THE FRACTURE OF GEOPOLYMERS

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ABSTRACT

The alkaline activation of Portland cement based composites, granulated blast-furnace slag and pozzolans opens new opportunities for the manufacture of special cements with properties different from those presented by the ordinary Portland cement.
In this work, a polymeric inorganic cement based on metakaolin, of early-high compressive strength and curable at room temperature called geopolymer[1], was obtained and the mechanical strengths were evaluated.
In order to stabilize the geopolymer cement matrix and improve its fracture toughness, micro-fibers of natural wollastonite were used in volumes from 0 to 5%. The methodology used was based on the non-linear fracture mechanics, developed for quasi-brittle materials[2]. The properties of fracture toughness, represented by the G_I^s curves, the fracture parameters K_{Ic}^s and $CTOD_c$ as well as the compressive, flexural strength and indirect tensile strength were evaluated and compared with those of a reference Portland cement composite with the same volumes of fibers.
The addition of wollastonite micro-fibers as stabilization elements and reinforcement yielding satisfactory results as to the improvement of the mechanical properties of the geopolymer cement composites. The results showed that the wollastonite micro-fibers are compatible with the alkaline matrix and develop a interfacial transition zone (matrix/fiber) as dense as the matrix. Toughness increase (K_{Ic}^s and $CTOD_c$) of the order of 26%, obtained for a fiber volume of 2%, were considered significant, when compared with the 8% gain obtained in the Portland cement composite. The effective critical crack extension (Δa_c) also showed a significant improvement. All the other mechanical properties were optimized, including the compressive strength, with addition of wollastonite.

keywords: geopolymer, nonlinear fracture mechanics, composite.

INTRODUCTION

The geopolymers, also called poly(sialate)s, are a new family of materials based on the oxide-aluminosilicates (pozzolans) polymerization, obtained by a similar process to that employed in the synthesis of crystalline zeolites [1]. The process consists of the hydrothermal polymerization of the pozzolan in a highly alkaline environment (pH $\simeq$14). The time of reaction depends on the processing temperature and of the radiation frequency used [2].

Depending on the Si/Al ratio, it is possible to obtain products with different characteristics. A 3D arrangement, with cross-linked bonds is formed when the Si/Al ratio is the equal or higher than 2. The polymeric mineral with those atomic ratios is called poly(sialate-siloxo), or PSS, and can be used a binder material in high-performance concretes and mortars [3].

When materials rich in amorphous silica (pozzolans) are added to the Portland cement, they react with the $Ca(OH)_2$, liberated during the formation of C-S-H by the hydration of C_3S and βC_2S, generating an extra production of C-S-H, even so, with more larger Si/Ca ratio. The consumption of $Ca(OH)_2$ and the extra formation of C-S-H, increase the matrix density and it contributes to the maintenance of a lower pH and therefore, more stable[3]. Even so, these alterations in the matrix increase its sensibility to such sharp defects as internal microcracks. Several researchers reveal that when reinforcement elements in the form of fibers are incorporated in the matrix, notable improvement in toughness is obtained.

In the case of the PS, countless microcracks are formed in the matrix due to the gradient of tensions generated during the polymerization. The employment of mineral fillers, in the form of fine particles minimizes those effects. In mortars and concretes, the stabilization can be associated to the reinforcement of the matrix, when particles in form of fibers are incorporate.

The RILEM Technical Committee 89 – Fracture Mechanics of Concrete – Test Methods[4], recommends the employment of the two-parameter fracture model (TPFM) based on the studies of Jeng and Shah[5] for determination of the fracture toughness of quasi-brittle materials such as mortars and concretes. The model considers the elasto-plastic deformations happening ahead of the tip of a macrocrack induced by a notch. The unloading compliance (C_u) measure in the unloading at 95% of the maximum load (post-peak load) in diagrams Load versus CMOD (crack mouth opening displacement) it allows the determination of the fracture properties of the material, indicated by the critical stress intensity factor (K_{Ic}^{s}), the critical crack tip opening displacement ($CTOD_c$) and the critical crack effective extension, $\Delta a_c = (a_c - a_0)$. The compliance in the initial loading (C_i) it supplies the modulus of elasticity (E) of the composite. The results obtained were used to calculate the deformation energy release rate (G_I^{s}).

This work presents a study of the fracture toughness of a mortar composite of PSS cement matrix with ratio Si/Al = 3, reinforced with natural wollastonite ($Ca[SiO_3]$) micro-fibers, a natural mineral of high modulus of elasticity (120 GPa) and aspect ratio (10-20) employed in the ceramic industry as a reinforcement and stabilization element. The volumes of fibers studied were of V_f = 0% (pure matrix) at V_f = 5%. The fracture parameters were measured and compared with the results obtained with the Portland cement mortar composites.

MATERIALS AND METHODS

In order to obtain PSS, the main source of aluminum and silicon was the metakaolin obtained by the kaolin calcination from Rio Grande do Norte (RN), Northeast of Brazil. The time and the temperature of calcination were objects of initial study, because they depend on the purity and of the degree of crystallinity of the kaolin. The calcination to 12 hours at 700 ^{o}C promote the desidroxylation of the kaolinite and the conversion of aluminum coordination number from VI to IV, disordering the lattice. Since the ratio between the silicon and the aluminum in the metakaolin is smaller than 3, an extra source of silicon, a commercial alkaline polysilicate was used. With the purpose of obtaining the necessary pH of 14, to initiate the polymerization, potassium hydroxide (Vetec P.A.) was also used as a complementary alkali source. The calcium source was granulated blast furnace slag (GBFS) supplied by Belgo Mineira S.A. In this work, the geopolymer studied was the sodium, potassium and calcium poly(sialate-siloxo), Na,K,Ca-PSS.

The reference Portland cement was the CPIIE-32 (type II of ASTM C 150), of marks Campeão/Mauá and the fine aggregate was the river sand supplied by IPT S.A. (Normal Brazilian sand). The proportion between binder and aggregate was 1:3, in weight for all the composites and the water/binder dry was 0,48 for the Portland cement composite and 0,38 for the PSS composite. The consistency index (flow table - ASTM C 230) for both composites it was of 165 $\pm$ 5 mm , with V_f = 0%.

The wollastonite used was the NYAD-G® grade (Figure 1) of Nyco Minerals Inc. (New York - USA). The Table 1 shows the main characteristics of the raw materials used in this study.

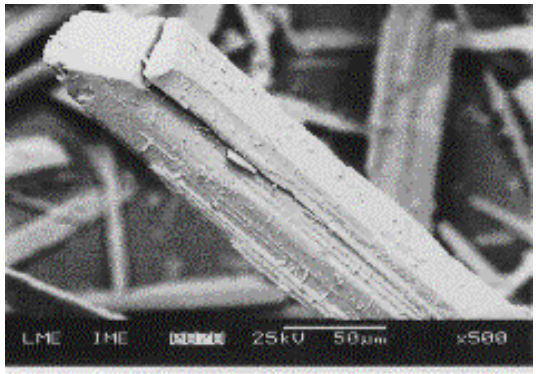

Figure 1 – Micrograph (SEM) of wollastonite micro-fibers used (500 X).

Table I – Chemical composition and physical properties.

Materials	Chemical Composition (%)									L.O.I.	Specific Area Blaine	Specific Weight
	CaO	MgO	Na_2O	K_2O	Fe_2O_3	SO_3	Al_2O_3	TiO_2	SiO_2	(%)	($m^2.Kg^{-1}$)	($g.cm^{-3}$)
Metakaolin	< 0,01	0,01	0,04	0,33	0,30	-	39,8	0,11	44,4	14,4	**1060,76**	2,56
Na-Silicate	-	-	17,3	-	-	-	-	-	35,6	44,3	**-**	1,75
GBFS	47,8	0,63	0,21	0,26	0,72	0,47	13,0	0,38	39,7	0,14	**345,43**	2,98
Wollastonite	46,55	0,15	0,01	0,05	0,75	-	0,28	0,04	51,37	0,34	**-**	2,90
CPIIE-32	60,4	1,4	-	-	1,6	3,9	5,0	-	20,0	6,30	**349,92**	3,04

Strength Activity Index (ASTM C 618) of pozzolan ∅ < 0,074 mm = 107,88%.
% Retained in the sieve # no. 325 Tyler-Mesh = 12,35%.
Aspect ratio of wollastonite: 10 to 20.
CPIIE-32 – Bogue composition (ASTM C 150): 46,60% C_3S; 22,18% βC_2S; 10,54% C_3A; 4,87 C_4AF.

The mixture of the basic constituent and the moldings of the specimens followed the procedures described in the NBR 7215 Brazilian standard. The wollastonite was dispersed in the water before mixing with other materials. Cylindrical test specimens of (∅10x20)cm for compressive strength (ASTM C 39) and splitting test (ASTM C 496) were moulded. To determination of the fracture toughness, the procedures established by TC-89 FMT of RILEM were adopted as already mentioned. The dimensions of the test specimens of toughness and the experimental configuration are shown in the Figures 2 and 3. The Na,K,Ca-PSS cement composites was cured to the air at 25 $\pm$ 2 ^oC, and the Portland cement composites was cured immerged in water at 22 $\pm$ 2 ^oC until the date of the tests. The G_{Ic}^s values were calculated based on relationship:

$$G_{Ic}^s = \frac{\left(K_{Ic}^s\right)^2}{E}$$

and G_I^s curves were obtained as function of Δa by interation.

After determination of the mechanical properties, samples of pastes and mortars were selected for scanning electron microscopy (SEM – Jeol 5800 LV) to identify the failure mechanisms.

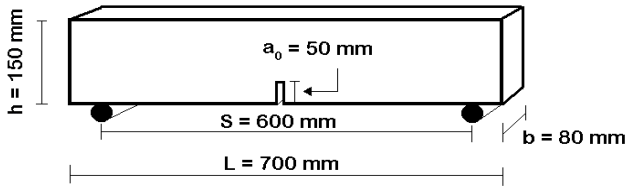

Figure 2 – Geometry and dimensions of the beams tested under 3-point bend.

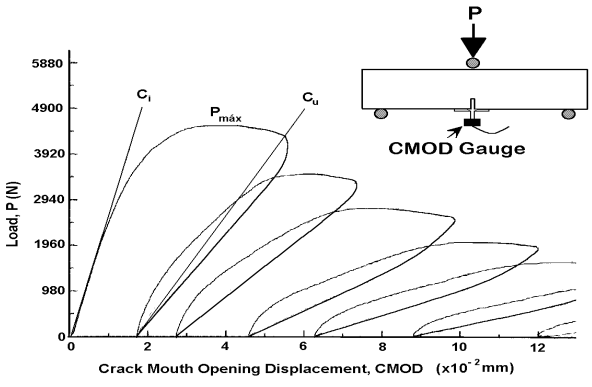

Figure 3 – A typical Load versus CMOD curve obtained from 3-point bend tests. The maximum load (P_{max}), initial compliance (C_i) and unloading compliance (C_u) are obtained from the graph and used as input for the TPFM.

RESULTS AND DISCUSSIONS

The Figures 4 and 5 show the results of characterization of the two matrices studied. The results reveal that the microstructure of the poly(sialate-siloxo) cement is formed by phase of sodium, potassium and calcium aluminosilicate - Na,K,Ca-PSS, without any traces of $Ca(OH)_2$, commonly present in the Portland cement matrix.

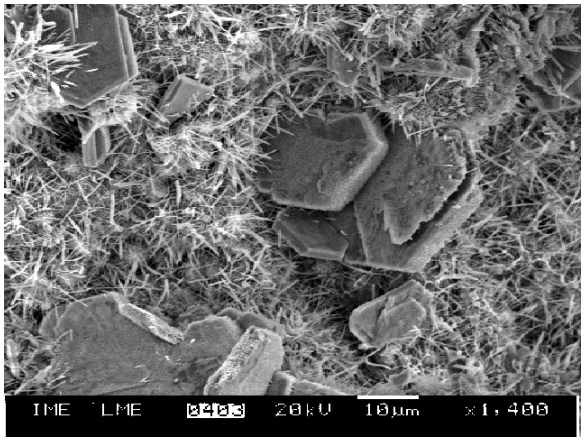

Figure 4 – Micrograph (SEM) of Portland cement composite bulk matrix (1400X). The big polygonal phases are $Ca(OH)_2$ crystals and the needle-like crystals are C-S-H particles.

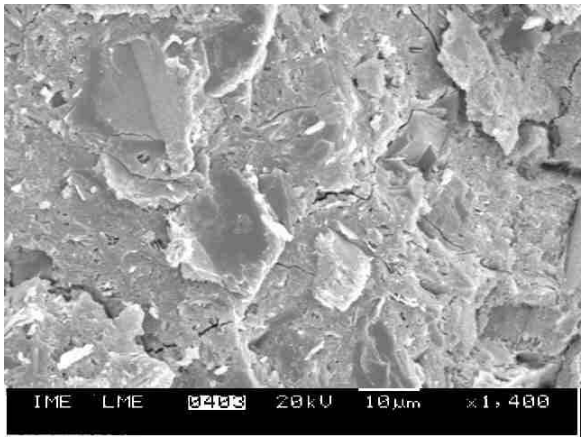

Figure 5 – Micrograph (SEM) of Na,K,Ca-PSS cement composite bulk matrix (1400X). Note as the microstructure is homogeneous and dense, but with microcracks.

The compressive strength tests results of normal mortar of cement CPIIE-32 and of cement Na,K,Ca-PSS specimens, without fiber reinforcement ($V_f = 0\%$), as function of age are shown in the Figure 6. When the Na,K,Ca-PSS is cured at 65 ^oC to 4 hours, it reaches an early compressive strength of 45 MPa. This same strength level is reached at three days of age, when the cure is realized at room temperature. At 28 days of age, a compressive strength of 60 MPa is reached, largely overcoming the Portland cement mortar.

Figure 7 shows the flexural strength and splitting tests results at 28 days of age, as a function of fibers volume. It can be noted that the optimum fiber volume and that presents the best results was of 2%. Above this value, there was strength reduction due to what may be an increase of mixture porosity, since the water/binder ratio stayed constant and chemical admixture was not used.

The Figures 8 and 9 show the results obtained in the three-point bend beam tests, for determination of modulus of elasticity (E) and of the toughness properties (K_{Ic}^s, $CTOD_c$ and Δa_c).

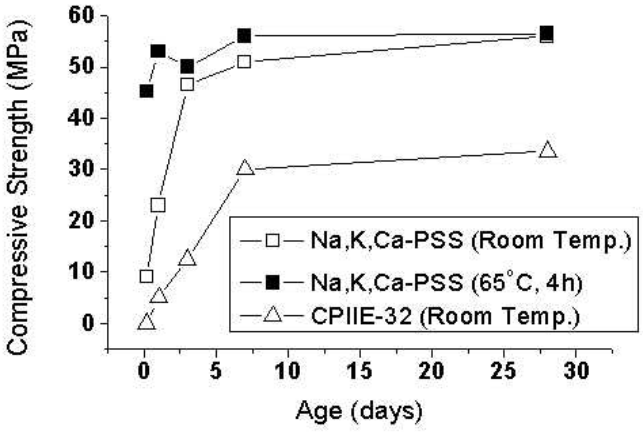

Figure 6 – Compressive strength of poly(sialate-siloxo) composite matrix and Portland cement composite matrix as function of the time and temperature.

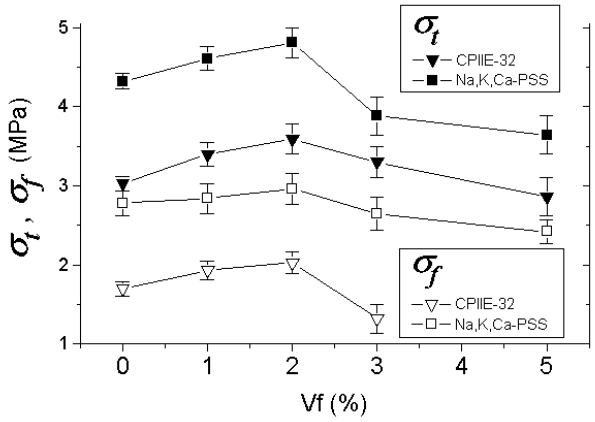

Figure 7 – Variation of tensile and flexural strengths as function of fiber volume. (at 28 days of age)

As shown in Figure 8, in both composites, K_{Ic}^{s} values increased until 2%. The toughness increase was of 26% to PSS composite and 8% to PC cement. The $CTOD_c$ values always growing with fiber addition. In the Portland cement composites, the $CTOD_c$ values decreased up to $V_f = 2\%$. Only to $V_f = 3\%$ that there was improvement of $CTOD_c$, however the values were low than the matrix with $V_f = 0\%$. Here is noted the importance of determination of two fracture parameters, because with only one these means, a equivocal can be performed in quasi-brittle materials toughness analysis. The addition up to 2% increased the modulus of elasticity to both composites system. However, above this fiber volume, there was decrease of E values, probably due the excessive porosity of the mixture.

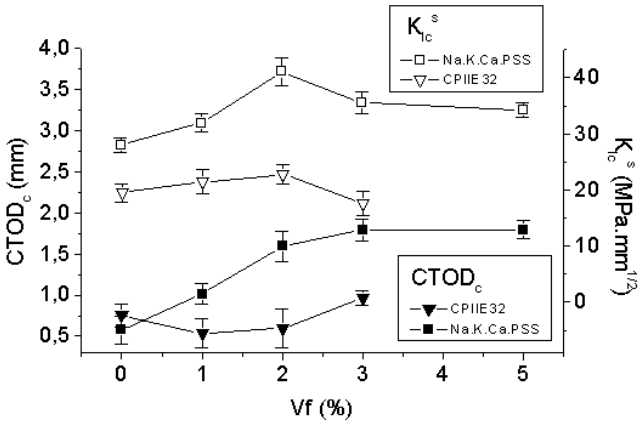

Figure 8 – Variation of $CTOD_c$ and K_{Ic} as function of fiber volume.

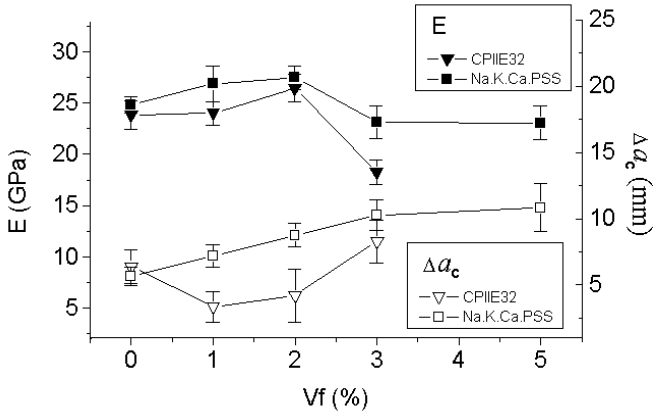

Figure 9 – Variation of modulus of elasticity and critical crack effective extension as function of fiber volume.

The critical effective crack extension increased to all fiber volume in the PSS cement composites. However, in the Portland cement composites, was observed a decrease in Δa_c to $V_f = 1$ and 2 %. These results indicates different actuation of wollastonite micro-fibers, depending of composite matrix. The G_I^s values obtained by PSS composites show its high performance. The fracture toughness determined by G_{Ic}^{s} for PSS was 100% higher than to presented by PC, for all fiber volumes, as shown in Figures 10 and 11.

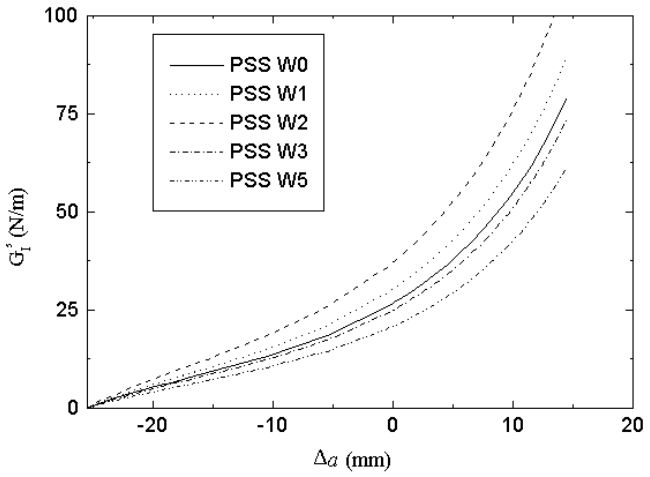

Figure 10 – Variation of deformation energy release rate, G_I^s as function of effective crack extension, Δa to PSS geopolymer cement with $V_f = 0\%$ to 5%.

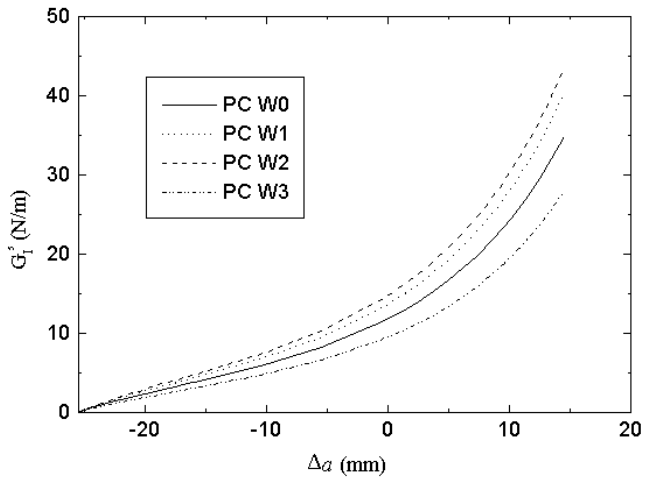

Figure 11 – Variation of deformation energy release rate, G_I^s as function of effective crack extension, Δa to CPIIE-32 Portland cement with $V_f = 0\%$ to 3%.

The Figure 12 shows a micrograph (SEM), obtained by secondary electrons of the fracture surface of the PSS composite. To notice the presence of fibers broken in traction in the level of the fracture surface and other, had gone pull-out of matrix. Figure 12 shows a micrograph (SEM) obtained by backscattering electrons of the polished surface, revealing the change happened in the crack trajectory when intercepting the

fiber. These observed mechanisms are the main ones responsible for the increasing of toughness of the material. The critical crack effective extension (Δa_c) increased 50% in PSS composite with V_f = 2%. In Portland cement composite, increasing occurs of 10% in Δa_c only occurs with at V_f = 3%.

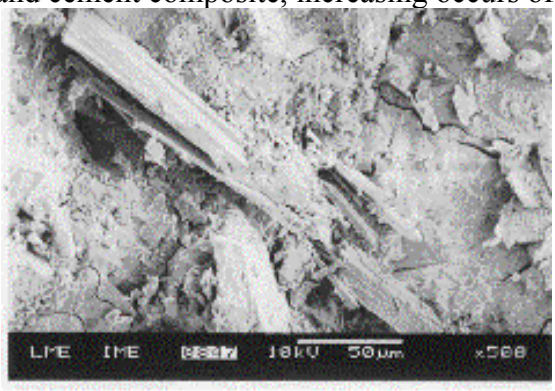

Figure 10 – Micrograph (SEM) of Na,K,Ca-PSS cement composite with 2% of wollastonite micro-fibers (500X).

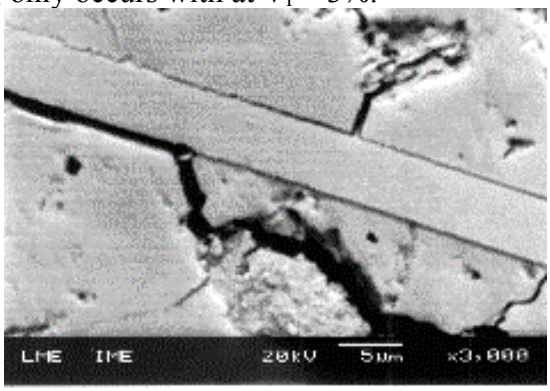

Figure 11 – Micrograph (SEM) of Na,K,Ca-PSS cement composite fracture surface polished. Note as the crack trajectory is modified by fiber (3000X).

CONCLUSIONS

The addition of wollastonite micro-fibers as reinforcement elements, supplies satisfactory results as the improvement of the mechanical properties of the geopolymeric composite type Na,K,Ca-PSS. The results reveal that the wollastonite micro-fibers present total compatibility with the alkaline matrix (pH = 13) and, they develop a interfacial transition zone (matrix/fibre) that is as dense as the bulk of the matrix. Increases of fracture toughness (K_{Ic}^s and $CTOD_c$) of the order of 26% to V_f = 2% were registered. The critical crack effective extension (Δa_c) also showed a significant improvement. The G_I^s curves calculated by K_{Ic}^s and $CTOD_c$ values showed the high performance of geopolymeric composites, always 100% higher the Portland cement composites to all fiber volumes. The other mechanical properties too were optimized with addition of wollastonite, including the compressive strength.

Acknowledgements

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