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► To cite this version:

A. Capmas, T. Bier. Possibilities of special cements in ceramic applications. Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-1341-C7-1346. 10.1051/jp4:19937206 . jpa-00251840

HAL Id: jpa-00251840

<https://hal.science/jpa-00251840>

Submitted on 1 Jan 1993

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Possibilities of special cements in ceramic applications

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ABSTRACT

About 25 years ago, the only way to have confinement material for high temperature applications was to prepare a ceramic by sintering or fusion at high temperature.

A new technology came, with the production of Low Cement Castables. This new product was obtained by a careful choice of the granulometry of the aggregates, an optimization of the defloculation of fine particles, including the cement (Calcium Aluminate Cement) and the addition of silica fume. Silica fume brought two improvements:

- a fluidifying effect, due partly to the low sensitivity of viscosity to pH, and partly to the geometric effect of the nicely spherical particle.
- a chemical effect, brought by the reaction of silica and Calcium Aluminate Cement to give a coherent zeolitic structure, through which water could escape during the first firing.

From a ceramist point of view, it is interesting to understand how this components, nearly colloidal system mixed in water can be heated up to ceramization without any noticeable change in mechanical characteristics and shrinkage.

From a more practical point of view, it is also interesting to realize that some characteristics, usually attributed only to ceramics, also apply with low cement castables technology: high compressive strength, flexural strength, corrosion resistance, abrasion resistance, impact resistance.

INTRODUCTION

Cementitious materials can be considered a class of materials by its own between bodies bonded just by cohesion and ceramics where a very strong bond is created by sintering [1]. Being composed of non-metallic, inorganic oxides, they are very close to ceramics, show their brittleness but do not exhibit their compressive strengths, temperature resistance or electrical properties.

On the other hand cementitious bonding has been looked at as one method of ceramic fabrication [2]. Recently the term CBC, chemically bonded ceramics, has been used-especially in the U.S. and even patented [3]. The CBC's can be considered a ceramic material which does not require much energy to be produced but shows properties similar to conventional (sintered) ceramics. Compressive strength performance has been improved and even the electrical insulating properties can match to those of normal alumina ceramics [4]. The so called MDF (macro defect free) cement patented by ICI [5] exhibits what bending and compressive strengths are concerned a behaviour close to that of aluminium, without having the ductility of course.

Although CBC's and MDF materials are true ceramics, they do not resist to high temperatures very well. Chemical and physical modifications of system can, however, lead to a much improved temperature behaviour and quite impressive compressive strengths for a hydraulically bound body.

TRADITIONAL CEMENTITIOUS BINDERS

Portland cement concrete

Figure 1 shows the development of compressive strength with increasing temperature for various concretes including even high strength concretes [6].

Fig.1: Compressive strength of various high strength and normal strength concretes

All these materials show quite some drastic degradation of compressive strength beyond 400-500°C which can even lead to the disintegration of the material for temperatures around 1200°C [7]. Several mechanisms are responsible for this behaviour -first of all the dehydration of the bonding phases but also spalling (high strengths concrete) due to high water vapour pressures upon heating which can not be released in a very dense matrix.

Conventional refractory concrete

Conventional castables for refractory applications are concretes with an alumina cement and aggregates such as chamotte, corundum or tabular alumina. Their behaviour upon firing is similar to that of Portland cement concrete for temperatures up to about 900°C, but different beyond 1000°C as shown in figure 2.

Fig.2: Development of surface hardness of a high alumina cement paste with temperature.

The strengths or hardness loss is due to the dehydration of the phases which gave the green body its strength. The increase in strength for higher temperatures, absent in PC systems, is due to a recrystallization or "ceramization" forming anhydrous, stable oxides. For pure pastes this is shown in figure 3.

Fig.3: Development of phases upon heating in a neat CAC paste.

For pure Al_2O_3 - CaO systems the stable oxides formed are CA and CA_2 . In the presence of siliceous aggregates like chamotte table 1 gives the phases changes upon firing.

Operation	Cement				Aggregate	
Before adding water	A	CA		CA2	S	A3S2
After curing at 20°C	A	CAH10		CA2	S	A3S2
After drying at 200°C	A	C3AH6+AH3			S	A3S2
After heating at 600°C	A	C12A7+AH			S	A3S2
at 1000°C	A	CA2	C2AS	CAS2	S	A3S2
at 1200°C	A	CA2	C2AS	CAS2	S	A3S2
at 1400°C		C2AS				A3S2

Table 1: Phase changes in a refractory concrete

The hydrated phases are the same as in a neat paste, during the process of recrystallization the silica from the aggregates are incorporated in the anhydrous oxides formed -gelhenite and anorthite.

It should be pointed out, however, that the strength losses between 400°C and 1000°C together with the accompanying dimensional changes limited the use of refractory concretes. The introduction of a new generation of concretes -LCC (low cement castables) and ULCC (ultra low cement castables)- changed this situation.

ADVANCED CEMENTITIOUS BINDERS

Development in refractories

Fig.4: Main components of LCC and ULCC mixes

The development towards more performing castable refractories led to systems as schematically shown in figure 4. The main difference to CC's (conventional castables) being the introduction of fine reactive fillers such as silica fume or reactive alumina and admixtures. These modifications allowed to reduce the water content while maintaining or improving workability and hence the mechanical performances as it is shown in table 2.

	ULCC	LCC	CC
Al ₂ O ₃	85,00	84,50	84,00
CaO	0,40	1,10	5,00
Apparent density (g/cm ³)			
110°C	2,96	2,94	2,66
1200°C *	2,96	2,93	2,49
Open porosity %			
110°C	10,00	9,00	15,50
1200°C *	12,00	18,00	29,00
Compressive strength N/mm ²			
110°C	75,00	125,00	105,00
1200°C	145,00	150,00	50,00
HMOR N/mm ²			
1000°C	14,00	18,00	4,00
1300°C	8,00	8,00	3,00
1500°C	5,00	2,50	0,00

* after 5 hours at 1200°C

Table 2: Comparison of different properties for CC, LCC and ULCC concretes.

While after oven drying, only the LCC shows slightly better strength, for high temperatures much higher compressive strength are obtained for the LCC + ULCC mix. Taking the hot MOR, the differences are more pronounced. At 1500°C a CC exhibits no hot MOR at all while the LCC at ULCC systems are still at a reasonable level. Contrary to cold crushing strengths (compression), the hot MOR declines always.

If we look at the temperature range between 400°C and 1000°C where normally a decrease in strength is observed, the LCC system shows an increase, even in hot MOR as described by [8] shown in figure 5.

Fig.5: Hot Modulus of Rupture for CC and LCC mixes as a function of temperature according to [8].

The same trends have been observed for the compressive strength, (cold crushing strength) development as shown in figure 6.

Fig.6: Cold crushing strength of a conventional and a low cement castable (fireclay aggregate) [9].

To explain the excellent strength performance in the intermediate temperature range, Clavaud [9] suggests the formation of a pseudo-zeolitic bond. This type of phase releases water in a wide range of temperature due to its weak bonding characteristics what has been shown by DTA measurements. The low amount of water together with its gentle release do not involve the same type of damages as they are found in normal concretes.

Kieser et. al [10] have found some evidence that zeolith-type phases are formed in LCC mixes containing silica. This is supported by findings of Fryda [11]. It seems that calcium aluminate cements in the presence of amorphous silica can form gel-like aluminosilicate structures which in consequence can transform at ambient temperatures (50°C) to zeolithes if the appropriate cations are present. This ongoing work will be complimented by ^{27}Al - NMR studies.

An interesting aspect for the calcium aluminate-silica systems concerning CBC's has been published recently by B. Borglum et. al [12]. This group found that with auto-claving at 300°C a calcium aluminate cement with 43% quartz will directly form the anhydrous hexagonal anorthite phase CAS₂. A material like this -processed at low temperatures- can not only exhibit remarkable strength (≈ 250 MPa)

but should also be stable upon firing because there is no dehydration taking place to alter or destroy the structure.

CONCLUSIONS

Recent developments have shown that it is possible to create ceramic materials based on calcium aluminate cements with additions of silica which overcome the strengths loss usually encountered when a cement based ceramic is heated. This strength loss is due to dehydration of the bonding phases and subsequent damage to the internal structure of the material.

To overcome this weakness two ways have been described:

- the formation of a pseudo-zeolitic structure which releases water more gently.
- the direct formation of anhydrous phases by hydro-thermal processing.

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