite itself. Table 2 collects the results of EDX (oxides) analysis.

Type 1 crystalline phase mainly appears at the interphase between anhydrite grains (Fig. 9), as small microcrystals. They are composed of S, Ca, Si and Na. Type 2 crystalline phase (Fig. 10) can be observed without etching but they are clearly prominent on the anhydrite grains after etching in dilute HCl (1 min), which partially dissolves the anhydrite, and almost disappear after etching for 2 min. They are composed of S, Si, Ca and Mg, but due to the small size of these crystals, there may be some interference from anhydrite on the EDX analysis. The Si, Ca and Mg content of these crystal is remarkable. Type 3 crystalline phase (Fig. 11) is mainly located at the interface between adjacent anhydrite grains. They are composed of Na–K, S, Ca and Si.

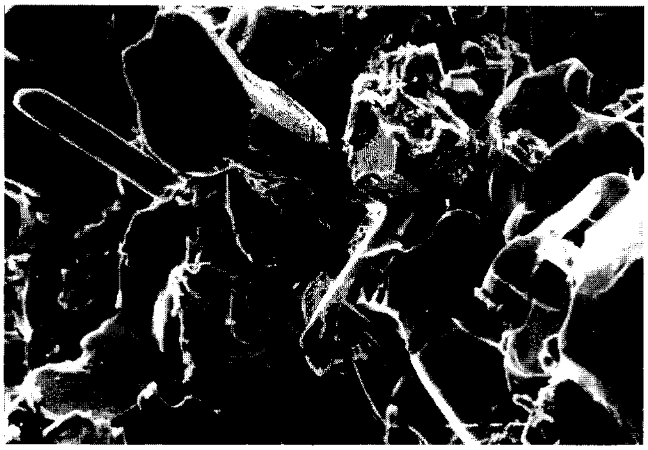

Fig. 6. Scanning electron micrograph (×750) of a sintered specimen of set B (see text).

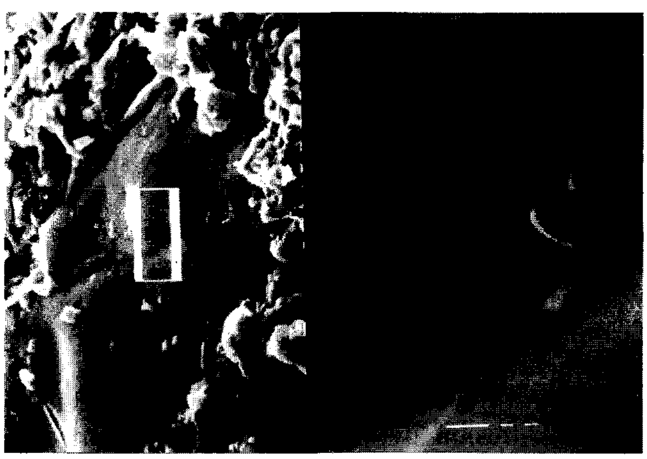

Fig. 7. Scanning electron micrographs of a sintered specimen of set B, showing neck linkage between two adjacent anhydrite grains (×1000 and ×10 000).

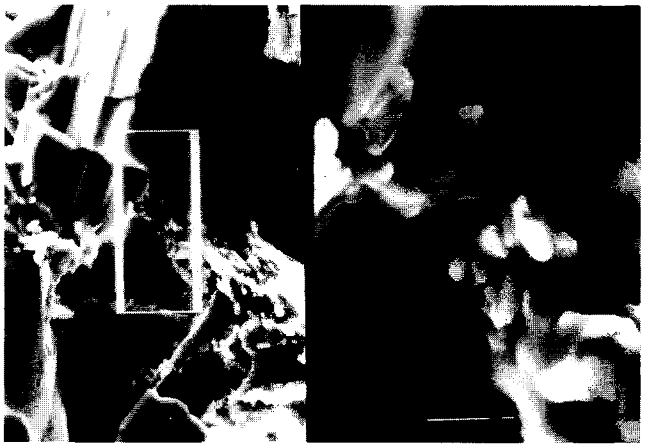

Fig. 8. Interface between two anhydrite grains, composed of a polycrystalline phase containing mainly Ca, Si, S, K, Na and Mg (×1500 and ×7500).

It appears that type 2 crystals are characterized by the Mg, and type 3 crystals by the K–Na contents. Nevertheless, type 1 crystals can be mixtures of type 2 and type 3 crystals, as the phase designated 'mixed' in Table 2, which can be observed in Fig. 8.

5 Water Reactivity

To assess the water reactivity of this new sintered material, two kind of tests have been carried out: (1) water immersion test and (2) water absorption by capillary suction.

Three sets of six similar specimens each were sintered to be tested, according to the procedure just described, namely: S1 (80 wt% NA and 20% glass); S2 (90 wt% NA and 10% glass) and S3 (85 wt% NA and 15% glass).

5.1 Water immersion tests

The specimens were entirely immersed in filtered water at approximately 15±5°C for 24 h. Set S1 shows the greater damage: expansivity and laminated fissuration along the main dimensions. Sets S2 and S3, however, show better behaviour, with minor or no damage.

Table 2. EDX analysis (wt%, oxides) of different phases in sintered anhydrite. Set B: anhydrite (80%) and glass (20%) powder

		Anhydrite	*Type 1*	*Type 2*	*Type 3*	*Mixed*
Na_2O	No etched		11·49		5·04	4·76
	1 min			0·19	14·34	
	2 min				15·78	11·24
MgO	No etched			8·01		4·38
	1 min			5·64		
	2 min			5·47		0·76
SiO_2	No etched		21·61	42·60	2·15	31·18
	1 min	0·77		32·84	8·91	
	2 min	1·10		52·42	7·10	17·20
SO_3	No etched	55·07	42·64	15·94	57·75	31·99
	1 min	54·39		27·19	60·10	
	2 min	55·98		6·73	66·80	48·33
K_2O	No etched				5·30	1·28
	1 min			0·40	2·39	
	2 min				0·37	3·98
CaO	No etched	44·93	24·26	33·43	29·76	26·40
	1 min	44·84		33·01	14·24	
	2 min	42·91		35·36	9·95	18·50

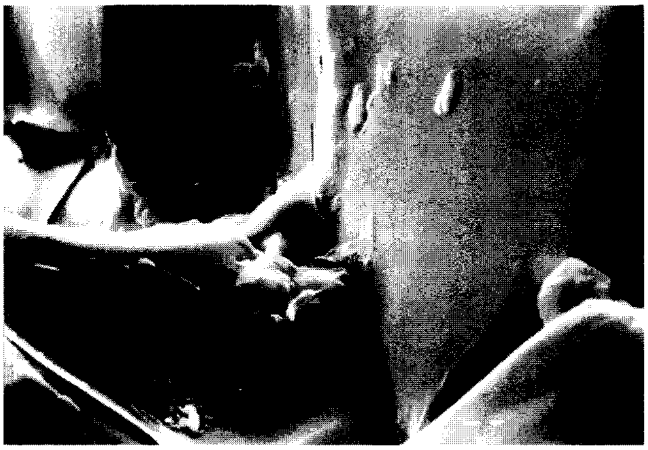

Fig. 9. Micrograph showing type 1 crystals (see text) between sintered anhydrite grains (×3500).

Fig. 11. Scanning electron micrograph of (×3500) type 3 crystals (see text).

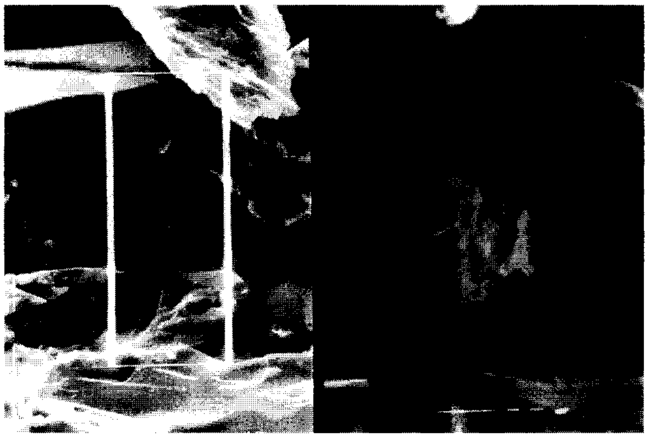

Fig. 10. Scanning electron micrographs showing type 2 (see text) crystals growing on anhydrite grains (×1500 and ×4500).

5.2 Water absorption tests

The specimens were placed for 24 h on a wet horizontal surface containing 2 mm of filtered water at 15±5°C, in a sealed receiver. Sets S1 and S3 show the main damage over the nonimmersed surface: flaws and expansivity. Set S2 shows much better behaviour, with minor damage.

6 Conclusions

A new solid phase sintered material based on pure natural anhydrite with some addition of glass powders, has been densified under very simple conditions of pressure and temperature. Also, NA without glass addition has been sintered in the solid phase, but it showed minor strength and compacting properties. The microstructure of this new material has been identified by means of scanning electron microscopy and EDX analysis. Further work is necessary to quantitatively assess the stoichiometry.

The manufacturing process and properties of this new material suggest that it may find many building applications, particularly as wall partition blocks, ceiling, steel protection against fire, and so on. The fire behaviour of this new material is really remarkable, as it is thermodynamically stable until 900°C, and probably above this temperature, without gas emission under fire.

Further research work is necessary to improve the water resistance of this material.

Acknowledgement

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