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High-strength aluminate cement produced by cold isostatic pressing

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High-strength cement was obtained by a simple process technique. Powders of Secar 71 were cold isostatically pressed (CIP) into green bodies with a relative density of 66 vol%. The green bodies were then immersed in water or kept in humid air for curing at various temperatures for different periods of time. Hydrated cements with high density and low porosity were obtained. The water uptake was more than 20% (by weight) after one day. Over the course of a few days the open porosity decreased to a few per cent. The three-point bending strength of the hydrated cement bodies was 50–80 MPa, and the compressive strength exceeded 200 MPa. The hardness measurement revealed a twofold increase, compared with the control specimens which were prepared by the conventional mixing method. The microstructure of the CIP-processed cements showed a macropore-free composite structure. It was concluded that, by applying CIP, high-strength cement could be produced using commercially available cement without any auxiliary additives. © *2000 Kluwer Academic Publishers*

1. Introduction

Conventionally processed and hydrated cement is a brittle material with relatively low strength. It contains a large number of defects, in particular, large pores. These pores are introduced during the processing and hydration of cement, in the form of entrapped air bubbles and voids caused by the evaporation of excess water and hydration volume changes. Pores or defects, especially the large ones, control the strength of brittle materials according to the Griffith model [1]. Kendall *et al.* [2] studied relationship between porosity, microstructure and strength of cement and concluded that freedom of macro-defects is essential in obtaining high strength.

Various processes, e.g. warm pressing [3], and, autoclaving [4], have been introduced in order to reduce these defects in the hydrated cement. Increased strength was also reported by adding auxiliary substances such as super-plasticizers [5]. This rendered the paste workable using less water. Silica fume [6] has also been used to fill the voids in the cement. For macro-defect-free (MDF) aluminate cement cured at an elevated temperature, the bending-strength achieved was approximately ten times greater than that of the same cement processed in a conventional manner [7]. However, the long-term stability of MDF cement is somewhat inferior, especially when exposed to damp environments. The degradation has been related to the superplasticizer employed [8].

We reported a CIP-process for making high-strength gypsum without additives [9, 10]. Water was sucked into the material by capillary forces. The total amount and the maximal size of single domains were limited by the reduced void fraction and pore size of the CIPed green body. In this study, the same process was applied to a commercially available aluminate cement. The strength and microstructure of the hydrated cement processed were evaluated.

2. Materials and methods

An aluminate cement, (Secar 71, Lafarge, France) was used as delivered throughout this study. The powder was packed in rubber bags and cold isostatically pressed for 10 minutes at a pressure of 320 MPa. The cross sections of the resulting green bodies were either circular or rounded quadratic with about 4 cm as a typical dimension. The green density and compressive strength were then measured. The green bodies were cut into lengths of approximately 40 mm and were hydrated by:

I. immersion in water at room temperature (referred to as 20 °C) and 37 °C for 1, 7 or 30 days;

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II. exposure to air saturated with water vapor at 37 °C for 1 or 7 days;

III. immersion in an aqueous solution of 0.5% Li_2CO_3 at 37 °C for 0.5, 1, 2, 4 and 24 hours.

For comparison, control samples were prepared by thoroughly mixing water (W) and cement (C) in a container. A W/C ratio of 0.32 (by mass) was used. About 30 g of the resulting mixtures were cast in a mold and cured in ambient air at 20 °C and 37 °C. Specimens were cut for examination after 1, 7, or 30 days.

2.1. Density and porosity measurements

The density of green bodies was determined by measuring the weight and volume of accurately cut samples. We then calculated these as a percentage of the theoretical density of the cement, which is close to 2.96 g/cm^3. The density of the hydrated bodies was determined by weighing dried samples in air and samples soaked in water.

To determine the open porosity, the bodies were weighed before and after centrifugation in water at 6000 rpm for 10 minutes. The weight increments corresponded to the volume of the pores which were filled with water. The calculations were based on the following equations:

$$D = \frac{W_a}{W_c - W_w} d; \quad \text{and} \quad P = \frac{W_c - W_a}{W_c - W_w} \times 100$$

where D = density of the body, d = density of the water, P = open porosity as a percentage by volume, and W = weight of the body, $_{a})$ in air, $_{w})$ in water and $_{c})$ after centrifugation in water.

2.2. W/C ratio determination

The penetration of water into CIPed cement was examined by weighing before soaking and after 10 minutes, 7 and 24 hours. The total porosity of the green bodies was calculated from the density of green bodies and from the density of actual phases as given in Table I.

2.3. Strength measurement

For strength measurement, test bars were cut from hydrated cement (a few also from green bodies). The dimensions of these bars were 30 × 4 × 3 mm for three-point bending and 6 × 4 × 4 mm for compression testing. The tests were conducted using a universal test machine (Alwetron, T50, Sweden) at a cross-head speed of 0.5 mm/min. The three-point bending test used a span of 22 mm between two supports.

TABLE I Density (g/cm^3) of the substances used

Substance	Density	Molecular weight
H	1.0	18.02
CA	2.98	158.03
CA_2	2.93	259.99
CAH_{10}	1.72	338.23
C_3AH_6	2.52	378.29
AH_3	c2.4	156.02

Where H = H_2O, C = CaO and A = Al_2O_3.

2.4. Microhardness and surface structure assessments

In order to facilitate the determination of Vickers microhardness a thin metal (Au-Pt) layer was used. This was about 10 nm thick and coated on a polished cement surface by ion sputtering prior to the indentation. The instrument used was from Shumazu Corp, Kyoto, Japan. The microstructure of the materials was then studied under both a stereo and a scanning electron microscope.

3. Results

3.1. W/C ratio

A relative density of 66% after CIPing means that 34% of the volume is made up of pores. This indicates that if these pores could be filled with water without any hydration, the W/C ratio would be 0.174. The corresponding density of the body would then be 2.29 g/cm^3. The actual W/C ratios obtained after soaking in water of green bodies are given in Table II. It is worth noting, that although the "ratio of the filled pores" is obtained after 7 h at 37 °C, the pores are filled to about 70% after soaking for only 10 minutes at that temperature. A much slower uptake proceeds after filling the pores. It is worth mentioning that at 20 °C mainly the low temperature hydrate (CAH_{10}) develops, and that at 37 °C the high temperature hydrates (C_3AH_6 and AH_3) occur. The hydrate formation rate is higher at the higher temperature, and a considerably higher fraction of the cement may be hydrated at the higher temperature.

3.2. Hydrated cement

The increase of density with time is shown in Table III for CIPed green bodies and for the control cement. A

TABLE II W/C ratio of CIPed cement cured at the different conditions

	Temperature	
Time	20 °C	37°C
10 min	0.122	0.132
7 h	0.152	0.172
1 d	0.235	0.272
7 d	0.235	0.277
30 d	0.261	0.277

TABLE III Density (g/cm^3) of hydrated cement CIP processed and cured in water at different temperatures

	20 °C		37°C	
Time (day)	CIPed	Control	CIPed	Control
1	2.45 ± 0.02	1.89 ± 0.02	2.51 ± 0.01	1.85 ± 0.02
7	2.45 ± 0.02	1.95 ± 0.02	2.53 ± 0.01	2.02 ± 0.01
30	2.49 ± 0.02	1.95 ± 0.03	2.56 ± 0.02	2.01 ± 0.01

TABLE IV Open porosity (%) of the hydrated cement CIP-processed and cured in water at different temperatures

	20 °C		37 °C	
Time (day)	CIPed	Control	CIPed	Control
1	8.4 ± 0.5	15.1 ± 0.9	2.5 ± 0.3	19.8 ± 2.0
7	7.7 ± 0.2	6.7 ± 0.3	2.3 ± 0.2	8.2 ± 0.5
30	3.8 ± 1.6	7.1 ± 0.5	2.1 ± 0.1	8.4 ± 1.1

higher density was obtained for the CIPed bodies compared with that of the control cement. The higher density at higher temperature is in accordance with the densities of the different phases.

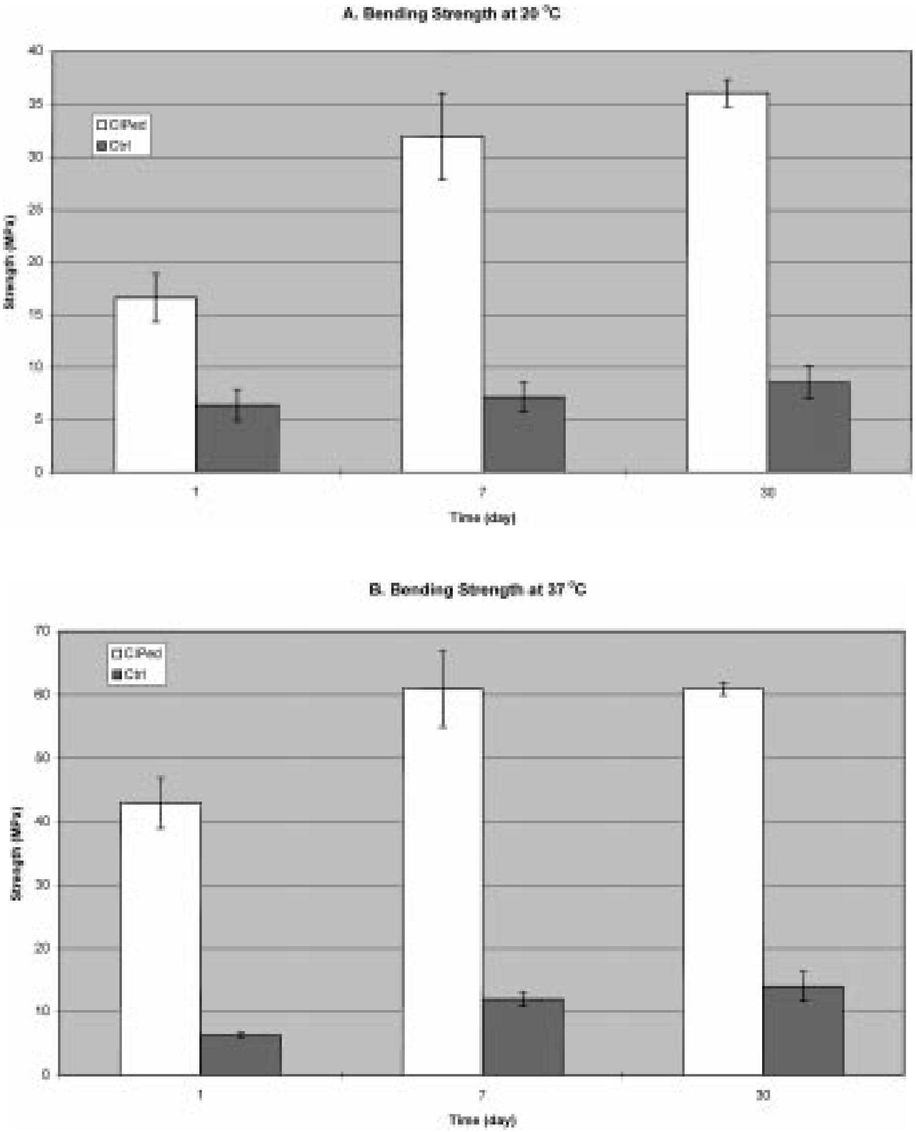
The open porosity of the hydrated cement is presented in Table IV. A significant difference was found between the control and the CIPed samples, and the high temperature cured CIPed samples showed the lowest open porosity.

The development of bending strength with time at two temperatures is shown in Fig. 1. A higher hydration temperature resulted in a higher strength. The strength of the control cement is in all instances inferior to that of CIPed samples. The bending-strength of the cement cured in water and in humid air is compared in Fig. 2. No significant difference was found between samples hydrated in water and samples hydrated in humid air. The compressive strength of cement green bodies was approximately 5 MPa. After water immersion the compressive strength of the CIPed bodies increased to over 200 MPa and the strength development followed the same pattern as the bending-strength.

The bending strength of green bodies hydrated in solutions containing the accelerator Li^+ is shown in Fig. 3. The strength developed fast, and is comparable after only 0.5 h to that of the control cement after one day. However, in the course of days there was no significant difference compared with the CIPed samples hydrated without an accelerator.

3.3. Microstructure and hardness

The microhardness of the cements measured is listed in Table V. CIP-processed cement had a twofold higher


A. Bending Strength at 20 °C

B. Bending Strength at 37 °C

Figure 1 Bending strength of CIP-processed cement cured in water (A) at 20 °C and (B) at 37 °C for 1, 7 and 30 days, compared with the control material.

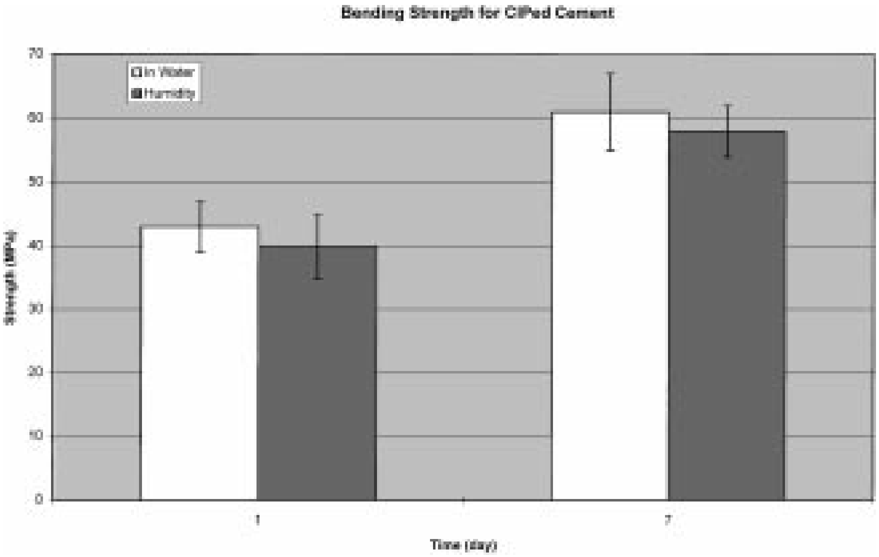


Figure 2 Comparison between bending strength of CIP-processed cement cured in water and humid air at 37 °C for 1 and 7 days.

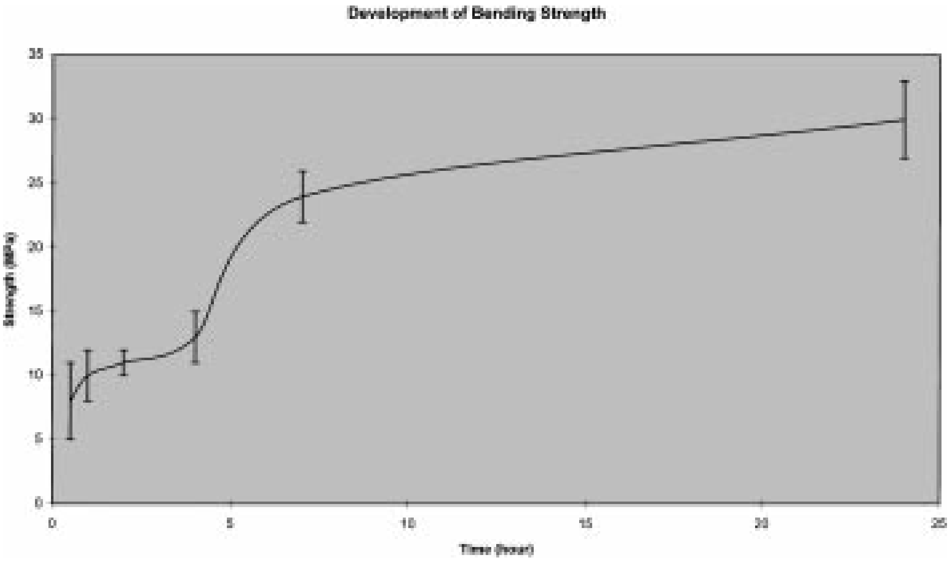


Figure 3 Development of bending strength of the CIP-processed cement cured in a 0.5% Li_2CO_3 solution at 37 °C.

TABLE V Compressive strength (MPa) and microhardness (VHN) of the cement (cured for 7 days)

	CIPed		Control	
Temperature (°C)	Strength	Hardness	Strength	Hardness
20	254 ± 50	158 ± 16	116 ± 11	67 ± 7
37	286 ± 35	155 ± 10	97 ± 18	71 ± 8

hardness than that of the control cement. SEM micrographs are shown in Fig. 4. The pore sizes observed in the CIPed cement are a few tens of micrometers compared to hundreds of micrometers for the control cement.

4. Discussion

The green bodies of CIP-processed cement block can withstand a certain amount of loading, and are also machinable. They can be easily cut or carved to a desired shape. It seems that the compacted green structure does not prevent or delay the water penetration into the cement green body. The flexural strength of the cement which was CIP-processed and cured in humid air was the same as that of the cement which was cured in water. This indicates that water vapor and liquid water react in a similar way with the green body. It was possible to produce a high early strength of CIPed cement by immersing the CIPed cement block in a 0,5% Li_2CO_3 solution. The strength development was not negatively influenced by the high hydration rate.

The CIP-processed cement after hydration had a much higher density (2.51 g/cm^3) than that of the green body filled with water. (theoretical value 2.29 g/cm^3). This is caused by further water penetration into the pore system that develops during the hydration process due to the volume changes of the system related to hydration of the phases. The additional water then reacts with the remaining unreacted aluminate cement. The

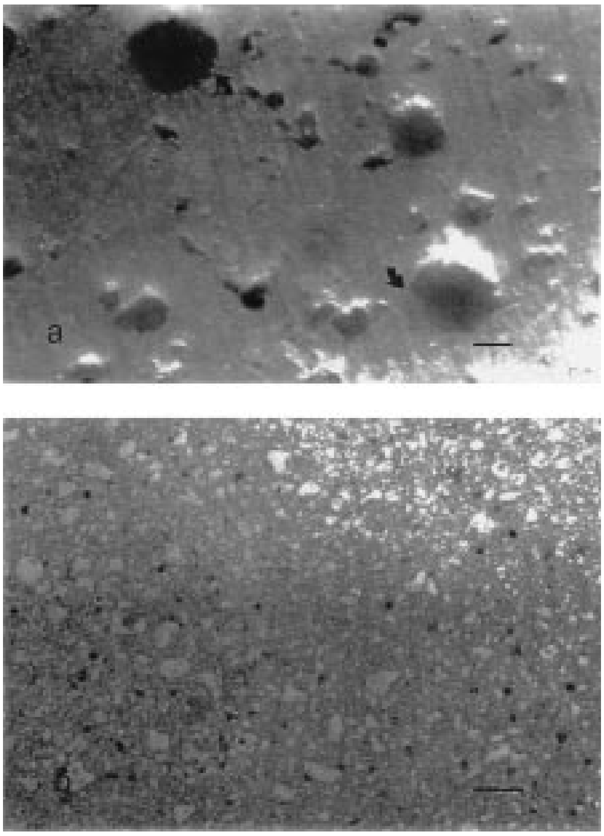


Figure 4 Micrographs of the control and CIP-processed cements, cured in water at 37 °C for one day. a) the control material, large defects appear (arrow, bar = 1 mm); b) CIP-processed cement with a macro-defect-free structure. The white spots are non-hydrated particles embedded in the hydrates formed (bar = 0.1 mm).

basic hydration reactions of aluminate cement are as follows;

$$\text{at } 20\,^\circ\text{C} \qquad CA + 10H \rightarrow CAH_{10} \qquad \text{(a)}$$

$$2CA_2 + 26H \rightarrow 2CAH_{10} + 2AH_3 \qquad \text{(b)}$$

$$\text{at } 37\,^\circ\text{C} \qquad 3CA + 12H \rightarrow C_3AH_6 + 2AH_3 \qquad \text{(c)}$$

$$3CA_2 + 21H \rightarrow C_3AH_6 + 5AH_3 \qquad \text{(d)}$$

For the main CA phase, the hydration will result in 15.7 vol%, 19 vol%, 25.3 vol% and 26.3 vol% reduction (chemical shrinkage) for hydration (a), (b), (c), and (d), respectively (11).

From the reactions above, it is seen that the W/C ratio of the reactions (a) and (b) is higher than the W/C ratio of the reactions (c) and (d). The slightly lower W/C observed for the CIP-cement at 20 °C compared to that measured at 37 °C, indicates that the hydration is a diffusion controlled process with faster hydration at higher temperatures.

The slight increase of density, with curing time, suggests that the hydration of cement is continuous. With negligible volume change of the CIPed cement block during hydration ($<1\%$), one can assume that the slight increase of density is due to the net increase of the water uptake. The volume reduction during hydration results in more space for further water uptake. However, due to the reduced permeability of the set cement, the water uptake slows down with time.

The CIP-cement has a similar level of W/C ratio as the control cement (0.277 compared to 0.32), but the strength is several times higher than that of the control cement. The results demonstrate the importance of the final microstructure developed, not just the degree of hydration. The CIP-processed cement showed a heterogeneous but macro-pore-free structure, a composite structure consisting of hydrates and non-reacted particles (Fig. 4). These non-reacted particles probably help to reinforce the material and contribute to the high strength of the hydrated cement. The CIP process creates a macro-defect-free structure of the cement before hydration, thus avoiding large defects in further processing.

A higher curing temperature yielded higher strength of CIP-processed cement, indicating the importance of the degree of hydration and the type of hydrates developed. The hydrates act as binders between the non-reacted particles. The CIP technique provides a way of producing cement materials without an excess of water, thus elimimating the formation of larger pores. Multifold strength increase of the CIP-processed cement emphasizes the importance of macro-defect-free structures, and indicates the potential of chemically cured ceramics in load-bearing applications.

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