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Promotion effect of C-S-H-phase nuclei on building calcium silicate hydrate phases

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Abstract

In this investigation the influence of C-S-H-phase nuclei on the $CaO\text{-}SiO_2\text{-}H_2O$ hydrothermal reaction was studied. $CaO\text{-}SiO_2\text{-}H_2O$ mixes ($C/S = 0.11$) were hydrothermally treated at 10 atm. of saturated steam with the addition of C-S-H-phase nuclei. The source of C-S-H-nuclei was ground waste sand–lime (WSL) products. WSL was added in amounts from 0 to 40% by weight of the total mix and in different surface areas. Hydration kinetic studies and physico-chemical tests were done on the hydrothermally-hardened specimens at different times of autoclaving. The modes of the hydrothermal reaction between silica, lime and WSL were fully discussed and related to the developed compressive strength of the final autoclaved samples. The results indicated that the C-S-H-phases in the WSL accelerated the nucleation period of the reaction between quartz and lime. The on the seeds crystals formed and later accumulated tobermorite $Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O$, as this represented the main hydration product it caused higher strength values for these autoclaved products. The role of C-S-H-phase nucleation as a decisive factor in $CaO\text{-}SiO_2$ hydrothermal reaction has been demonstrated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium silicate hydrates; Hydrothermal reactions; Physical and chemical properties; Waste sand lime

1. Introduction

The reaction mechanism of a $CaO\text{-}SiO_2\text{-}H_2O$ system at high temperature and pressure has been thoroughly investigated [1–3]. It has been observed that reaction of $Ca(OH)_2$ and SiO_2 at temperatures of about 125–200°C proceeds through different stages. The first reaction product is a lime-rich phase, generally called lime-rich tobermorite gel, with a probable composition of $C_7S_4H_n$. This phase reacts with residual SiO_2 to form $C_5S_4H_n$ and further reactions with residual SiO_2 result in the formation of lime-arm calcium silicate hydrate such as $C_2S_3H_2$. By using a raw mix with a low C/S ratio as used in industry (~0.1) residual silica remains. Researchers [4,5] have reported that the rate-determining step (RDS) for the reaction was the rate of dissolution of SiO_2, or, more specifically, the availability of the silicate ions in the reaction zone. Recently it has been proved [6] that the addition of alkali to a $CaO\text{-}SiO_2$ reaction medium increases the solubility of SiO_2 and causes an increase in the reaction rate. On the other hand, some researchers [7,8] are of the opinion that the RDS of the $CaO\text{-}SiO_2$ reaction is the rate of diffusion of the silicate ions through the deposits that surround the quartz grains. However, this is only restricted in the latter periods of the reaction [9].

Nucleating agents are solids that possess cell-size domains of about the same size as that of the solid to be nucleated. Funk [10] reported that the addition of the nucleating agent, tobermorite gel, increased the rate of hydration of $\beta\text{-}C_2S$. Miskiewicz [11] used the C-S-H-phase nuclei as an accelerator for the hydration of $Ca_3SiO_4Cl_4$. Miskiewicz attributed the acceleration to the nucleation effect. Little information about the mechanism of nucleation in the $CaO\text{-}SiO_2$-hydrothermal reaction has been reported. This work studied the effect of C-S-H-phase nuclei, present in WSL, on the $CaO\text{-}SiO_2$ reaction in autoclaving, and to study the possibility of introducing WSL as a raw ingredient in the sand–lime brick industry, i.e. for waste recycling.

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2. Experimental details

Used CaO was prepared by ignition of analytical grade $CaCO_3$ at 1000°C for 1.5 h. SiO_2 was natural silica ($SiO_2 = 99.7\%$). The source of C-S-H-phase nuclei was waste sand–lime brick (WSL). Sand–lime mixes ($C/S = 0.11$) were prepared and WSL was added in amounts from 0–40% by weight to the dry mix. The required amount of water was added. The samples, after homogenization, were moulded (400 kg/cm^2) and autoclaved at 10 atm. (183°C) for 6–12 h. The hardened specimens were dried at 50°C for 24 h and then subjected to chemical investigation and X-ray diffraction analysis. In addition, the physico-mechanical properties were also studied.

WSL was crushed and separated into the following fractions: <2.0, 2.0–1.0, 1.0–0.5, 0.5–0.125 and <0.125 mm. The main constituents of WSL were sand, calcium silicate hydrate and $CaCO_3$, which was a result of carbonation of the unreacted $Ca(OH)_2$.

This study has three parts: (A) the influence of the whole WSL <2.0 mm; (B) the influence of WSL with different grain sizes; and (C) the influence of the finest WSL fraction (<0.125 mm) using different autoclave times.

3. Results

3.1. *Influence of the whole WSL <2.0 mm*

3.1.1. *Kinetics of hydration*

Analysis of the autoclaved products was carried out to determine the chemically-combined water, free lime and combined silica, as well as to calculate the C/S molar ratio. The results are graphically represented in Figs. 1 and 2. The results indicate that the addition of WSL (<2.0 mm) enhanced the rate of lime–silica reaction. Free lime content continuously decreased with increasing amounts of WSL (Fig. 1); whereas the amount of combined silica continued to rise with increasing amounts of WSL. Consequently, the calculated C/S molar ratio of the formed calcium silicate hydrates showed a continuous decrease as shown in Fig. 2. Also, the combined water was increased by up to 20% WSL addition, and then starts to decrease with any further additions (Fig. 2).

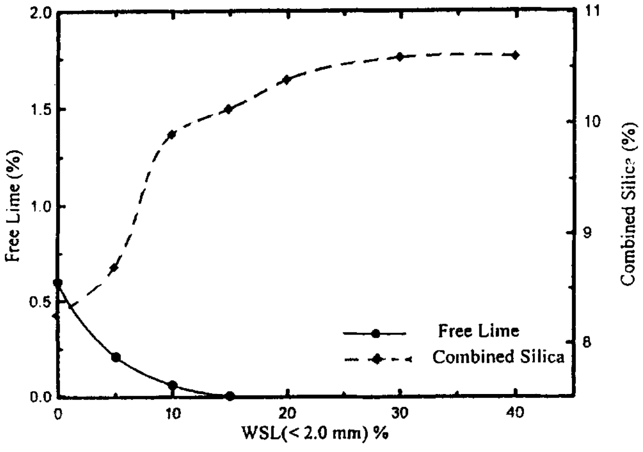

Fig. 1. Effect of WSL (<2.0 mm) on the free lime and combined silica contents of sand – lime products.

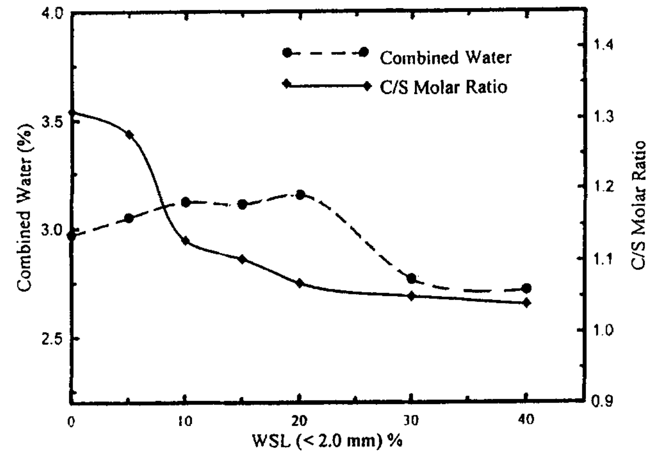

Fig. 2. Influence of WSL (<2.0 mm) additions on the amounts of combined water and C/S molar ratio of sand–lime products.

3.1.2. *Physico-mechanical properties*

The physico-mechanical properties of the different hardened samples are graphically represented as a function of the percentage of added WSL (<2.0 mm) in Fig. 3. This clearly indicates that compressive strength increased with increasing amounts of WSL up to 15%, and then smoothly decreased with further additions. Samples with a WSL content of up to 30% showed higher compressive strength than the control sample (without WSL).

Apparent porosity increased with increasing additions of WSL, whereas bulk density decreased. Generally, there is a reverse relationship between bulk density and apparent porosity, as seen in Fig. 3.

3.2. *Influence of WSL with different grain size*

The effect of WSL with different grain sizes on the physico-mechanical properties of sand–lime bricks was studied. Crushed WSL was separated into four fractions: 2.0–1.0, 1.0–0.5, 0.5–0.125 and <0.125 mm, using the corresponding standard sieves. Each fraction was added separately to the total mix. The coarse fractions were added in amounts of 5, 10, 15, 20 and 30% of the total mix. The finest fraction (<0.125 mm) was added in amounts of 1, 3, 5 and 10% of the total mix. The moulded samples were hydrothermally processed at 10 atm. (183°C) for 8 h. The hardened specimens were

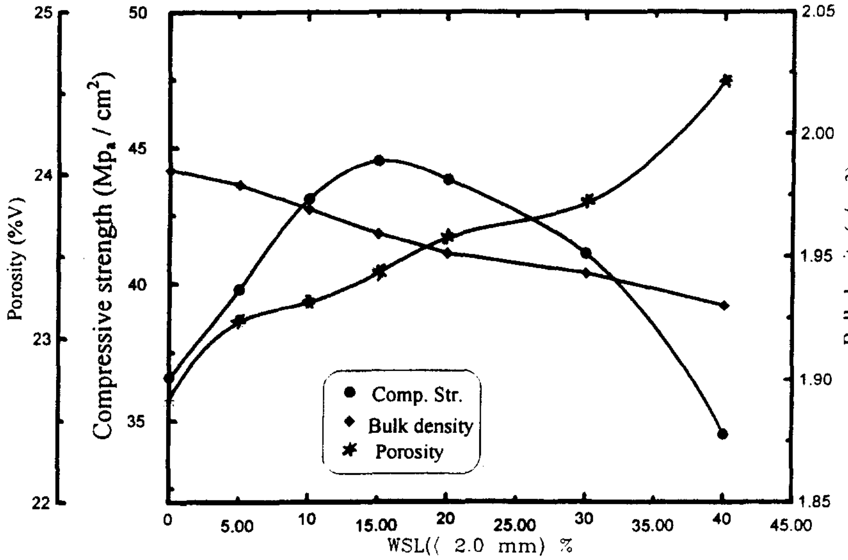

Fig. 3. Influence of WSL (<2.0 mm) additions on the physico-mechanical properties of sand–lime products.

investigated for their physico-mechanical properties (Table 1). Strength is graphically represented against the percentage of WSL added in Fig. 4. The results of compressive strength shows that the addition of the 2.0–1.0 mm grain size fraction caused a slight decrease in strength. Both fractions 1.0–0.5 mm and 0.5–0.125 mm showed nearly the same trend in strength: it increased with up to 15% WSL additions, but then declined with further additions. Generally, addition of the 1.0–0.5 mm fraction resulted in an increase in strength of more than that caused by the addition of the 0.5–0.125 mm fraction.

Table 1

Grain size (mm)	WSL (%)	Physical properties		
		Comp. strength (Mp_a/cm^2)	Bulk density (g/cm^3)	Porosity (% V)
2.0–1.0	0	36	1.985	22.63
	5	36	1.975	23.22
	10	35	1.963	23.5
	15	35	1.955	23.88
	20	34	1.942	24.38
	30	32	1.925	25.21
1.0–0.5	5	39	1.971	23.43
	10	41	1.955	23.37
	15	41	1.94	23.5
	20	38	1.93	24.18
	30	32	1.916	25.08
–0.125	5	37	1.969	23.51
	10	39	1.932	24.55
	15	39	1.922	24.98
	20	37	1.908	25.5
0.5	30	31	1.875	27.03
<0.125	1	50	1.979	22.78
	3	56	1.98	23.36
	5	60	1.98	23.58
	10	58	1.963	25.12

The addition of the finest fraction of WSL (<0.125 mm) increased the strength markedly up to 5% WSL addition, whereas 10% addition caused a slight decline in strength, as shown in Fig. 4.

The influence of the addition of WSL (in different grain sizes) on the porosity and bulk density of the autoclaved

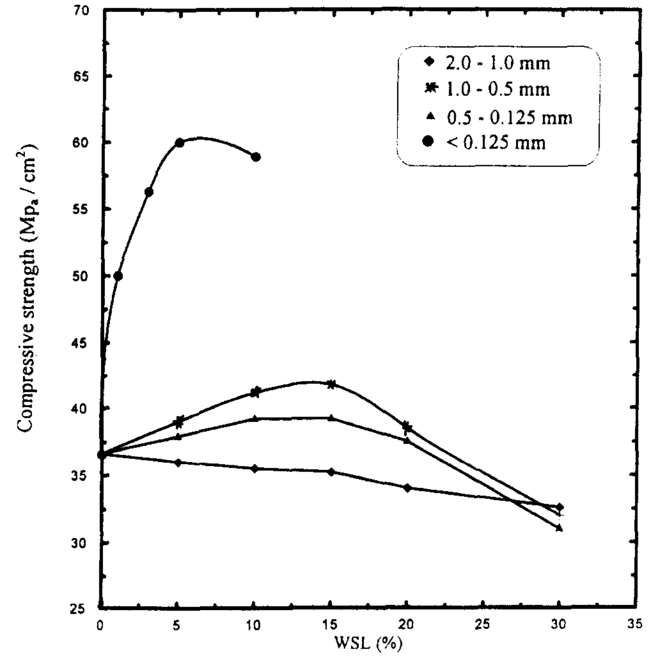

Fig. 4. Influence of the addition of WSL with different grain sizes on the compressive strength of sand–lime products.

products is shown in Table 1. The results show that the addition of WSL generally increased the porosity and bulk density was decreased. The addition of any grain size fraction (2.0–1.0, 1.0–0.5, 0.5–0.125 or <0.125 mm) of WSL increased the porosity and decreased the bulk density to a higher extent than the addition of whole WSL (<2.0 mm). On the other hand, the addition of the 0.5–0.125 mm fraction caused a maximum increase in porosity and a maximum decrease in the bulk density.

3.3. Influence of the finest WSL (<0.125 mm) fraction using different autoclave times

From the previous results it can be concluded that maximum strength was obtained by the addition of the finest WSL (<0.125 mm) fraction. Accordingly, autoclaving was planned to optimize this fine fraction. Thus, the added amounts of WSL (<0.125 mm) were kept as in the previous section (1, 3, 5 and 10% of the total mix). The samples were autoclaved at 10 atm. (183°C) for 6, 8 and 12 h. The products were dried at 50°C for 24 h, and assessed for their physico-mechanical properties, kinetics of hydration and X-ray diffraction analysis.

Table 2 shows the results for hydration kinetics as well as those for the physico-mechanical properties of the final products prepared with the finest WSL additions and autoclaved for different periods.

3.4. Kinetics of hydration

The results of free lime and combined silica for specimens autoclaved for different periods (6, 8 and 12 h) are plotted as a function of WSL (<0.125 mm) (Fig. 5). Generally, the values of free lime decreased with increasing WSL, or with increasing autoclave time. Samples with 3, 5 and 10% WSL, were found to contain no free lime after autoclaving periods of 8 and 12 h.

The values for combined silica increased with increasing WSL content. The results show a sharp increase with increase in processing time from 8 to 12 h for samples containing 5 and 10% WSL, compared with that of the control sample.

The C/S molar ratio of the binder, as calculated from the results of chemical analysis and combined water, are given in Fig. 6. The C/S molar ratio decreased as the WSL content increased for all autoclaving times. The values of combined water show a large increase up to 3% WSL addition, followed by smooth increase.

3.5. X-ray diffraction analysis

The samples that contained 0, 1, 5 and 10% WSL (<0.125 mm) and were autoclaved under 10 atm. for 8 h were investigated by X-ray diffraction analysis. The diffraction patterns of these samples are given in Fig. 7. The results can be summarized as follows:

1. The intensity of the $CaCO_3$ peaks increased as the amount of added WSL was increased because WSL contained considerable amounts of $CaCO_3$.
2. The intensity of the peaks characterizing free CaO was in a good agreement with the results of the chemical analyses given in Table 2. Free lime was detected easily in the control samples. However, only traces appeared in the sample with 1% WSL.
3. Calcium hydrosilicate (tobermorite) was detected at trace levels in the control sample (without WSL),

Table 2

Auto. conditions	WSL <0.125 mm (%)	Physical properties			Kinetics of hydration					
		Comp. strength (Mp$_a$/cm^2)	Bulk density (g/cm^3)	Porosity (% V)	Comb. water (%)	Free lime (%)	Free silica (%)	Comb. silica (%)	Comb. lime (%)	C/S ratio
h.	0	28.0	1.975	22.79	2.80	0.80	78.54	6.91	9.80	1.52
6	1	30.3	1.975	22.93	3.33	0.25	76.90	8.68	10.35	1.25
x	3	33.5	1.978	22.32	3.93	0.08	75.29	9.46	10.57	1.20
b	5	36.3	1.974	23.82	3.90	0.06	72.40	11.28	10.65	1.01
10	10	44.6	1.966	24.60	3.95	0.06	70.66	11.84	10.82	0.98
h.	0	36.6	1.985	22.60	2.97	0.62	78.00	8.26	9.96	1.30
8	1	50.0	1.979	22.78	3.51	0.18	76.14	9.59	10.37	1.16
x	3	56.3	1.98	23.36	3.80	0.01	75.07	10.07	10.59	1.13
b	5	60.0	1.98	23.58	3.71	0.00	72.24	12.11	10.70	0.95
10	10	58.9	1.963	25.12	3.62	0.00	70.20	12.64	10.85	0.92
h.	0	43.5	1.986	22.59	3.13	0.40	77.17	9.02	10.25	1.22
12	1	46.9	1.982	22.64	3.42	0.06	74.22	10.84	10.52	1.04
x	3	51.7	1.976	23.44	3.95	0.00	71.96	12.36	10.60	0.92
b	5	53.2	1.958	23.50	3.95	0.00	70.25	13.63	10.67	0.84
10	10	50.0	1.954	25.02	4.15	0.00	68.13	14.73	10.86	0.79

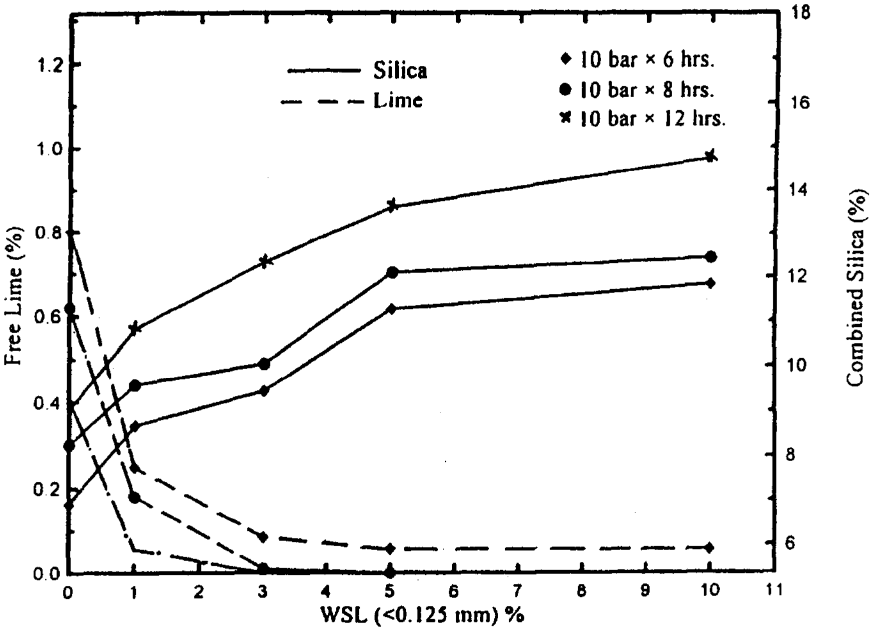

Fig. 5. Influence of WSL (<0.125 mm) additions on the free lime and the combined silica contents of sand–lime products.

and the amount of it increased with increasing content of WSL. The sample with 10% WSL was characterized by the presence of traces of xonotlite.

3.6. Physico-mechanical properties

Fig. 8 shows the compressive strength of the samples with the finest fraction of WSL autoclaved under 10 atm. for 6, 8 and 12 h represented as a function of the amount of WSL (<0.125 mm) added.

The results indicate that the compressive strength increased with increasing WSL at all autoclave times, except for the samples with 10% WSL at 8 and 12 h, which showed a slight decrease. The strength of the control samples (without WSL), increased with increase in autoclave time from 6 to 12 h. For the samples made

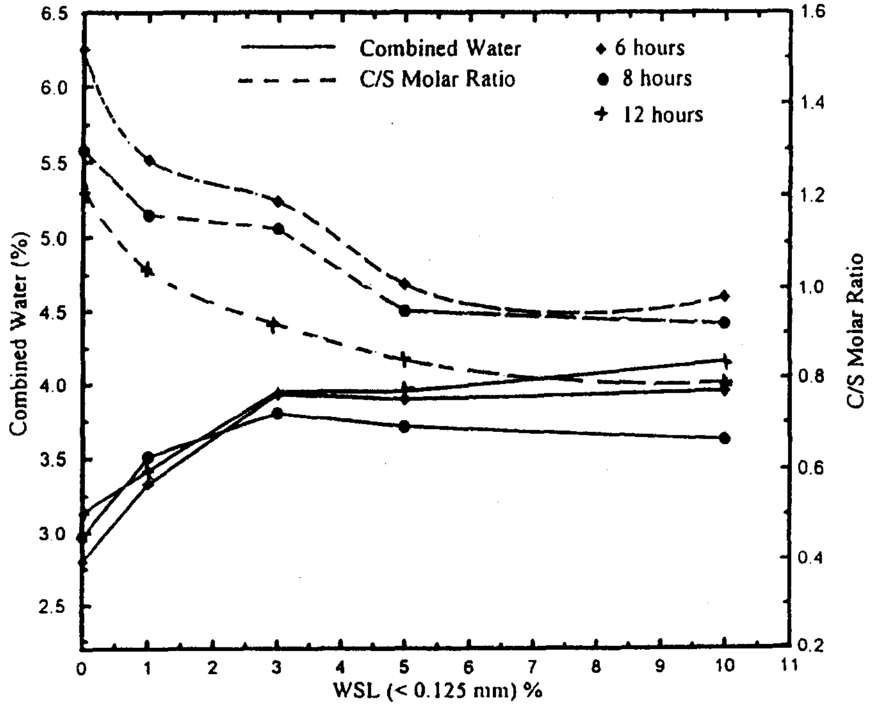

Fig. 6. Effect of WSL (<0.125 mm) additions on the combined water and C/S molar ratio of SL-bricks.

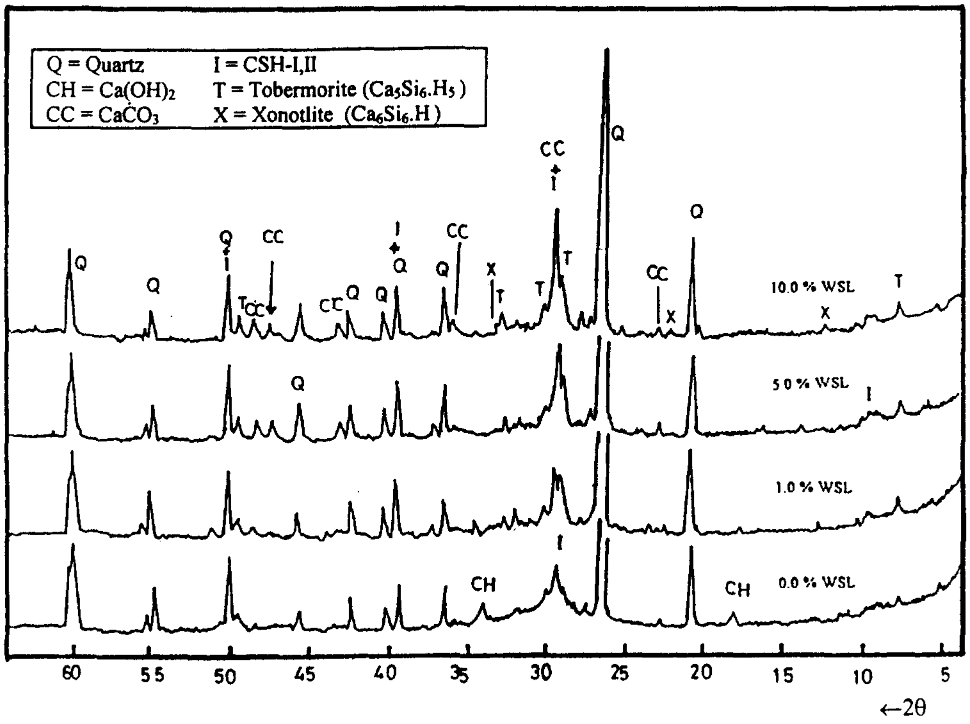

Fig. 7. XRD patterns of autoclaved sand–lime products with different amounts of WSL (<0.125 mm) (10 bars × 8 h).

with WSL, the increase in autoclave time from 6 to 8 h caused a sharp increase in strength values. A further increase in autoclave time from 8 to 12 h is reflected in a corresponding decrease in strength. Maximum strength was obtained with 5% WSL and 8 h autoclaving time.

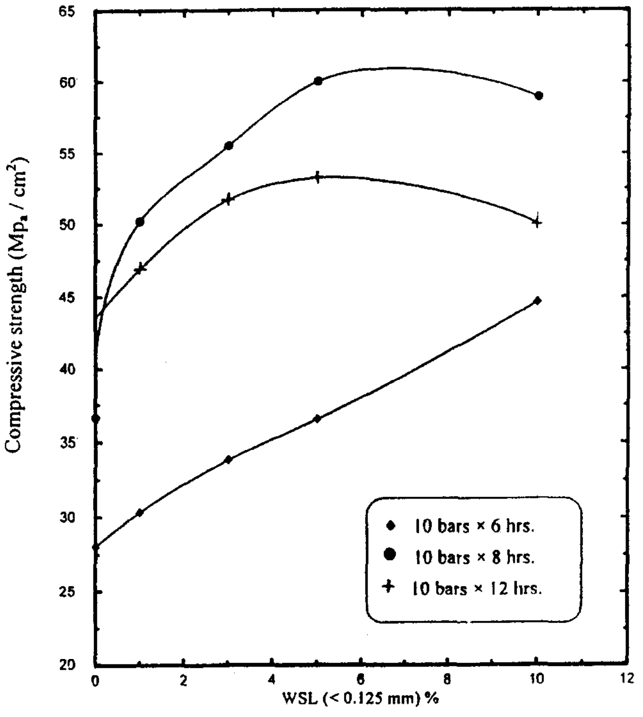

Fig. 8. Effect of WSL (7 < 0.125 mm) additions on the compressive strength of sand–lime products (10 bar for 6, 8 and 12 h).

Table 2 illustrates the bulk density and apparent porosity of the autoclaved specimens in relation to the amount of the added WSL. Generally, the porosity increased and the bulk density decreased with increasing amounts of WSL at all autoclaving times used. Samples with 5 and 10% WSL possessed the highest porosity and the lowest bulk density at autoclaving time of 12 h.

4. Discussion

As the amount of the added WSL (<2.0 mm) increased the measured C/S molar ratio of the binder decreased to approach the C/S molar ratio of the tobermorite phase (Fig. 2). This indicates that the ratio of crystalline/amorphous content of the binder increased [12] and consequently the strength of the products increased (Fig. 3) to reach its maximum at ~15% addition. Further additions of WSL resulted in a lowering of strength because of the sharp increase in porosity of the product. It may be concluded that the addition of WSL (<2.0 mm) generally accelerated the hardening process during autoclaving and improved the physico-mechanical properties of the product. The optimum amount of added WSL must be experimentally determined in situ.

Before discussing the effect of WSL with different grain sizes, it is important to state that the mechanical separation of different grain size fractions of WSL results in them having different chemical compositions. The coarsest grains (2.0–1.0 mm) have higher concentration of quartz sand and the lowest amount of calcium hydrosilicates. On the other hand, the finest fraction (<0.125 mm), have the lowest amount of quartz sand and the highest amount of calcium hydrosilicates.

To explain the influence of WSL at different grain sizes on the physico-mechanical properties of the product, two factors must be considered. The first is the amount and number of seed crystals of Ca-hydrosilicates in each grain size, which accelerate the lime–silica reaction and the transformation of amorphous to crystalline phases. The second is the extent of change in compaction of the samples caused by the change in grain size distribution of the starting mix.

The addition of the coarse fraction of WSL (2.0–1.0 mm) caused no effective change in strength at up to 30%, as seen in Fig. 4. Because this fraction contained the lowest amount of seed crystals of C-S-H, it would be expected that the positive influence of calcium hydrosilicates on compressive strength would be matched by the negative influence of reducing the lime content in the raw mix. For example, in the mix with 30% WSL coarse fraction, the mixing lime was reduced to 8.5% of the total mix, compared with 11% for the control sample.

Addition of the fractions that had 1.0–0.5 and 0.5–0.125 mm grain sizes increased the strength, since they contain considerable amounts of Ca-hydrosilicates. However, they were not fine enough to provide many nuclei for crystallization.

The sharp increase in strength with increasing the percentage addition of WSL (<0.125 mm), up to 5% (Fig. 4), is caused by the presence of higher amounts of calcium hydrosilicates in this fraction, with considerable fineness. The fineness is very important because the finer the calcium hydrosilicates the higher the number of nuclei of crystallization within the reaction medium, which accelerates the reaction rate.

The results of the samples prepared with the addition of the finest WSL (<0.125 mm) and different autoclaving times revealed the following. With a relatively short processing time, 6 and 8 h, the addition of WSL increased the rate of the reaction, increased the amount of hydration products (C-S-H-phases) and accelerated the transformation of C-S-H-I into 1.1-nm tobermorite (see Fig. 7). Increasing the autoclaving time to >8 h increased the reacted silica values in the samples that contained WSL (Fig. 5). It also increased the crystallinity of the binder. As a net result, a destruction of the quartz-calcium hydrosilicate interface through the dissolution of silica and the diffusion of $H_2SiO_4^{2-}/H_3SiO_4^-$ ions occurred outwards [13]. All the above factors lead to a decrease in the strength value (see Fig. 8).

Some authors [14,15] have demonstrated that a change in crystal form or structure of the binder, or the inversion of tobermorite to xonotlite or gyrolite, is associated with strength loss. These factors may also take part in the strength decrease with increasing autoclaving time. The calculated C/S molar ratio showed a large decrease as autoclave time was increased from 8 to 12 h (Fig. 6).

It may be concluded that the kinetics of the CaO-SiO_2-H_2O reaction are rather complex and involve several processes. In the early stage of reaction, after mixing, Ca^{2+} and $H_2SiO_4^{2-}/H_3SiO_4^-$ ions pass into solution. This process is a dissolution controlled reaction. The dissolution of CaO and SiO_2, as mentioned earlier [16], is greatly affected by many factors such as the nature of the raw materials, their surface area and autoclaving conditions. This is followed by nucleation of calcium hydrosilicates and growth of their crystals. This process, in our view, is a nucleation controlled reaction. This suggestion [17,18] is supported by the large increase in rate of the CaO-SiO_2-H_2O reaction, which is provided by the C-S-H-nuclei in the reaction medium that act as seeds for growing calcium hydrosilicate crystals. In the later stage of the reaction, the initially formed lime-rich C-S-H-phases react with the dissolved silica to form lime-arm phases. This stage, the phase transformation, is a totally diffusion controlled reaction.

5. Conclusions

The addition of WSL accelerates the hydration reaction between lime and silica, and leads to quicker hardening of the products at shorter autoclaving times. The calcium hydrosilicates present in WSL act as seed crystals or nuclei for the formation of C-S-H phases, and accelerates the transformation of the lime-rich phases into low-lime phases. This is confirmed by decreasing the C/S molar ratio of the binder and by increasing the amounts of calcium hydrosilicate, as determined by chemical analysis (Table 2). As the transformation of amorphous lime-rich phases into more crystalline, low-lime phases proceeds, further calcium and silicate ions enter into the reaction to stabilize the metastable state. These results give support to the view that the nucleation of C-S-H is a rate-determined step in the lime–silica hydrothermal reaction, especially in the early stages of the reaction.

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