

# Investigations on mix design of tungsten mine waste geopolymeric binder

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## Abstract

Strength data show that the parameters, which lead to optimum strength for 7 days curing, remain the same for long curing ages. However, when calcium hydroxide percentages above 10% are used, strength decrease after 14th curing day is noticed. In order to explain this behaviour several hypotheses are discussed. The use of an activator with a sodium hydroxide concentration of 24 M leads to a compressive strength of almost 70 MPa. The strength performance is typical of a very reactive binder, being suggested that it is due to the calcium hydroxide and also to the nucleation centers provided by the iron oxide of the mine waste mud. Results allow foreseeing that even higher strength performance could be achieved if lower water/sodium molar ratios were used.

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## 1. Introduction

International commitments under Kyoto Protocol, related to greenhouse gas reductions [1,2], led to an increasing boost in the developing of construction materials with low CO<sub>2</sub> emissions. Portland cement is the most used material in the construction industry worldwide, it has a high level of CO<sub>2</sub> emissions (1 ton of cement generates 1 ton of CO<sub>2</sub>) and its use tends to become less competitive when compared to alternative ecological new binders [3]. Alkali-activated binders based on industrial by-products such as fly ash and blast furnace slag represent a greener alternative to ordinary Portland cement due to their low CO<sub>2</sub> emissions [4]. Furthermore, alkali-activated cementitious systems possessing very good chemical resistance [5,6], and can be used as fireproof building materials [7], as protective

coating for concrete surfaces [8] and to immobilize toxic metals with long term stability [9–11].

The alkali-activation of aluminosilicate waste materials is a complex chemical process evolving dissolution of raw materials, transportation or orientation and polycondensation of the reaction products. Some authors [12] mentioned the existence of two different models of alkali-activation. The first one is the alkali-activation of blast furnace slag (silicon and calcium) in which C–S–H is believed to be the main reaction process. In the case of the second model, the alkaline activation of metakaolin (silicon and aluminium) with high alkaline solutions yielding polymeric bonds can be taken as an example. Previous studies concerning the alkali-activation of different minerals suggest that a wide range of Al–Si based minerals could be used as primary materials [13]. However, it must be noted that studies have used highly pure materials so far and it is expected that mine waste mineral will hardly behave just like them.

Previous studies, concerning the alkali-activation of tungsten mine waste mortars together with a small percentage of calcium hydroxide, suggest that a geopolymeric binder with extremely high early age strength can be produced [14,15].

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The present work studies the joint effect of several parameters that could influence strength development with curing time, such as calcium hydroxide percentage, sodium hydroxide concentration and waterglass/sodium hydroxide mass ratio.

## 2. Experimental work

### 2.1. Materials

Tungsten mine waste mud used in this study was subject to a thermal treatment at 950 °C during 2 hours. Mineralogical composition and thermal conditions were described elsewhere [16]. The XRD patterns indicate that mine waste mud is composed mainly of muscovite and quartz which were identified by their characteristic patterns as follows: muscovite (card 46-1409) and quartz (card 46-1045). For those thermal conditions XRD patterns indicate that dehydroxylation did not result in a complete collapse of muscovite structure. Calcination results in a formation of an amorphous phase causing an increased general background (BG) in XRD patterns and dominantly taking place in the calcinations interval from 850 to 950 °C with a thermal behaviour similar to other phyllosilicate clay minerals. The main muscovite peak ( $2\theta = 8.8^\circ$ ) persisted even after the sample had been heated at 950 °C, although it diminished considerably. Peak area measurements reveal that about 12% of muscovite survived calcination at 950 °C. Molecular changes during dehydroxylation were also examined with infrared emission confirmed by the diminishing absorption peaks at 3600–3700 (OH stretch); however, the peak does not disappear totally, indicating only a partial transformation.

The chemical composition and specific surface of the mine waste mud are shown in Table 1.

The fine aggregate used was a crushed sand from the same mine with a specific gravity of 2.7, 24 h water absorption of 0.9%, and a fineness modulus of 2.8.

### 2.2. Mixture operations and compressive strength testing

The factors considered in this investigation led to the manufacture of several mixes. Distilled water was used to

Table 1  
Chemical composition and specific surface

Constituents (%)	Mine waste mud
SiO <sub>2</sub>	53.48
Al <sub>2</sub> O <sub>3</sub>	16.66
Fe <sub>2</sub> O <sub>3</sub>	12.33
K <sub>2</sub> O	7.65
Na <sub>2</sub> O	0.62
MgO	1.27
SO <sub>4</sub>	3.10
TiO <sub>2</sub>	1.39
As	1.28
Other minor oxides	2.22
Blaine fineness (m <sup>2</sup> /kg)	357

dissolve the sodium hydroxide flakes to avoid the effect of unknown contaminants in the mixing water. The alkaline activator was prepared prior to use. The sand, mine waste mud and calcium hydroxide were dry mixed before adding the activator. To produce a workable mix extra water was added, and the mass ratio of water/dry solid content was 4%.

Compressive strength data were obtained using 50 × 50 × 50 mm<sup>3</sup> cubic specimens according to ASTM C109. The fresh mortar was cast and allowed to set at room temperature for 24 h before being removed from the moulds and kept at room temperature for another 6 days until tested in compression. Compressive strength for each mortar mixture was obtained from an average of 3 cubic specimens.

## 3. Results and discussion

### 3.1. Influence of Ca(OH)<sub>2</sub> and sodium hydroxide concentrations

For a waterglass/sodium hydroxide mass ratio of 2.5:1, a set of mixtures were made containing several calcium hydroxide percentages (10%, 15%, 17.5%, 20% and 22.5%) and with sodium hydroxide concentrations from 6 M to 16 M (Table 2).

Fig. 1 shows compressive strength versus sodium hydroxide concentration according to calcium hydroxide percentage. The mortar mixtures with a 10% calcium hydroxide percentage present the maximum compressive strength, almost 30 MPa, for a sodium hydroxide concentration of 16 M (to which corresponds an H<sub>2</sub>O/Na<sub>2</sub>O molar ratio of 13.4). These results confirm the ones already obtained for early age compressive strength [15].

The mixtures, in which calcium hydroxide percentage is higher than 10%, show strength decrease after 14 days curing. This strength loss related behavior is confirmed by others [18]. According to these authors, who studied alkali-activated metakaolin/slag mixtures, the maximum compressive strength has been achieved for a percentage

Table 2  
Mortar composition (C105–C116)

Compound	Concentrated Hydroxide	Waterglass: hydroxide	Ms (silica modulus)	H <sub>2</sub> O/Na <sub>2</sub> O molar ratio	Calcium hydroxide (%)
C105	16 M	2.5:1	1.34	13.7	17.5
C106				13.9	22.5
C107	14 M		1.41	14.3	17.5
C108				14.6	22.5
C109	12 M		1.49	15.1	17.5
C110				15.3	22.5
C111	10 M		1.59	16.0	17.5
C112				16.3	22.5
C113	8 M		1.72	17.2	17.5
C114				17.5	22.5
C115	6 M		1.90	18.7	17.5
C116				19.1	22.5

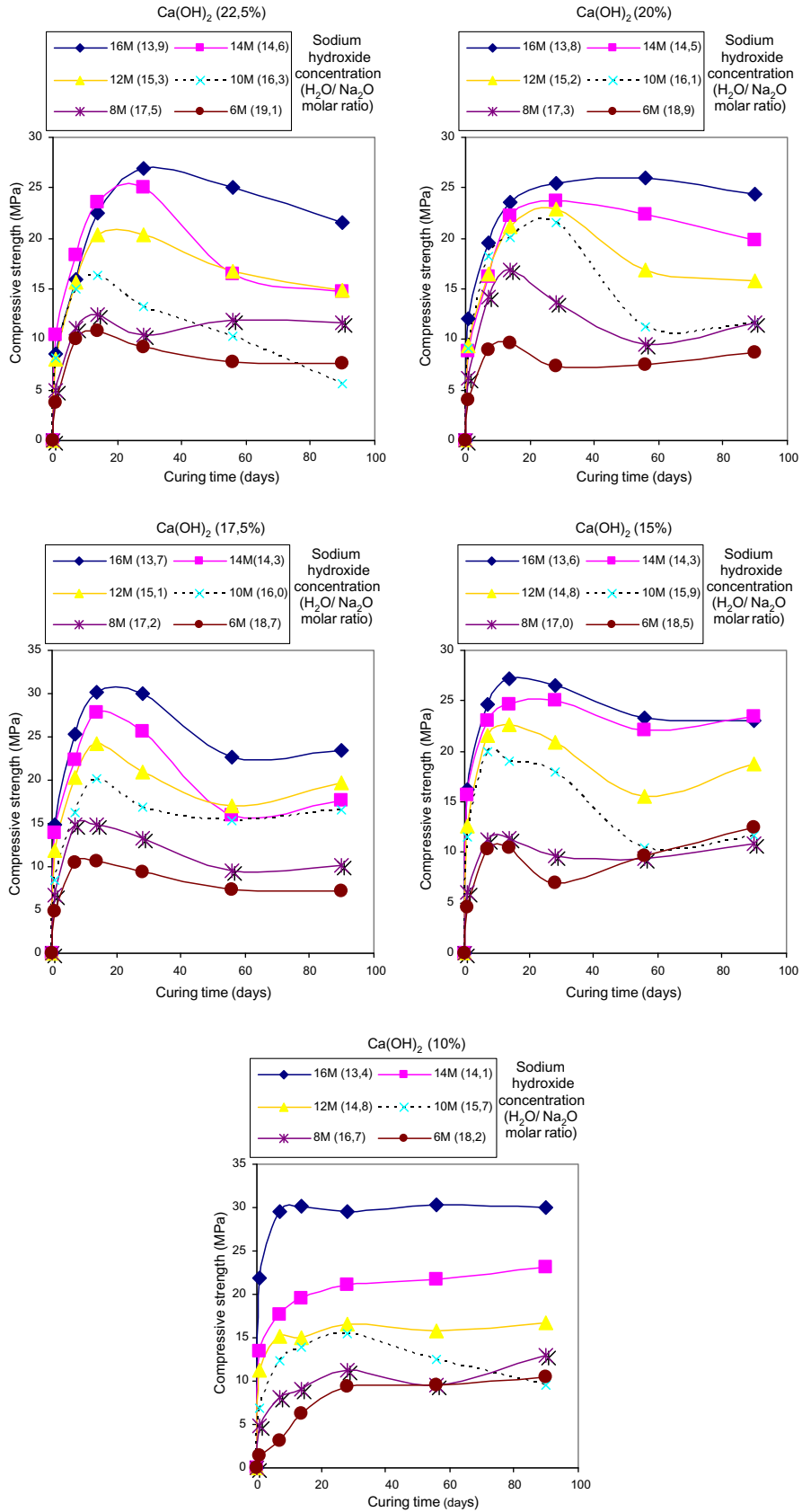


Fig. 1. Compressive strength versus sodium hydroxide concentration according to calcium hydroxide percentage (22,5%; 20%; 17,5%; 15% and 10%).

of 20% of slag (which corresponds to a calcium oxide content of 8.6%). The explanation for this is related to the formation of two different phases, geopolymeric gel and calcium silicate hydrates, and the former acts as microaggregates [17].

However, when high slag percentages are used, for instance 40% of slag (17% calcium oxide), compressive strength decreases when curing time goes from 7 to 14 days curing. These authors believe that strength loss with curing time, is probably due to the fact that CSH reaction and the geopolymeric reaction will compete against each other for soluble silicates, gives rise to a binder composed of two porous phases which leads to strength loss.

An alternative explanation is related to the possibility of the occurrence of shrinkage cracking near the aggregates,

originating a clear tensile strength reduction, which could only be confirmed when shrinkage and tensile strength were studied. And a third explanation is related to the formation of gel similar to the one that takes place in ASR of portland cement binders, so the gel volume increase would explain strength loss.

Fig. 2 shows compressive strength versus  $H_2O/Na_2O$  molar ratio, for several calcium hydroxide percentages according to curing time. The results show a compressive strength increase with the  $H_2O/Na_2O$  molar ratio decrease. It is more clear for mixtures with a 10% calcium hydroxide percentage a  $H_2O/Na_2O$  molar ratio lower than 15 and higher curing ages. The rest of the mixtures with higher calcium hydroxide percentages sometimes show a strength increase for  $H_2O/Na_2O$  molar ratio decrease, and that

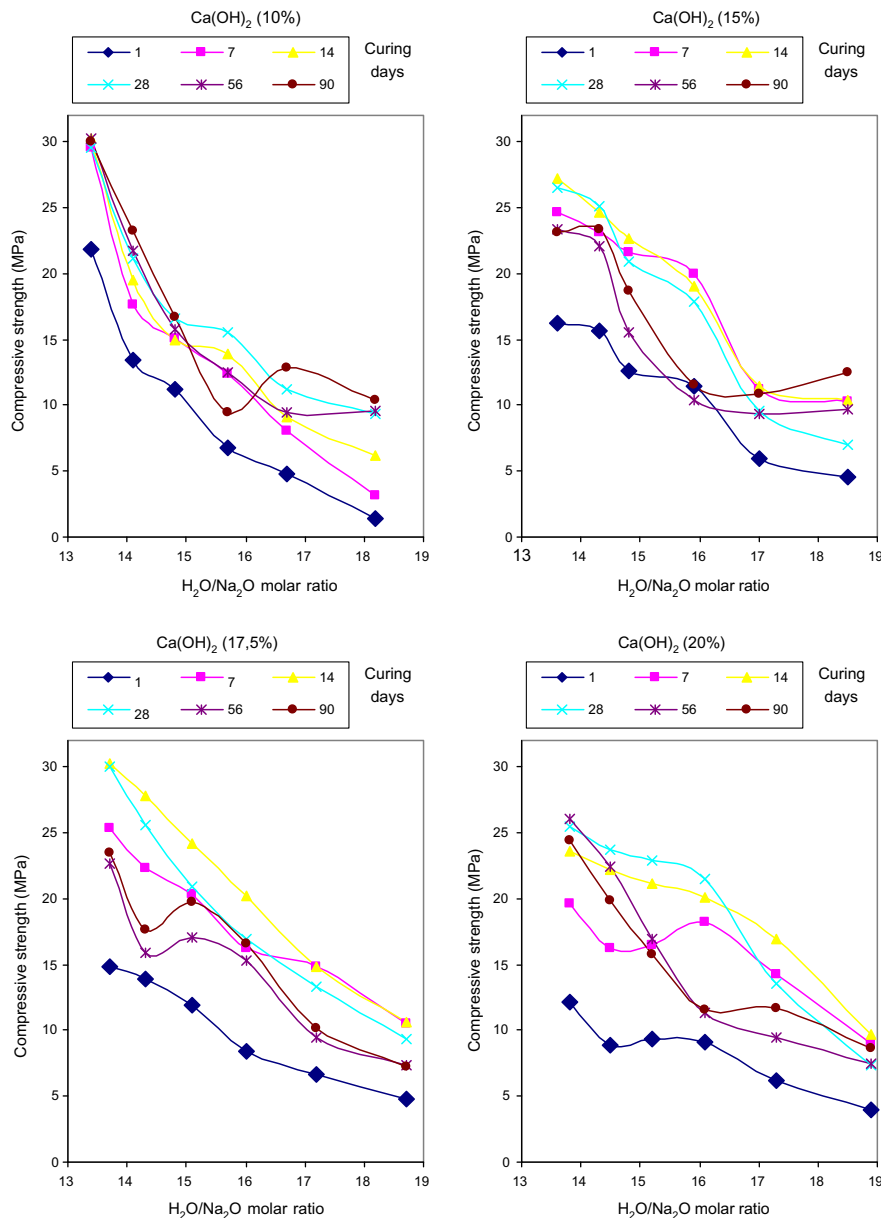


Fig. 2. Compressive strength versus  $H_2O/Na_2O$  molar ratio according to calcium hydroxide concentration (10%, 15%, 17.5% and 20%).

occurs starts after 14 days curing. However, sometimes they also present a strength decrease when  $H_2O/Na_2O$  molar ratio decreases. This behaviour has to do with calcium hydroxide solubility in high alkaline environment

and with the formation of calcium hydroxide and NSCH precipitates. Therefore, it seems that higher compressive strength results could be expected for lower  $H_2O/Na_2O$  molar ratios.

Table 3  
Mortar composition (C117–C125)

Compound	Concentrated hydróxide	Waterglass: hydroxide	Ms (sílica modulus)	$H_2O/Na_2O$ Molar ratio	Calcium hydroxide (%)
C117	16 M	4:1	1.54	15.2	20
C118		5:1	1.72	15.8	
C119		6:1	1.86	16.3	
C120		4:1	1.54	14.9	15
C121		4:1	1.54	14.7	10
C122		4:1	1.54	14.5	5
C123		5:1	1.72	15.5	15
C124		5:1	1.72	15.3	10
C125		5:1	1.72	15.0	5

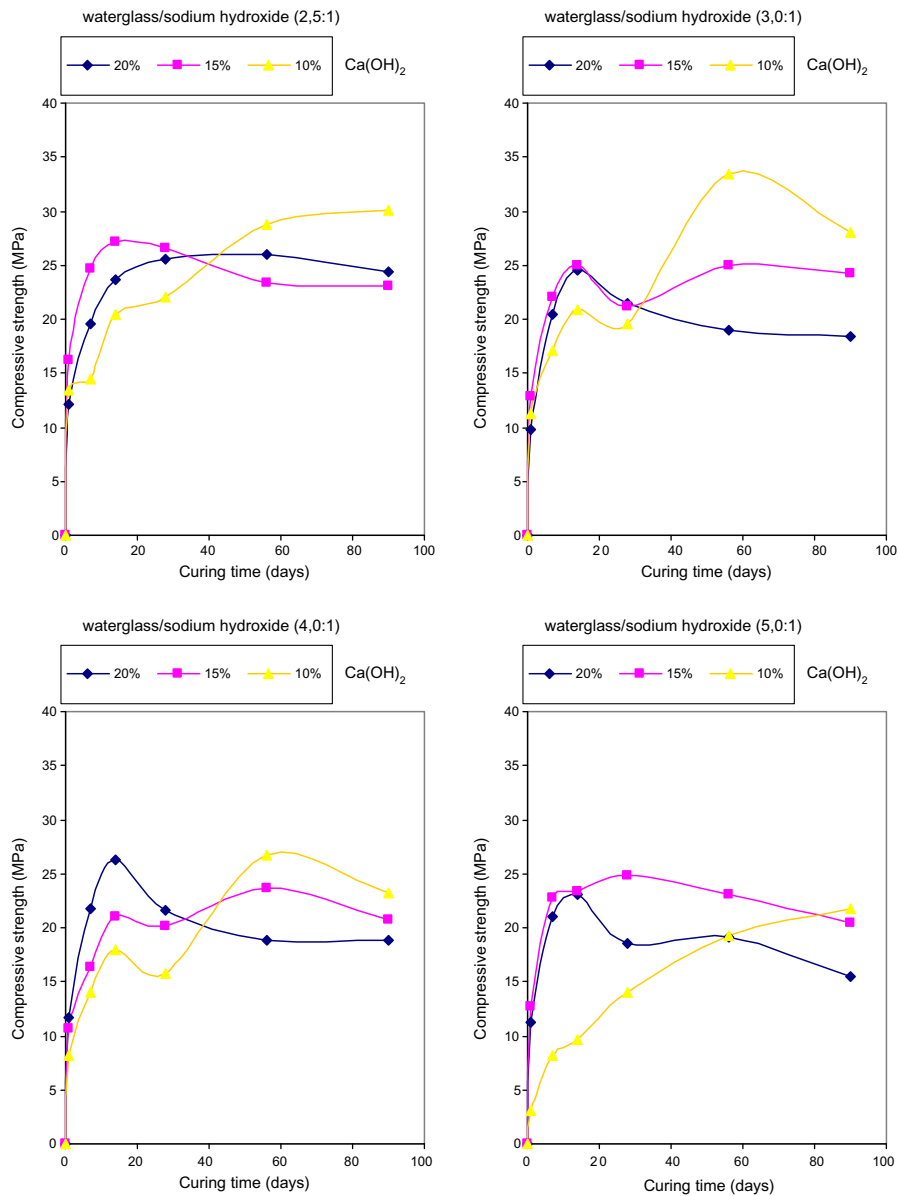


Fig. 3. Compressive strength according to curing time for several calcium hydroxide percentages and waterglass/sodium hydroxide mass ratios.

3.2. Influence of waterglass/sodium hydroxide mass ratio

To confirm if the optimum waterglass/sodium hydroxide mass ratio of 2, 5:1, which was obtained for 7 days curing, does not change with curing age, several mixtures were studied, Table 3 presents some information related to these mixtures.

Figs. 3 and 4 show the compressive strength results according to curing age. The strength results due to the waterglass/sodium hydroxide mass ratio of 6:1 are not presented, because their low workability prevented mixing and placement operations. The results confirm that a waterglass/sodium hydroxide mass ratio of 2,5:1, associated to a calcium hydroxide percentage of 10%, leads to the highest

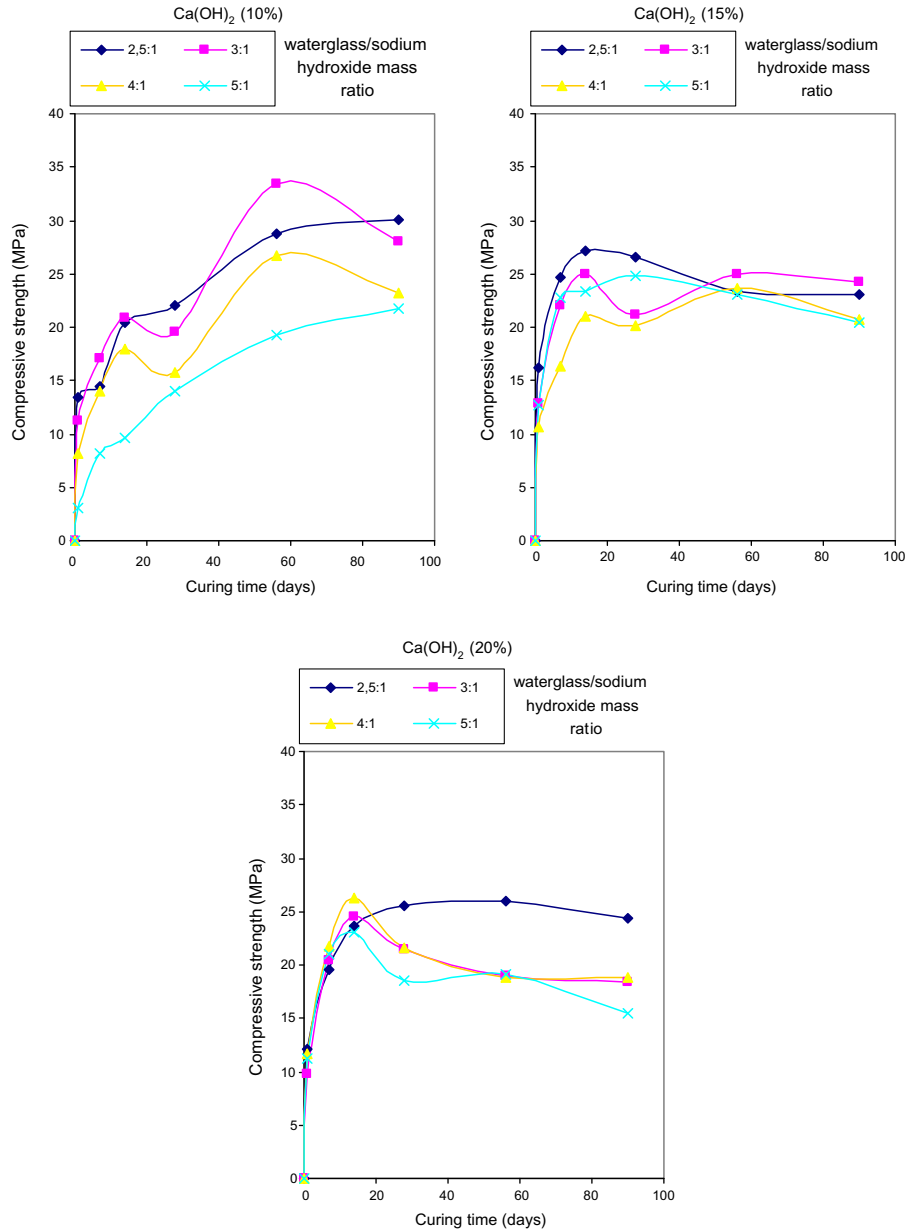


Fig. 4. Compressive strength according to curing time for several calcium hydroxide percentages and waterglass/sodium hydroxide mass ratios.

Table 4  
Mortar composition (C126–C128)

Compound	Concentrated hydroxide	Waterglass: hydroxide	Ms (sílica modulus)	H <sub>2</sub> O/Na <sub>2</sub> O Molar ratio	Calcium hydroxide (%)
C126	24 M	2,5:1	1,17	10,3	10
C127				10,7	25
C128				10,2	5

compressive strength. It was also noticed that the water-glass/sodium hydroxide mass ratio and therefore, the amount of soluble silica in the mixture are influenced by the amount of calcium hydroxide also present in the mixture. For a calcium hydroxide percentage of 10%, increasing waterglass leads to strength decrease for 14 days curing and in a more pronounced form for 56 days. For calcium hydroxide percentages of 15% and 20% the strength loss occurs for 14 days curing. When the amount of waterglass present in the mixture is raised, strength results present a random behaviour, which could be due to the fact that more waterglass means less workable mixtures and thus more porous and with lower strength.

### 3.3. Influence of $H_2O/Na_2O$ molar ratio

Aiming to study the influence of the water/sodium mass ratio in strength increase, three nem mixtures have been

made having a sodium hydroxide concentration of 24 M (Table 4).

The option for this kind of concentration was due to the fact that it was the maximum concentration possible, because, although attempts have been made to synthesize a 25 M sodium hydroxide concentration they reveal to be due to the fact that sodium pellets were not completely dissolved.

However, after noticing that the use of less aggregates means less extra water and thus a lower water/sodium mass ratio, it was decided to use an aggregate/binder mass ratio of 1. After several previous mixes it was found that the extra water needed to properly mix and place the specimens is about 1.8% over the aggregate and binder mass. Fig. 5 shows compressive strength according to curing age. The results show a major strength increase, with 30 MPa after just 1 day, reaching almost 70 MPa after 28 days curing. This performance is mainly related to the use of less

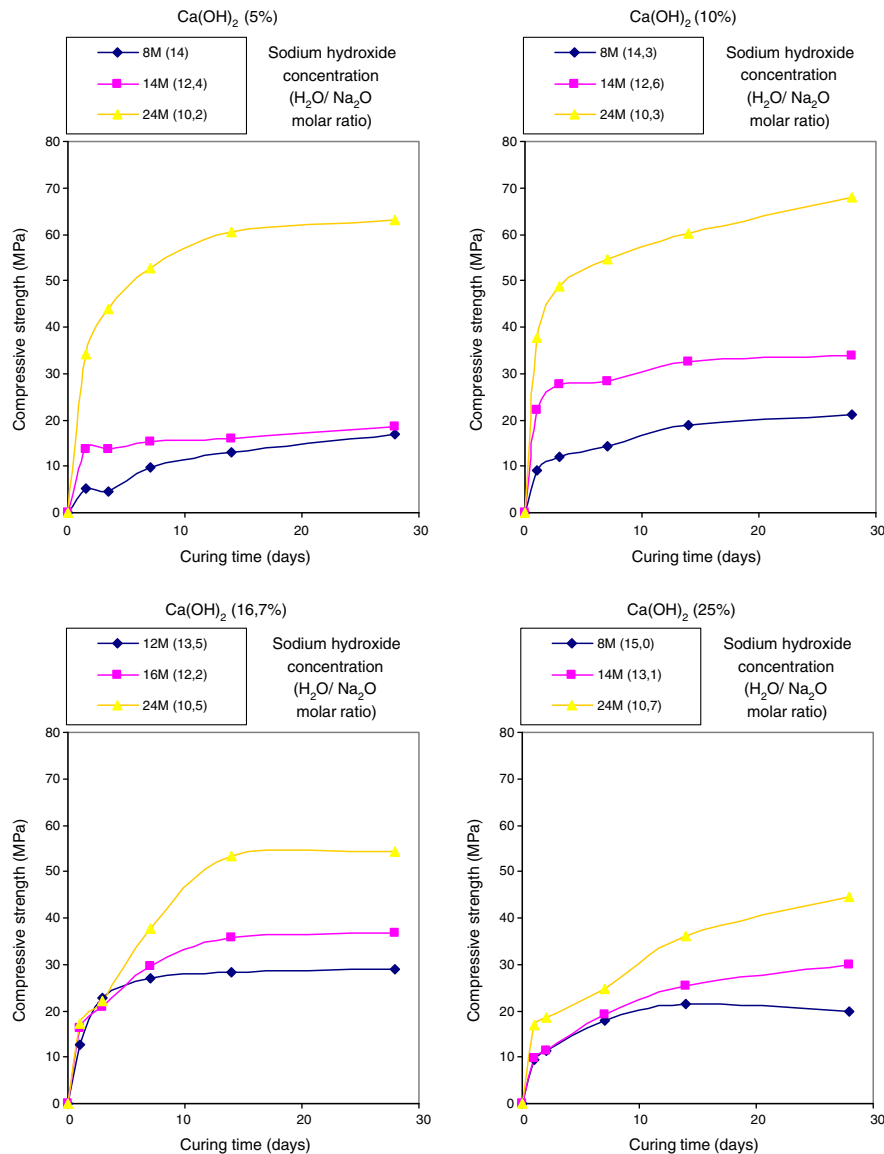


Fig. 5. Compressive strength according to curing time for several calcium hydroxide percentages and waterglass/sodium hydroxide mass ratios.

aggregates and thus less extra water. The use of mixtures containing 5% of calcium hydroxide leads to lower strength after long curing time ages than when 10% calcium hydroxide mixtures were used. The strength differences are much higher for the initial curing days: after just 1 day the mixtures with 5% calcium hydroxide have just half the strength of the 10% calcium hydroxide mixtures.

The extraordinary strength increase is due to the use of a low  $H_2O/Na_2O$  molar ratio, which influences strength development. When the alkaline concentration raises, which implies a higher amount of dissolved aluminosilicate species, more cementitious material is available to react. In the previous section it was reported that, with the exception of the composition with 10% calcium hydroxide all the others showed a strength decrease after 14 days curing, but now only the mixture with 25% calcium hydroxide and 8 M concentration shows a strength decrease with curing time.

The adverse effect reported by others [18] related to reduction in strength due to excess of alkali has not been confirmed. It's thought that it must be a subject related to setting rate, because faster rates give less time for dissolution leading to more unreacted particles and strength reduction, so it may be expected that these authors used more reactive material (fly ash and kaolin) than mine waste mud used in the present work.

Results show that compressive strength is influenced by the percentage of calcium hydroxide, and the highest strength is achieved for a 10% calcium hydroxide percentage. However, the use of a 5% calcium hydroxide percentage leads to similar strength results for long curing ages. This means that for this mixing conditions compressive strength is not so much influenced by calcium hydroxide percentage. An explanation for such behaviour may rely on the fact that aluminosilicate (geopolymeric) compounds are being formed.

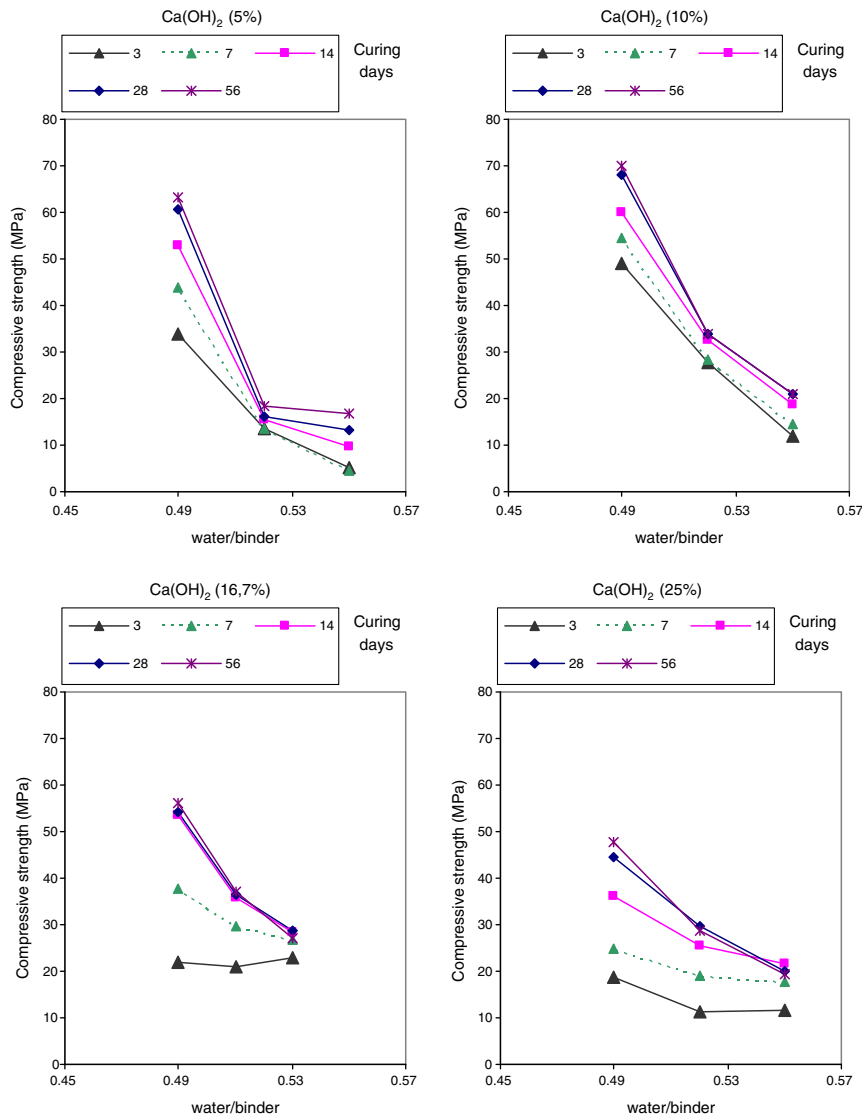


Fig. 6. Compressive strength versus water/binder mass ratio for several calcium hydroxide percentages (5%, 10%, 16,7% and 25%).



The use of 16.7% and 25% calcium hydroxide percentages, although associated with a strength rise due to the use of a 24 M concentration, achieved a far lower strength than the 10% calcium hydroxide percentage. This behaviour can be explained by the use of less aluminosilicate mine waste (replaced by calcium hydroxide) as well by the increase of unreacted particles, due to less setting time, because calcium hydroxide shortens setting time. As for the water/binder ratio (Fig. 6), strength results show that for mixtures with 16.7% and 25% calcium hydroxide percentages it has some influence but only for long curing ages. For the mixtures with a 10% calcium hydroxide percentage, compressive strength has a linear relationship with the water/binder mass ratio, which is almost the same until the 56th curing day. As for the mixtures with a 5% calcium hydroxide percentage, strength is only influenced by the water/binder mass ratio only below 0.52. Since the strength behaviour is related to the  $H_2O/Na_2O$  molar ratio, they

cannot be explained per se, unless the comparison was made between mixtures with the same ratio.

As for the sodium/binder percentage ratio (percentage of sodium mass over binder mass), it can be seen (Fig. 7) that when the parameter increases compressive strength also increases. Lower percentages of calcium hydroxide show to be more influenced than when 16,7% and 25% calcium hydroxide percentages were used at early ages. The explanation for this behaviour could be due to the nature of the reaction products formed which are influenced by calcium hydroxide solubility in high alkaline environment. The use of a sodium/binder percentage of 17% is higher than the percentages reported in the current literature. This maybe due to the low Blaine fineness of mine waste mud ( $3570\text{ cm}^2/\text{g}$ ) which needs a higher sodium concentration to increase dissolution.

As for the  $H_2O/Na_2O$  molar ratio (Fig. 8), the strength results show that the use of low water/sodium ratios is

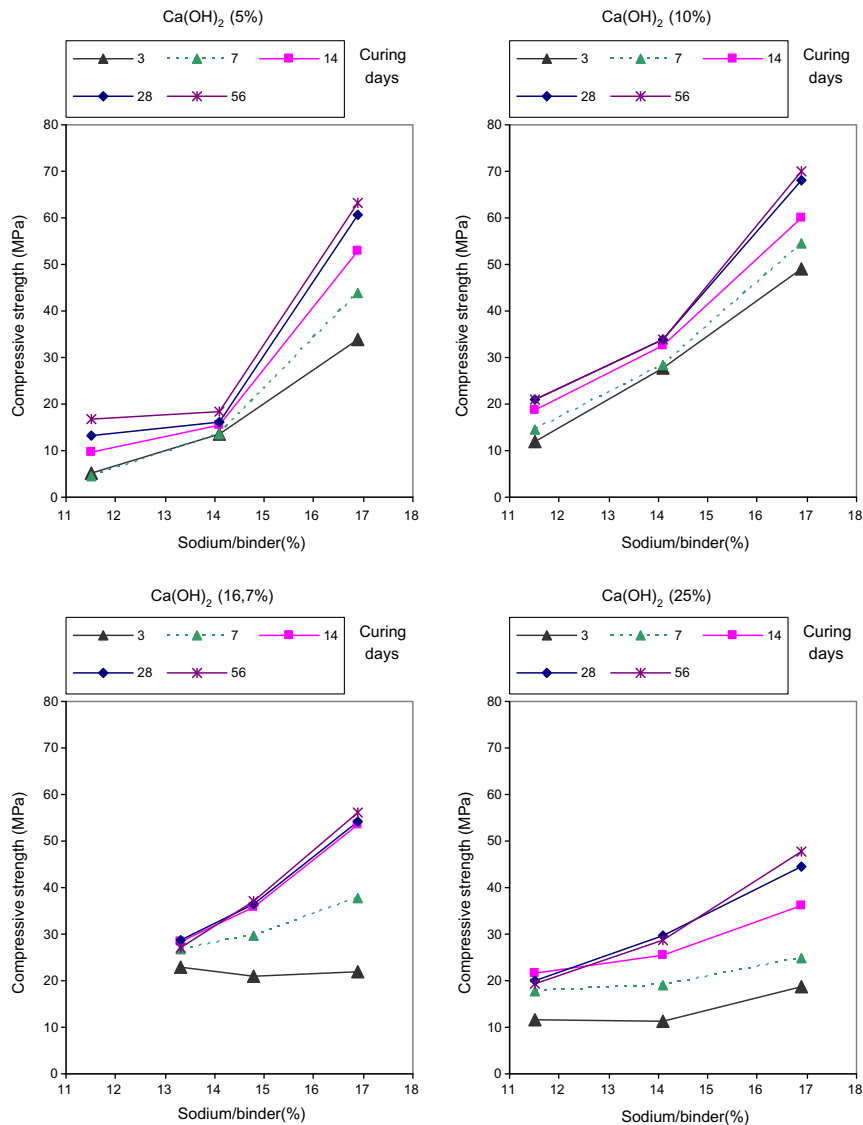


Fig. 7. Compressive strength versus sodium/binder percentage for several calcium hydroxide percentages (5%, 10%, 16,7% and 25%).

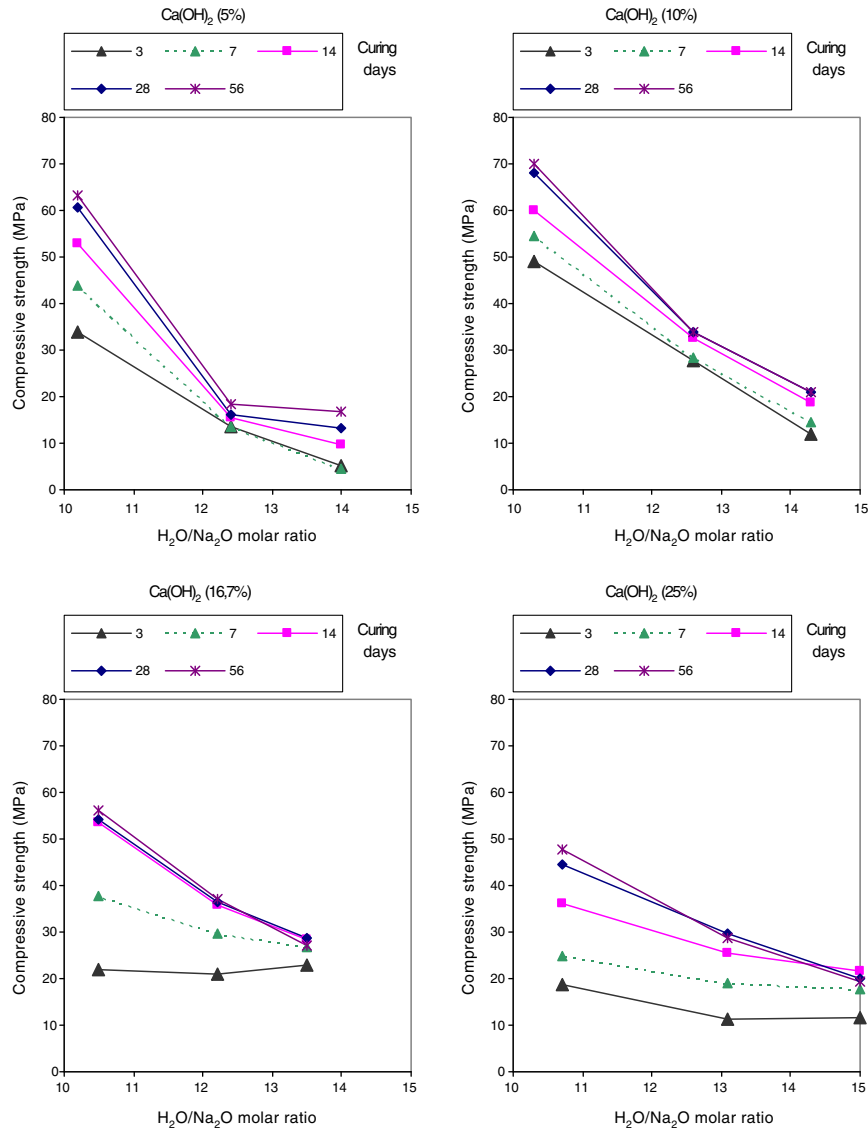


Fig. 8. Compressive strength versus H<sub>2</sub>O/ Na<sub>2</sub>O molar ratio for several calcium hydroxide percentages (5%, 10%, 16.7% and 25%).

crucial for achieving high strength performances, below 12.5 for low calcium hydroxide percentages. For H<sub>2</sub>O/Na<sub>2</sub>O molar ratios below 10, higher strength performance could even be expected. This, however, implies more extra water reductions, or even the use of lower activator/binder ratios, which may lead to workability problems.

#### 4. Conclusions

The strength data for long curing ages show that the parameters, which lead to optimum strength for 7 days curing, remain the same, however, when calcium hydroxide percentages above 10% are used, a relevant strength decrease after 14th curing day is noticed. In order to explain this behaviour several hypotheses are analyzed: the possibility of the geopolymeric reaction and the CSH reaction compete for soluble silicates, leading to a more porous and less strength phase; the possibility of shrinkage crack occurrence near the aggregates or the formation of

alkali-silica gel similar to the one that takes place in ASR. The use of mixtures with a waterglass/sodium hydroxide above 3:1 could not even be properly mixed due to the viscosity of waterglass.

The use of an activator with a sodium hydroxide concentration of 24 M leads to very high compressive strengths, for early ages with 30 MPa after just 1 day as well as after just 28 days (70 MPa). The highest compressive strength is obtained with a mixture containing 10% of calcium hydroxide. The use of a 5% calcium hydroxide percentage, gives rise to much lower strength after just one day but has almost the same strength performance after 28 days curing. The strength performance is typical of a very reactive binder, being suggested that it is due to the calcium hydroxide and also to the nucleation centers provided by the iron oxide of the mine waste mud. Results allow foreseeing that even higher strength performance could be achieved if lower water/sodium molar ratios were used.

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