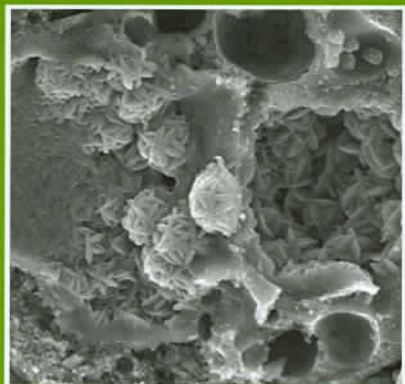# Geopolymers

Structure, processing, properties and industrial applications

Edited by John L. Provis and
Jannie S. J. van Deventer

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A geopolymer is a solid aluminosilicate material usually formed by alkali hydroxide or alkali silicate activation of a solid precursor such as coal fly ash, calcined clay and/or metallurgical slag. Today the primary application of geopolymer technology is in the development of reduced-CO_2 construction materials as an alternative to Portland-based cements. *Geopolymers: structure, processing, properties and industrial applications* reviews the latest research on and applications of these highly important materials.

Part I discusses the synthesis and characterisation of geopolymers with chapters on topics such as fly ash chemistry and inorganic polymer cements, geopolymer precursor design, nanostructure/microstructure of metakaolin and fly ash geopolymers, and geopolymer synthesis kinetics. Part II reviews the manufacture and properties of geopolymers including accelerated ageing of geopolymers, chemical durability, engineering properties of geopolymer concrete, producing fire- and heat-resistant geopolymers, utilisation of mining wastes and thermal properties of geopolymers. Part III covers applications of geopolymers with coverage of topics such as commercialisation of geopolymers for construction, as well as applications in waste management.

With its distinguished editors and international team of contributors, *Geopolymers: structure, processing, properties and industrial applications* will be a standard reference for scientists and engineers in industry and the academic sector, including practitioners in the cement and concrete industry as well as those involved in waste reduction and disposal.

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Utilization of mining wastes to produce geopolymer binders

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Abstract: This chapter discusses the utilization of mining wastes to produce geopolymeric binders. It includes the influence of calcination operations in the reactivity of mine wastes; in what way mix design parameters influence strength gain; it covers physical and mechanical properties and also durability and environmental performance.

**Key words**: mine wastes, geopolymeric binders, properties, durability, adhesion.

13.1   Introduction

Mineral waste can be defined as the 'residues, tailings or other non-valuable material produced after the extraction and processing of material to form mineral products' (Harrison *et al.*, 2002). Nevertheless there is no universally recognized classification of mineral wastes. For the past fifteen years many countries have carried out surveys about mining waste materials (Mitchell *et al.*, 2004). The main reasons for undertaking such surveys are the need to conserve scarce natural resources, reduce environmental pollution and to conserve energy (Hammond, 1988). Not very long ago the failure cases of Aznalcollar mine in Spain (1998) which affected 2656 ha of Donana Nature Park with pyrite sludge, Baia Mare mine (2000) in Romania clearly showed that in the short-term and environmentally speaking, mine wastes represent a clear and present danger as important as greenhouse gas emissions (BRGM, 2001; Puura *et al.*, 2002). Mining and quarrying wastes represent 15% of total wastes in Western Europe and 31% in Eastern Europe (Eurostat, 2003). Western Europe's mining and quarrying sector is the most concentrated and active in the world. Furthermore it makes a highly significant contribution to Europe's economy. Overall the extractive industry has an output of some 3 billions tonnes, with a value of about €50 billion, and employs around 500 000 people. It is estimated that over 20% of European Union's Gross Domestic Product is dependent in some form or other on the extractive industry (Brodkom, 2000). Therefore significant efforts must be made by the scientific community to find alternative uses for mining and quarrying

wastes, but also ways of stabilizing them to prevent them from spreading, and polluting surrounding areas in order to preserve natural biodiversity, as well as to protect drinking water supply and urban environments. Since alumino-silicate minerals are the most abundant in the Earth's crust, most mining wastes are likely to be of this kind. Therefore alumino-silicate wastes might become sources of geopolymerization. This chapter analyses the utilization of mining wastes to produce geopolymeric binders. It includes the influence of calcination operations in the reactivity of mine wastes; in the way mix design parameters influence strength gain; it covers some physical and mechanical properties particularly the adhesion between the mine waste binders and ordinary Portland cement concrete; it describes durability performance from abrasion and acid resistance and also assesses environmental performance from leaching tests. A more detailed coverage about the geopolymerization of mine wastes is presented elsewhere (Torgal et al., 2007a, 2007b, 2007c, 2008).

13.2   Influence of calcination operations in the reactivity of mine wastes

The thermal treatment of aluminosilicate materials causes changes in their structure with an increase in the amorphous phase. Therefore, the mechanical strength of alkali-activated binders depends on the structural conditions of the alumino-silicate materials, as natural materials lead to lower mechanical performance. Higher mechanical strength is associated with materials submitted to calcination like metakaolin or formed as by-products of high-temperature processes such as fly ashes, blast furnace slag. As happens in pozzolanic reactivity, alkali-activation reactivity depends on the amorphous content of silica and aluminium. The reactivity is linked to the material structure, being higher for higher amorphous content. Recent authors' investigations have focussed on alumino-silicate wastes from a tungsten mine. Geochemistry of Portuguese tungsten deposits is composed of blue schist formations with some quartz veins (Neiva, 1987). Schist is a very common metamorphic rock formed by dynamic high-temperature, high-pressure metamorphism that involves a lot of strain. For tungsten mine wastes the authors report that thermal treatment is responsible for increase reactivity. XRD patterns (Fig. 13.1) indicated that mine wastes used consisted mainly of muscovite and quartz which were identified by their characteristic patterns using the Materials Data JADE 6.0. software as follows: muscovite (card 46 – 1409) and quartz (card 46 – 1045). The chemical formula of muscovite is as follows:

$$(K, Ba, Na)_{0.75} (Al, Mg, Cr, V)_2 (Si, Al, V)_4 O_{10} (OH)_2$$
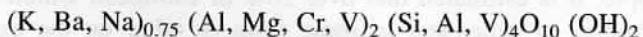
The chemical composition and specific surface of the mine waste mud are shown in Table 13.1. Phase transformations on calcination were monitored by
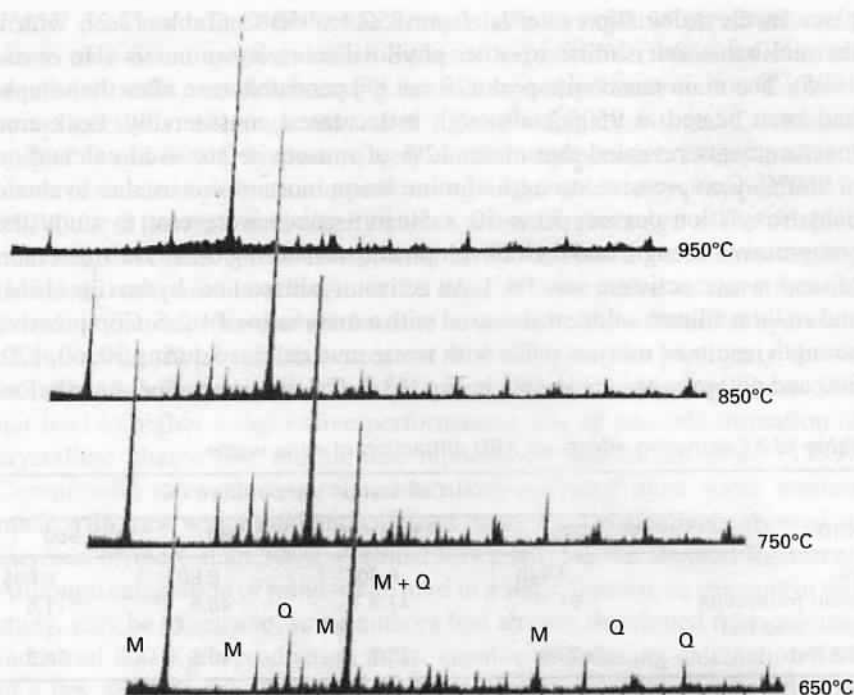
13.1 XRD patterns of mine waste treated at different temperatures (M – muscovite; Q – quartz).

Table 13.1 Chemical composition and specific surface

Constituents (mass %)	Mine waste mud
SiO_2	53.48
Al_2O_3	16.66
Fe_2O_3	12.33
K_2O	7.65
Na_2O	0.62
MgO	1.27
SO_4	3.10
TiO_2	1.39
As	1.28
Other minor oxides	2.22
Blaine fineness (m^2/kg)	357

XRD of waste powder quenched to room temperature to avoid crystallization of amorphous muscovite. Samples were placed in the static furnace only after the temperature treatment had been reached. After thermal treatment, the static furnace was opened to remove the samples. Results show that calcination leads to formation of an amorphous phase, causing an increase in the general background (BG) of XRD patterns and dominantly taking

place in the calcination interval from 850 to 950°C (Table 13.2), with a thermal behaviour similar to other phyllosilicate clay minerals (He *et al.*, 1995). The main muscovite peak ($2\theta = 8.8°$) persisted even after the sample had been heated at 950°C, although it decreased considerably. Peak area measurements revealed that about 12% of muscovite survived calcination at 950°C. Compressive strength of mine waste mortars was used to evaluate dehydroxylation degree, 50 × 50 × 50 mm cubes were cast to study the compressive strength and their development with curing time. The mass ratio of sand: waste: activator was 1:1:1. An activator with sodium hydroxide (12M) and sodium silicate solution was used with a mass ratio of 1:2.5. Compressive strength results of mortars made with waste mud calcined during 30, 60, 120, 300 and 480 minutes are shown in Fig. 13.2. Calcination temperature below

Table 13.2 Calcination effects on XRD diffraction of mine waste

XRD	Calcination temperature (°C)			
	650	750	850	950
2θ	8.845	8.807	8.803	8.806
Main muscovite peak area (%)	51	47.4	40.8	11.5
BG (%)	33.5	33.7	40.5	58.3
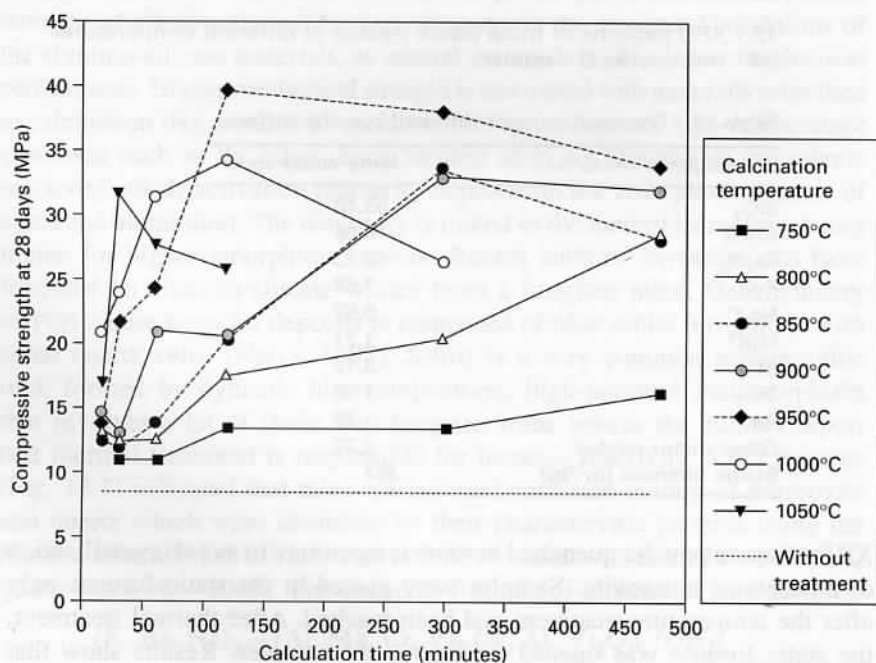
13.2 Compressive strength of mine waste mortars according to the thermal treatment of the waste.

750°C does not contribute to the compressive strength of alkali-activated waste mud-based mortars, which means it has no effect whatsoever in the reactivity of the waste. Increasing calcination temperature to 800°C shows some reactivity, although only after a long calcination time. Calcination at 850°C and 900°C leads to a very similar compressive strength after 5 hours of calcination but underperform against a calcination temperature at 950°C for 2 hours, which clearly shows a structural change in the calcined material. Calcination of waste powder at 950°C for 120 min considerably increases compressive strength at 28 days of curing due to the structural dehydroxylation process which leads to an amorphous product of dehydration of muscovite. This result is consistent with XRD results previously shown in Table 13.2. Furthermore increased calcination time and temperature does not lead to higher compressive performances due to possible formation of crystalline phases like mullite and reported by Mazzucato et al. (1999). Compressive strength data related to alkali-activated mine waste mortars made with, raw waste mud and calcined waste mud respectively showed an increase of more than 300% (Table 13.3) justifying the thermal treatment. Although calcination of mine waste mud in a static furnace, as happens in this study, may be expensive, some authors had already developed flash calciner industrial 800 Kg/h production units, capable of reducing calcination time to a few seconds and with the additional advantage of no further grinding operations (Salvador, 1995, 2000) which will cut down the cost of down mine waste mud thermal treatment.

13.3   Strength gain and mix design parameters

13.3.1 Influence of Ca(OH)$_2$ and sodium hydroxide concentration

Previous investigations showed that mine waste mixtures without calcium hydroxide have a very low compressive strength performance. The mortar mixtures (Table 13.4) with a 10% calcium hydroxide percentage present the maximum compressive strength, almost 30 MPa, for a sodium hydroxide

Table 13.3 Compressive strength of alkali activated mine waste mud mortars

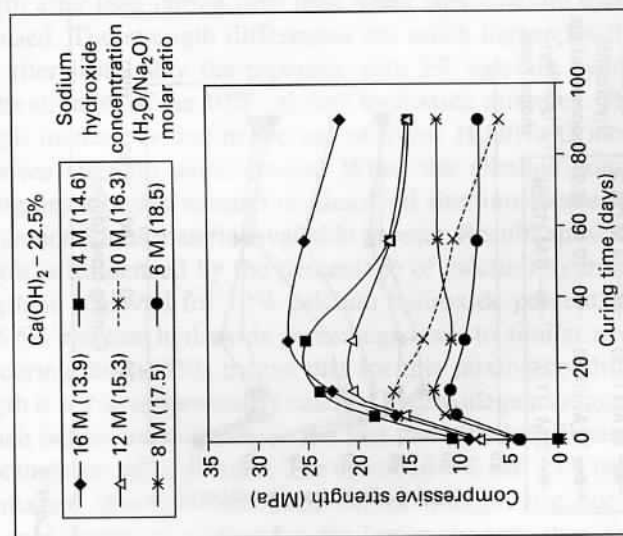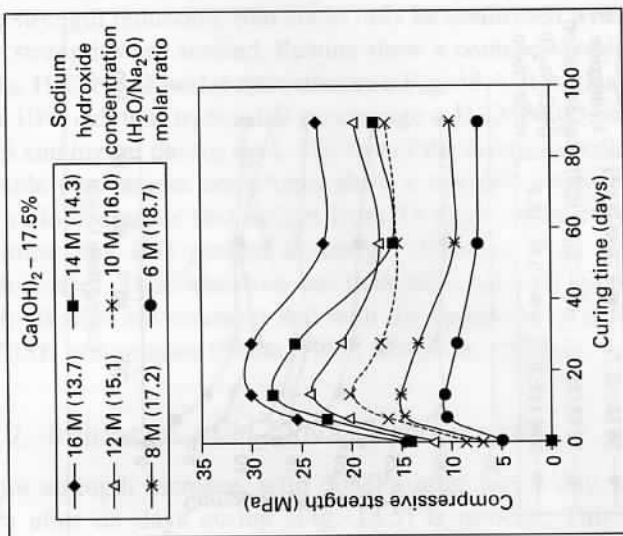|	Compressive strength (MPa)	
Curing (days)	Raw mine waste	Waste calcined at 950°C for 2 h
7	8.4 (1.2)	28.4 (1.8)
14	9.3 (4.3)	37.0 (1.1)
28	11.2 (1.8)	39.6 (1.8)

Bracketed values are the standard deviation
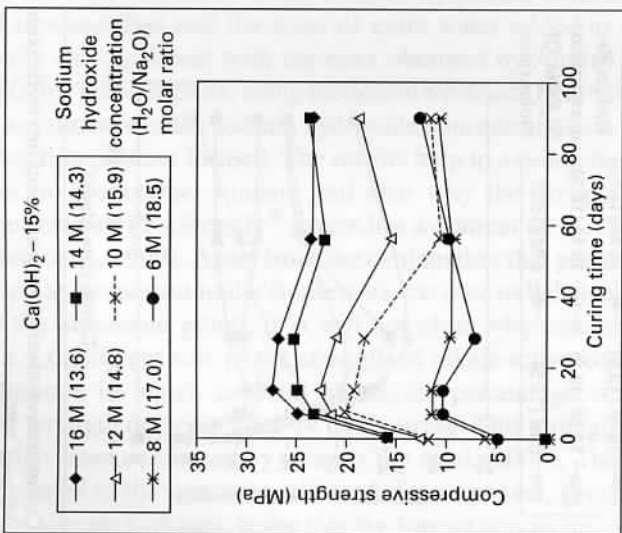
Table 13.4 Mortar composition (C105–C116)

Comp.	Conc. hydróxide	Waterglass: hydroxide	Ms (silica modulus)	H_2O/Na_2O Molar r.	Calcium hydrox.(%)
C105			1.34	13.7	17.5
	16M				
C106				13.9	22.5
C107			1.41	14.3	17.5
	14M				
C108				14.6	22.5
C109				15.1	17.5
	12M				
C110			1.49	15.3	22.5
		2.5:1			
C111				16.0	17.5
	10M				
C112			1.59	16.3	22.5
C113				17.2	17.5
	8M				
C114			1.72	17.5	22.5
C115				18.7	17.5
	6M		1.90		
C116				19.1	22.5

concentration of 16M, (to which correspond a H_2O/Na_2O molar ratio of 13.4 (Fig. 13.3)). The total mass of water used to determine the water-binder ratio is the sum of water contained in the sodium hydroxide solution, the water contained in waterglass and the mass of extra water added to the mixture. These results are consistent with the ones obtained by Alonso and Palomo (2001a, 2001b). These authors, using metakaolin/calcium hydroxide mixtures, reported the influence of the sodium hydroxide concentration on the nature of the final reaction product formed. The results help to explain the importance of calcium in geopolymer binders and also why the composition of the geopolymer cement PZ-Geopoly® patent has a content of 11.1% of calcium oxide (Davidovits, 1999). Apart from the explanation that positive ions such as Ca^{2+} need to be present in the framework cavities to balance the negative charge of the aluminate group, it is still not clear why calcium hydroxide plays such a significant role in the strength of alkali-activated binders.

The mixtures in which calcium hydroxide percentage is higher than 10%, show strength decrease after 14 days curing. This strength loss related behaviour has been confirmed by others (Yip et al., 2005). The explanation for that is related to the formation of two different phases, geopolymeric gel and calcium silicate hydrates, being that the former acts as microaggregates. These authors believe that strength loss with curing time is maybe due to the fact that CSH reaction and the geopolymeric reaction will compete against each other for soluble silicates, giving rise to a binder composed of two porous phases that leads to strength loss. More recently Yip et al. (2008) studied the

Figure (top graph): Ca(OH)$_2$ – 17.5%

Legend — Sodium hydroxide concentration (H$_2$O/Na$_2$O) molar ratio:
16 M (13.7); 14 M (14.3); 12 M (15.1); 10 M (16.0); 8 M (17.2); 6 M (18.7)

Axes: Compressive strength (MPa) versus Curing time (days)

Figure (bottom graph): Ca(OH)$_2$ – 22.5%

Legend — Sodium hydroxide concentration (H$_2$O/Na$_2$O) molar ratio:
16 M (13.9); 14 M (14.6); 12 M (15.3); 10 M (16.3); 8 M (17.5); 6 M (18.5)

Axes: Compressive strength (MPa) versus Curing time (days)
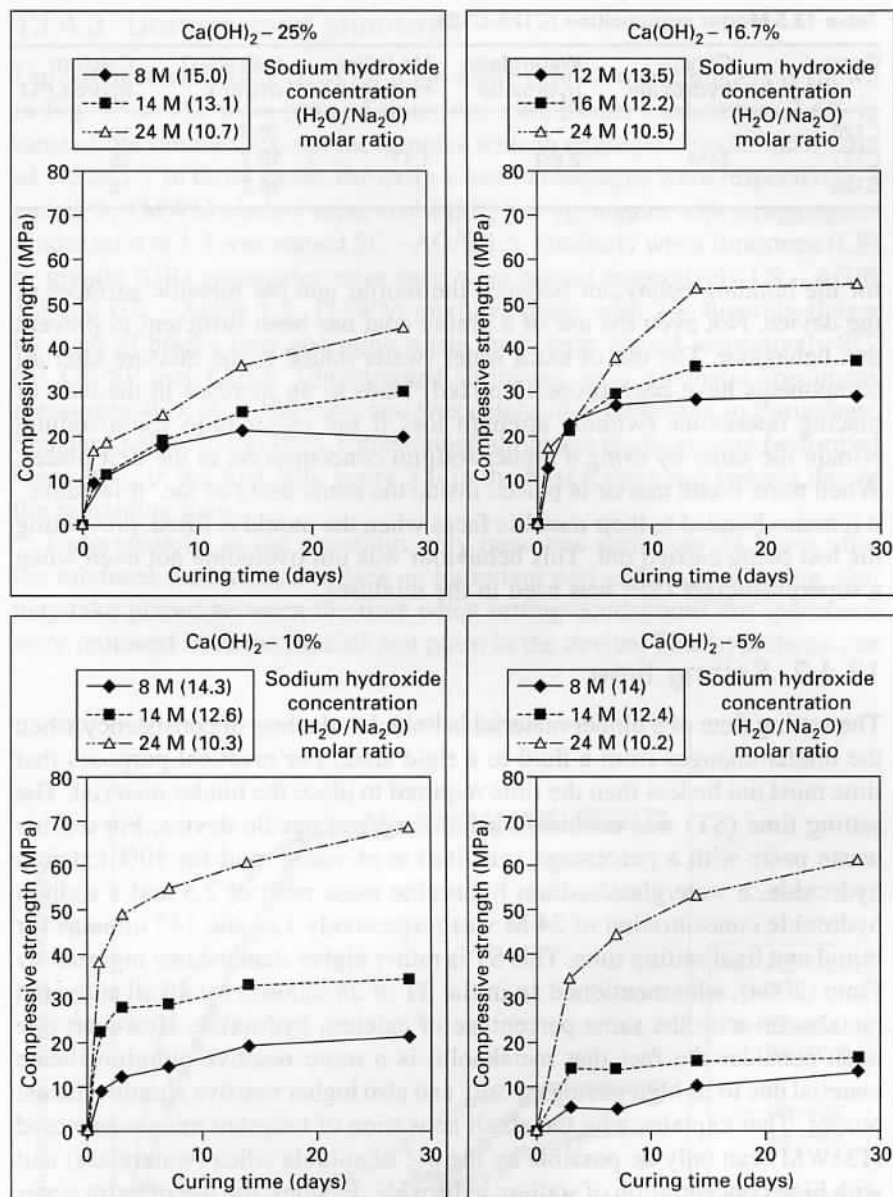
13.3 Compressive strength versus sodium hydroxide concentration according to calcium hydroxide percentage (22.5; 17.5; 15 and 10%).

Ca(OH)$_2$ – 10%

Sodium hydroxide concentration (H$_2$O/Na$_2$O molar ratio)

- 16 M (13.7)
- 14 M (14.1)
- 12 M (15.1)
- --*-- 10 M (15.7)
- 8 M (17.2)
- 6 M (18.2)

Compressive strength (MPa) — Curing time (days)

Ca(OH)$_2$ – 15%

Sodium hydroxide concentration (H$_2$O/Na$_2$O molar ratio)

- 16 M (13.6)
- 14 M (14.3)
- 12 M (14.8)
- --*-- 10 M (15.9)
- 8 M (17.0)
- 6 M (18.5)

Compressive strength (MPa) — Curing time (days)

13.3 Cont'd
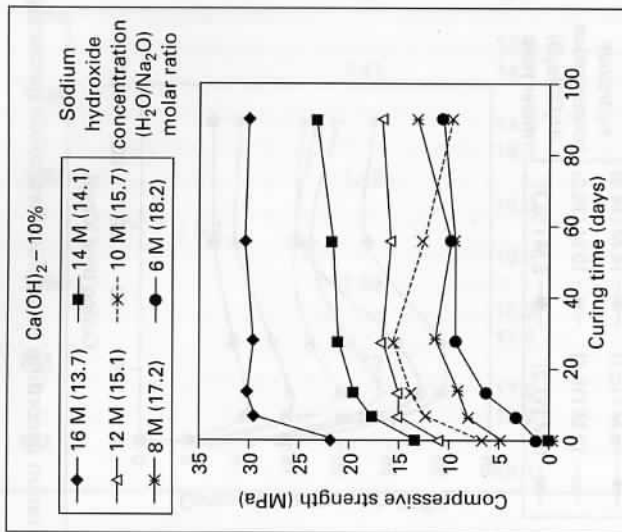
effect of calcium sources on the geopolymerization stating that lower strengths were due to the unreacted mineral particles that disrupt the geopolymeric gel network. An alternative explanation is related to the possibility of the occurrence of shrinkage cracking near the aggregates, originating a clear tensile strength reduction, that could only be confirmed when shrinkage and tensile strength were studied. Results show a compressive strength increase with the H_2O/Na_2O molar ratio decrease Fig. 13.4. It is clearer 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 decreases that occurs from 14 days curing forward. 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 CNSH precipitates (Stade, 1989; Macphee, 1989).

13.3.2 Influence of H_2O/Na_2O molar ratio

A major strength increase, with 30MPa after just 1 day, reaching almost 70MPa after 28 days curing (Fig. 13.5) is noticed. This performance is mainly related to the use of less aggregates and thus less extra water (Table 13.5). The use of mixtures containing 5% calcium hydroxide leads to lower strength after long curing time 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 rises, that implies a higher amount of dissolved aluminosilicate species, meaning more cementitious material available to react. Results show that compressive strength is influenced by the percentage of calcium hydroxide: the highest strength is achieved for 10% calcium hydroxide percentage. However the use of 5% calcium hydroxide percentage leads to similar strength results for long curing times. This means that for this mixing condition compressive strength is not so influenced by calcium hydroxide percentage. An explanation for such behaviour may rely in the fact that aluminosilicate (geopolymeric) compounds are being formed. The use of 16.7% and 25% calcium hydroxide percentages, although associated with a strength rise due to the use of a 24M 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 as from the increase of unreacted particles, due to less setting time, because calcium hydroxide shortens setting time.

Ca(OH)₂ – 25%

	Sodium hydroxide concentration (H₂O/Na₂O) molar ratio
◆— 8 M (15.0)	
■-- 14 M (13.1)	
△⋯ 24 M (10.7)	

Ca(OH)₂ – 16.7%

	Sodium hydroxide concentration (H₂O/Na₂O) molar ratio
◆— 12 M (13.5)	
■-- 16 M (12.2)	
△⋯ 24 M (10.5)	

Ca(OH)₂ – 10%

	Sodium hydroxide concentration (H₂O/Na₂O) molar ratio
◆— 8 M (14.3)	
■-- 14 M (12.6)	
△⋯ 24 M (10.3)	

Ca(OH)₂ – 5%

	Sodium hydroxide concentration (H₂O/Na₂O) molar ratio
◆— 8 M (14)	
■-- 14 M (12.4)	
△⋯ 24 M (10.2)	

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

and finished (Neville and Aitcin, 1998). Neville (1997) also mentioned the flowability capacity as an important property related to workability. It was not possible to evaluate the workability of mine waste mortars using the 'flow table' device, due to the adhesiveness of the waterglass which is responsible
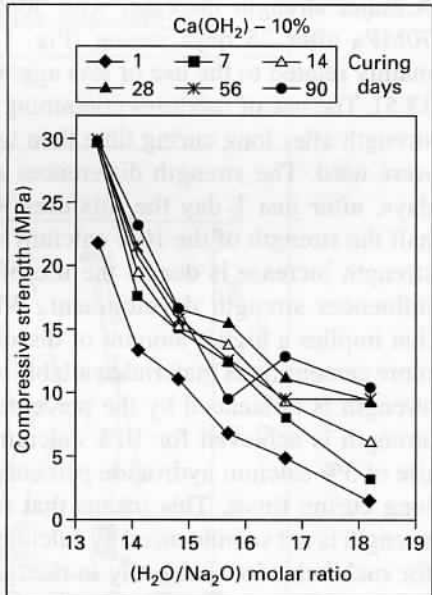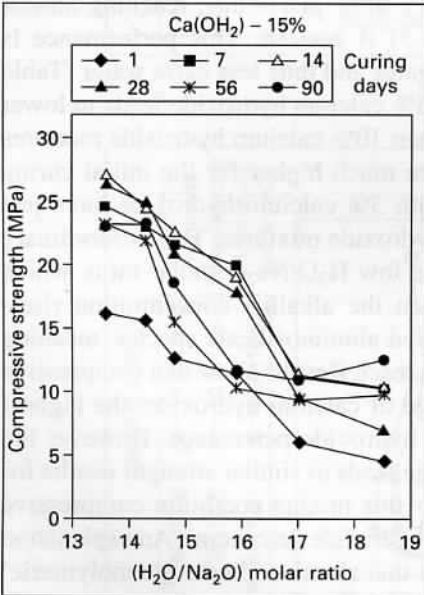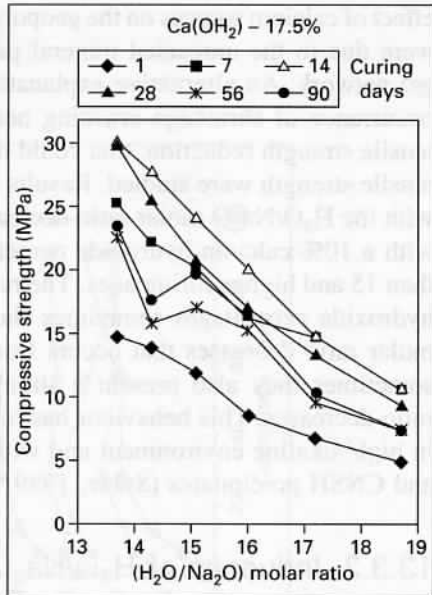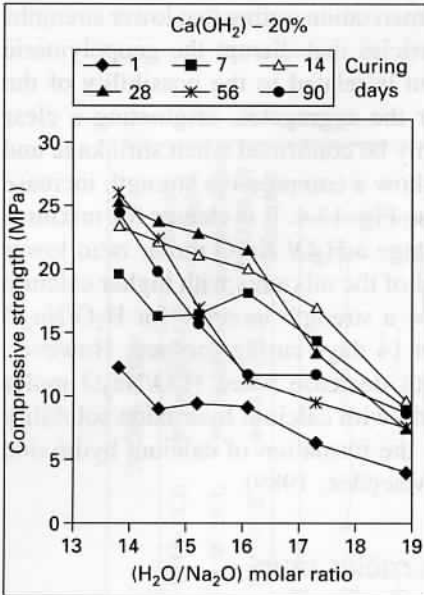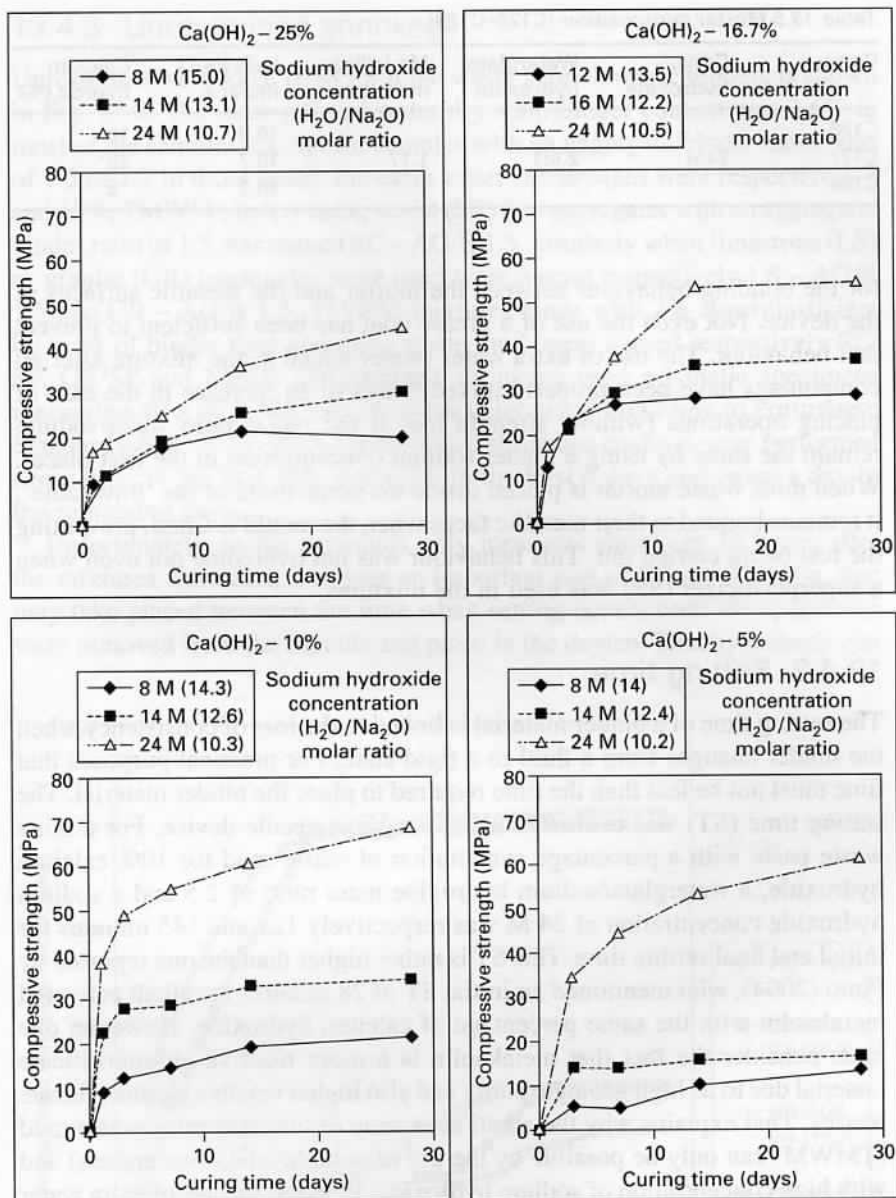
13.4 Compressive strength versus H_2O/Na_2O molar ratio according to calcium hydroxide concentration (10, 15, 17.5 and 20%).

13.4   Physical and mechanical properties

13.4.1 Workability

Workability is a property of a freshly mixed binder (mortar or concrete) that determines the ease with which it can be mixed, placed, consolidated

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

and finished (Neville and Aitcin, 1998). Neville (1997) also mentioned the flowability capacity as an important property related to workability. It was not possible to evaluate the workability of mine waste mortars using the 'flow table' device, due to the adhesiveness of the waterglass which is responsible

Table 13.5 Mortar composition (C126–C128)

Comp.	Conc. hydróxide	Waterglass: hydroxide	Ms (sílica modulus)	H_2O/Na_2O molar r.	Calcium hydrox.(%)
C126				10.3	10
C127	24M	2.5:1	1.17	10.7	25
C128				10.2	5

for the bonding behaviour between the mortar and the metallic surfaces of the device. Not even the use of a grease coat has been sufficient to prevent that behaviour. The use of extra water (water added to the mixture after all components have been properly mixed) leads to an increase in the ease of placing operations (without strength loss if the molar ratio water/sodium remain the same by using a higher sodium concentration in the first place). When mine waste mortar is placed inside the conic mold of the 'flow table', it remains bonded to their metallic faces when the mould is lifted, preventing the test being carried out. This behaviour was not overcome not even when a superplasticizer (SP) was used in the mixtures.

13.4.2 Setting time

The setting time of a binder material is linked to the loss of consistency when the binder changes from a fluid to a rigid state. For practical purposes that time must not be less than the time required to place the binder material. The setting time (ST) was evaluated using the Vicat needle device. For a mine waste paste with a percentage substitution of waste mud for 10% calcium hydroxide, a waterglass/sodium hydroxide mass ratio of 2.5 and a sodium hydroxide concentration of 24 M was respectively 125 and 145 minutes for initial and final setting time. This ST is rather higher than the one reported by Pinto (2004), who mentioned an initial ST of 28 minutes for alkali activated metakaolin with the same percentage of calcium hydroxide. However, one must consider the fact that metakaolin is a more reactive aluminosilicate material due to its high geologic purity and also higher reactive aluminosilicate phases. That explains why the alkali activation of tungsten mine waste mud (TMWM) can only be possible by the use of soluble silica (waterglass) and with high concentration of sodium hydroxide. Besides, the use of extra water to increase the workability of the mixtures may explain part of the ST delay. Furthermore, the ST may also be influenced by the moment when the extra water is added to the mixture. Depending on that particular time, different amount of dissolved aluminosilicate particles will be in the mixture. This means that contrary to OPC binders for which the paste ST gives a good estimation of ST for concrete mixtures, in the case of alkali activated based binders such estimation is not possible.

13.4.3 Unrestrained shrinkage

Unrestrained shrinkage (US) for mine waste geopolymeric binders is shown in Fig. 13.6. The mass ratio of water/dry solid binder content was 3.6% in most of the samples, except for samples with an aggregate/binder mass ratio of 1.5 or 1.7 in those cases, the extra water percentages were respectively 7 and 10%. TMWM binders using schist (SC) fine aggregates with an aggregate/binder ratio of 1.5 was named SC – AG/B 1.5. Similarly when limestone (LS) or granite (GR) aggregates were used were named respectively LS – AG/B 1.5 and GR – AG/B 1.5. TMWM mixtures made with 2% superplasticizer by mass of binder lime and mine waste mud, were named respectively SC/SP, GR/SP and LS/SP. Unrestrained shrinkage used prismatic specimens measuring $40 \times 40 \times 160$ mm^3 and was determined according to Portuguese Standard LNEC E398-1993. Unrestrained shrinkage readings were performed every hour in the first 10h, every 3 h in the next 6 days and twice a day in the remaining days.

Unfortunately, as the apparatus only measures shrinkage 24 hours after the mixtures were cast, it misses an important part of US deformation, that may take placed between the time when setting occurs until the specimens were removed from the moulds and place in the device. That hypothesis can
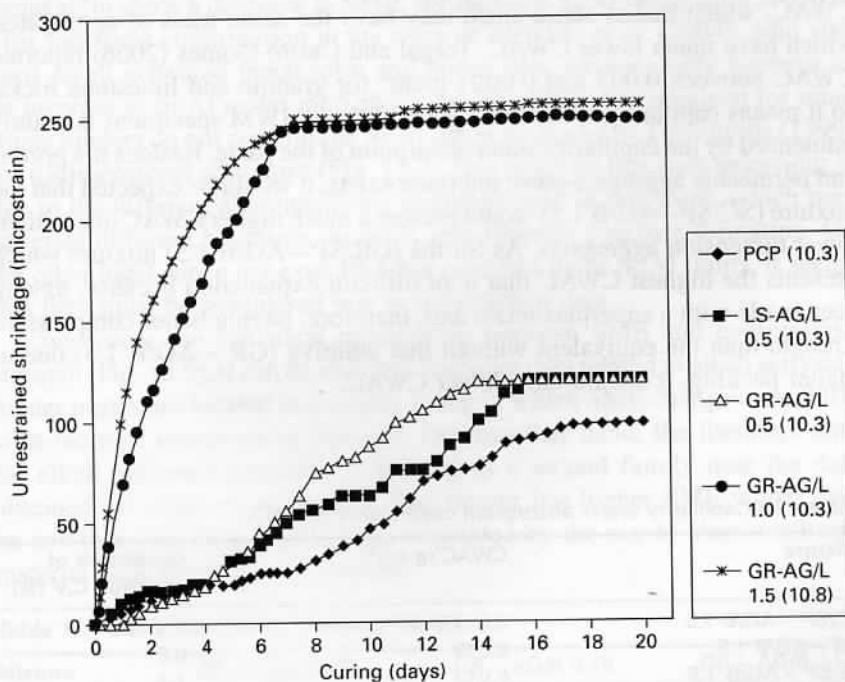
13.6 Unrestrained shrinkage.

only be confirmed using a test device that could measure US deformation since the beginning of setting, something that cannot be done with the Vicat penetration test which is currently used for OPC technology, where the shrinkage deformation in the first 24 h is disregarded (Aitcin, 2001). The US data shows a different behaviour for mine waste mortars with an aggregate/binder mass ratio between 1.0 and 1.5 and the ones with the equivalent 0.5, which have higher shrinkage than the pastes. As the aggregates percentage used in the mortars is much lower than for concretes, i.e mortar aggregate/binder mass ratio is below 2.0 versus between 4 and 5 for concrete, it follows that aggregates act as a set of inclusions trapped in a continuous paste matrix and do not form a rigid skeleton which help to diminish US deformation (Aitcin, 2001; Tazawa and Myazawa, 1995). So increasing aggregate content in terms of aggregate/binder mass ratio from 0.5 to 1.5 is not enough to achieve a US reduction. Besides the volume change associated to the shrinkage behaviour is also dependent on the mass of specimens, i.e the US will be higher for lower mass and higher porosity.

13.4.4 Water absorption

The capillarity water absorption coefficients (CWAC) in terms of (g/cm^2) are shown in Table 13.6. It can be seen that several mixtures have similar CWAC, which makes sense since they have the same mass of aggregates, which have much lower CWAC. Torgal and Castro Gomes (2006) reported CWAC between 0.005 and 0.0007 g/cm^2 for granitic and limestone rocks, so it means capillarity water absorption of the TMWM specimens is mainly influenced by the capillarity water absorption of the paste. Besides if a porous and permeable aggregate-paste interface exists, it would be expected that the mixture (SC/SP – AG/B 1.5) would present a much higher CWAC due to their lower dimension aggregates. As for the (GR/SP – AG/B 1.5) mixture which presents the highest CWAC that is of difficult explanation because, having been made with a superplasticizer and, therefore, having better compressive strength than the equivalent without that additive (GR – AG/B 1.5) due to higher packing, it should have lower CWAC.

Table 13.6 Capillarity water absorption coefficients (CWAC)

| Mixture	CWAC (g.cm^2)	Coefficient of variation C.V (%)
SC/SP – AG/B 1.5	0.012	0.9
GR – AG/B 1.5	0.013	0.8
LS/SP – AG/B 1.5	0.012	1.2
GR/SP – AG/B 1.5	0.015	1.6

13.4.5 Static modulus of elasticity (SME)

The SME allows separation of the elasticity behaviour of the mixture with granitic aggregates (GR) from the ones with schist (SC) (Table 13.7). From the same mass amount of aggregates different static modulus of elasticity were obtained (the SME of mixture with granitic aggregates is 85% of mixture with schist aggregates). That is probably related to aggregate dimension, as a higher dimension and a lower volume led to lower SME. For mixtures with granitic aggregates, an increase of 100% in aggregate amount lead to 14.5% higher SME. The SME data are similar to that obtained by others (Pinto, 2004; Hardjito et al., 2004; Duxson et al., 2005; Wang et al., 2005; Kirschner and Harmuth, 2004). That can be explained by the influence of the aggregates. In fact some authors considered aggregates to be the most important parameter concerning OPC modulus of elasticity (Teychenné, 1978; Zhou et al., 1995; Rashid et al., 2002). While Hardjito et al. (2004) and Pinto (2004) measured SME in concrete specimens, Duxson et al. (2005), Wang et al. (2005) and Kirschner and Harmuth (2004) evaluated the SME for pastes, which may explain their strangely lower results. Previous investigations on mine waste binders with SEM/EDS microanalysis led to the following data; $Si/Al = 3.3$ for (GR – AG/B 1.5) and $Si/Al = 3.2$ for (XS – AG/B 1.5). The investigations done by Davidovits (1999) using high purity alkali activated metakaolin show a decrease in SME, for increase Si/Al molar ratio above 3. This has some confirmation in the work of Fletcher et al. (2004), who also used alkali activated metakaolin and stated that decrease only happens to an increase in Si/Al molar ratio above 24. The SME data obtained for mine waste binders do not confirm the Si/Al limits proposed by Davidovits (1999) for tridimensional structures (Fig. 13.7). It is believed that such behaviour is due to the different aluminosilicate materials used in this work, which may generate different hydration products and different structure formation. On the other hand, since not even Fletcher confirms those Si/Al limits, it seems that they must be considered just as information data.

Concerning the statistical relationship between SME and compressive strength (Fig. 13.8), it can be seen that literature data related to alkali activated binder pastes are located as a family group in which SME changes very little with increase compressive strength. On the other hand, the literature data for alkali activated concretes is located as a second family near the data obtained for mine waste binders. The former has higher SME which may be due to a coarser microstructure originated by the use of aluminosilicate material with lower Blaine fineness.

Table 13.7 Static modulus of elasticity (SME)

| Mixture	SC – AG/B 0.75	GR – AG/B 0.75	GR – AG/B 1.5
SME (GPa)	34.9	29.7	34.0
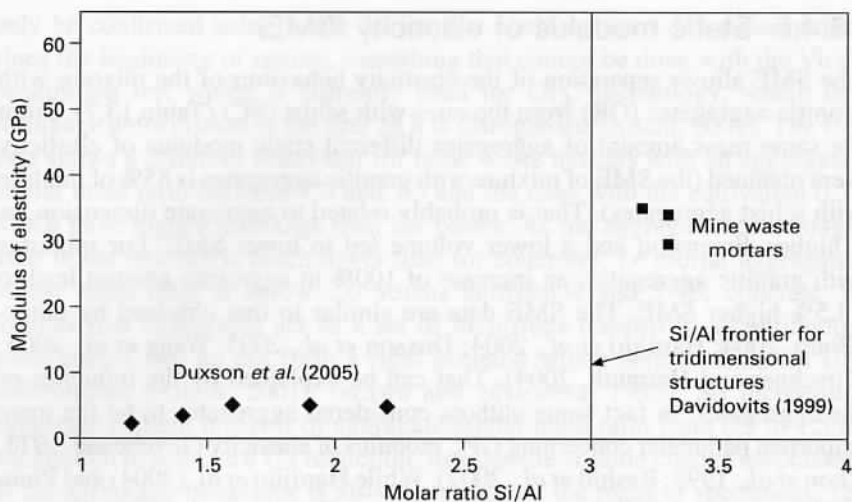
13.7 Modulus of elasticity versus molar ratio Si/A.
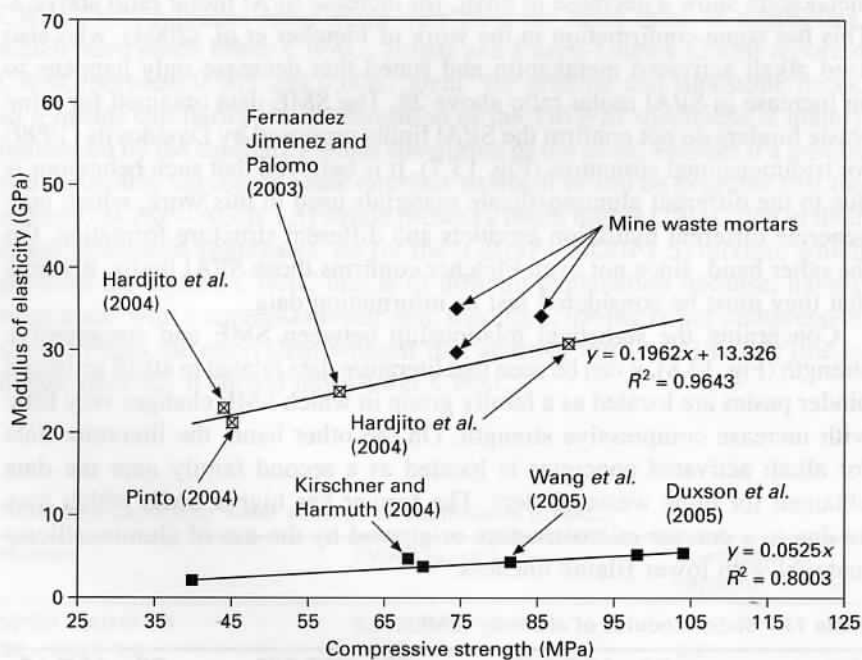
13.8 Relationships between compressive strength and modulus of elasticity.

13.4.6 Adhesion characterization of mine wastes geopolymeric binders

The failure modes were characterized by the location of the failure in the slant specimens. An adhesive failure is defined when the plane of failure is along the interface surface. Figure 13.9 shows a slant shear specimen failed in a monolithic failure mode. The values of bond strength in slant specimens with a monolithic failure mode are a lower estimate. The specimens were named after the name of repair material and the concrete substrate surface treatment. Specimens using concrete substrate repaired with commercial product R1 with and without surface treatment were named respectively, R1 – ES (Etched surface) and R1 – NTS (No treatment surface). Similarly when TMWM geopolymer binder was used to bond the two halves they were named respectively GP – ES and GP – NTS. Slant specimens with substrate surface treatment as cast against metallic formwork, and as cast against wood formwork were also used repaired with TMWM geopolymeric binder and
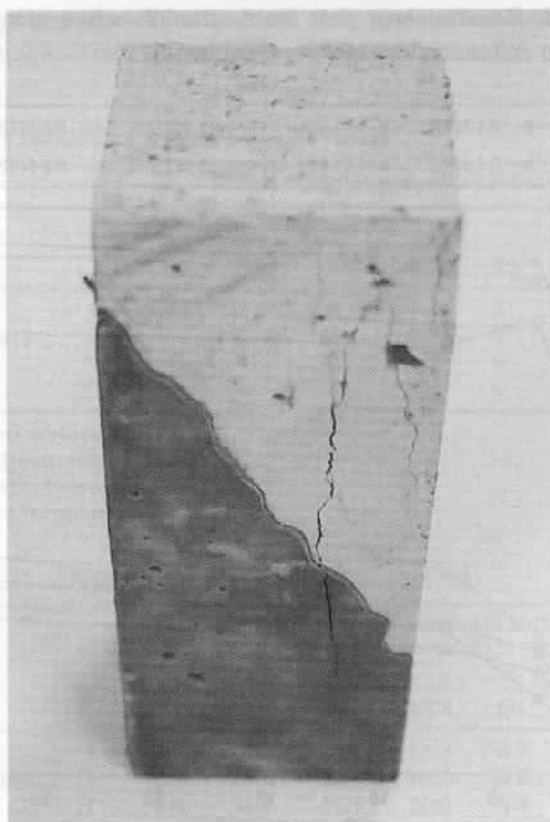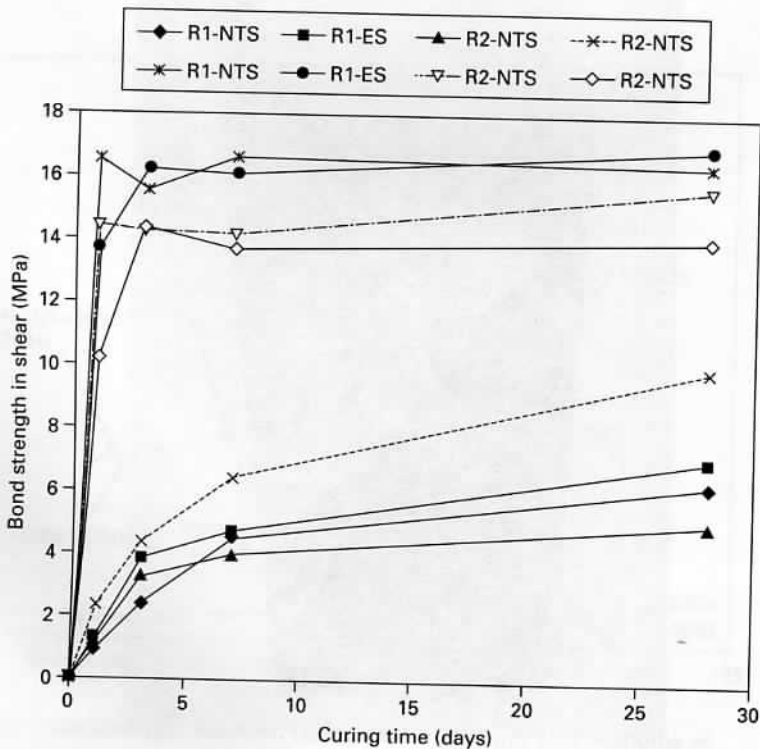

13.9 Slant specimen with a monolithic failure.

were respectively, GP-MF and GP-WF. It can be seen that specimens repaired with mine waste geopolymeric binder present the high bond strength even at early ages (Fig. 13.10). Specimens repaired with geopolymer binder with 1 day curing have higher bond strength than specimens repaired with current commercial products even after 28 days curing. Specimens repaired with mine waste geopolymeric binder are influenced not by chemical treatment in sawn concrete surface substrate, but by the use of concrete surfaces as cast against formwork. Those kinds of surfaces are rich in calcium hydroxide but lack exposed coarse aggregates which could contribute to improve bond strength due to silica dissolution from aggregate surface.

Commercial repair products used in the investigation were supplied as pre-packed blend of graded aggregates with a maximum size 2 mm, Portland cement, silica fume, fibres and other additives. The typical density of the fresh material is 2100 kg/m^3. The repair products are ready for on-site mixing and use, requiring only the addition of clean water.

The strength performance of commercial repair products is very dependent on the curing time and that constitutes a serious setback when early bond strength is required. Results show that bond strength when using repair product R2 are clear influenced by surface treatment.

13.10 Slant shear test results.

Table 13.8 shows the number of the specimens that had an adhesive failure. As can be seen, only the slant specimens repaired with geopolymeric binder and saw concrete substrates present monolithic failures due to its high bond strength. The failure mode for specimens repaired with current commercial repair products R1 and R2 are identical and occurs in the interface section, independently of the concrete substrate surface treatment. Table 13.9 shows the coefficient of variation (COV) of bond strength results according to curing age. The results show that in all cases COV decreases with curing age and shear strength increase except in the case of specimens repaired with mine waste geopolymeric binder and with chemical surface treatment (GP-ES). Specimens repaired with current commercial repair products R1 and R2 present very high COV at early ages. However, after 28 days curing this factor show acceptable values. For both commercial repair products COV results are clearly influenced by surface treatment. Specimens repaired with mine waste geopolymeric binder shows low COV values even at early ages which are not influenced by the chemical treatment. When comparing COV results in specimens repaired with current commercial repair products and geopolymeric binder it seems clear that the last repair solution is much more reliable. The explanation to that behaviour relies on the fact that OPC

Table 13.8 Specimens with an adhesive failure

		Repair material and substrate surface treatment							
		R1		R2		GP			
		ES	NTS	ES	NTS	ES	NTS	MF	WF
	1	4	4	4	4	2	0	4	4
Curing days	3	4	4	4	4	0	0	4	4
	7	4	4	4	4	0	0	4	4
	28	4	4	4	4	0	0	4	4

ES (etched surface)
NTS (no treatment surface)
MF (metallic formwork)
WF (wood formwork)

Table 13.9 Coefficient of variation of bond strength (%)

| | | Repair material and substrate surface treatment | | | | | | | |
		R1		R2		GP			
		ES	NTS	ES	NTS	ES	NTS	MF	WF
	1	23.0	33.3	21.7	27.3	6.7	6.7	12.5	14.8
Curing days	3	13.1	20.8	20.4	24.2	5.6	6.4	8.4	6.3
	7	8.5	17.7	14.1	20.0	5.6	6.0	7.7	5.8
	28	10.0	16.1	12.1	16.0	6.0	6.1	7.0	1.4

concrete substrate surfaces are rich in calcium hydroxide that will react to geopolymeric based binder due to the need of positive ions such as Ca^{2+} to be present in the framework cavities to balance the negative charge of AlO_4 groups and also to the mechanical interlock yield by silica ions release from aggregate surface when subject to the high alkaline activator. Therefore concrete substrates will chemically bonds to the geopolymeric phase as it can be seen by the absence of a clear interfacial transition zone in a microstructural level (Fig. 13.11).

13.5   Durability and environmental performance

For the durability performance, abrasion and acid resistance were assessed for mine waste geopolymeric mixtures and comparable OPC binders. The environmental performance was assessed with leaching tests.

13.5.1 Abrasion resistance

The abrasion resistance was evaluated using the Los Angeles abrasion apparatus (ASTM C 131-06), which consists of a metal cylinder, where eight $50 \times 50 \times 50$ mm^3 cubic specimens have been placed together with eight steel spheres. The cylinder is then submitted to 1000 full rotations,
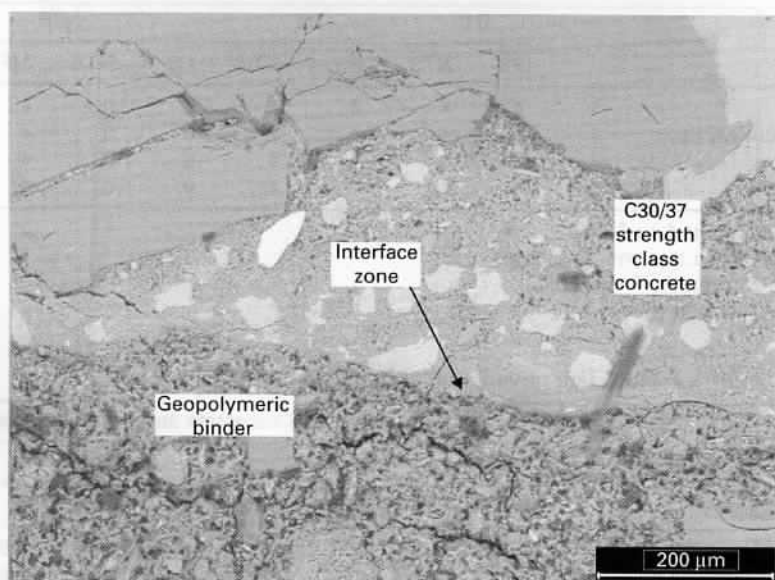

13.11 SEM micrograph of interfacial transition zone between concrete substrate and mine waste geopolymeric binder.

and after every 100 full rotations the specimens are weighed to detect the weight change. Mine waste binder specimens show a low level of weight loss while in OPC specimens a severe weight loss was observed. For mine waste binders the higher abrasion resistance was achieved in paste specimens (Fig. 13.12). This result is related to the fact that mine waste paste had the highest compressive strength. As for OPC specimens, abrasion resistance seems to be more influenced by the compressive strength than for the aggregates used in the mix.

13.5.2 Acid resistance

Acid resistance of OPC C30/37 concrete and mine waste binders as weight loss is shown in Fig. 13.13. The resistance to acid attack was tested by immersion of the mine waste binders and OPC concrete $50 \times 50 \times 50$ mm^3 specimens in 5% sulphuric, hydrochloric and nitric acid solutions during 28 days. To keep a constant pH, acid solutions were replaced after 14 days. After 28 days the specimens were oven-dried to achieve constant weight, and detachable particles were removed. The acid resistance was assessed by the differences
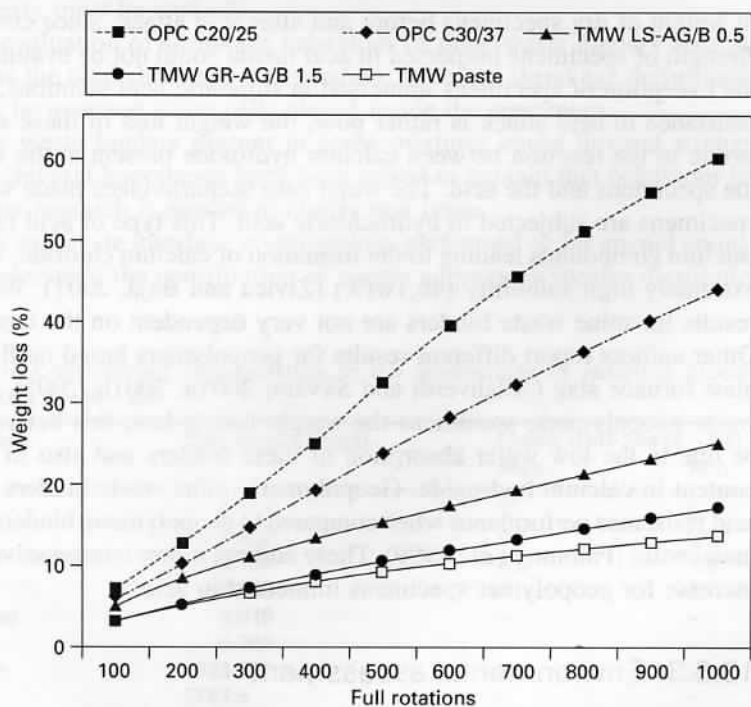
13.12 Abrasion resistance with the Los Angeles test for OPC and tungsten mine waste mud binders (TMWM).
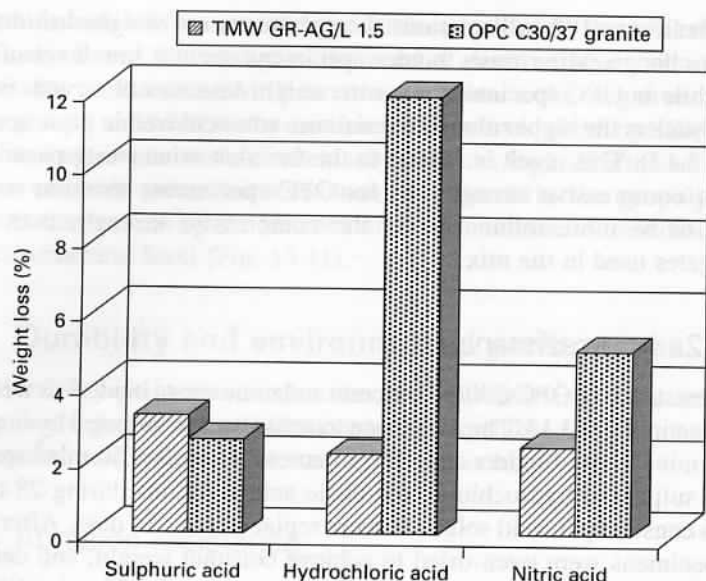
13.13 Weight loss after acid attack.

in weight of dry specimens before and after acid attack, since compressive strength of specimens immersed in acid media could not be evaluated. With the exception of specimens immersed in sulphuric acid solutions, the OPC resistance to acid attack is rather poor, the weight loss of these specimens is due to the reaction between calcium hydroxide present at the surface of the specimens and the acid. The worst case scenario takes place when OPC specimens are subjected to hydrochloric acid. This type of acid reacts with calcium compounds leading to the formation of calcium chloride, which has extremely high solubility (46,1wt%) (Zivica and Baja, 2001). Weight loss results for mine waste binders are not very dependent on the type of acid. Other authors report different results for geopolymers based on fly ash and blast furnace slag (Allahverdi and Skvára; 2001a, 2001b, 2005). For mine waste geopolymeric specimens the weight loss is low; this behaviour may be due to the low water absorption of these binders and also to their low content in calcium hydroxide. Geopolymeric mine waste binders have low acid resistance performance when compared to geopolymeric binders based on metakaolin (Palomo *et al.*, 1999). These authors report compressive strength increase for geopolymer specimens immersed in acid.

13.5.3 Environmental assessment

The use of new binder as a building material requires the assessment of its environmental performance. For that, leaching tests have been carried

out according to DIN 38414 – S4. Leaching results show that all chemical parameters are below the limits established by the standard and can be considered an inert material (Table 13.10). As to the limits for water contamination set by the Portuguese Decree 236/98 (Table 13.11), it can be stated that although some chemical parameters are above the limits for drinkable water, all limits are met concerning water for irrigation purposes.

13.6   Future research trends

Further investigations about geopolymeric mine waste based binders are needed in order to clarify several aspects that current knowledge does not, such as:

- Since water content influences the amorphous nature of reaction products, it means that mine waste binders with low water level must be studied.
- The workability of mine waste mortars lacks the knowledge of which additives can overcome some stiff behaviour.
- In OPC binders the setting time is evaluated using pastes and the Vicat needle. Since the setting time for mine waste binders is influenced by the volume and nature of the aggregates, other ways to evaluate this property must be studied.
- The evaluation of shrinkage behaviour of mine waste binders does not assess the total shrinkage deformation, therefore shrinkage deformation must be assessed using cells placed inside the specimens.
- Mine waste binders present in some mixtures cause flexural strength loss. Several hypotheses have been raised to explain that behaviour but further research is needed to clarify that issue.
- Paste aggregate interface investigations performed so far are not enough to understand the contribution of coarse aggregates species dissolution

Table 13.10 Contaminant concentration in the wastewater by leaching process standard DIN 38414 – S4

Contaminant	Test results (mg/l)	Limits (DIN 38414 – S4)	
		Max.	Min.
Zinc	0.011	2	5
Arsenic	< 0.002	0.1	0.5
Lead	0.197	0.5	1.0
Copper	0.062	2	5
Manganese	0.019	–	–
Iron	0.203	–	–
Potassium	123.75	–	–
Sodium	3792.5	–	–
Magnesium	0.163	–	–
Sulphates	< 0.003	500	1500

Table 13.11 Water quality according to the Portuguese Decree 236/98 (mg/l)

Constituents	Appendix I						Drinkable water Appendix VI		Irrigation water Appendix XVI	
	A1		A2		A3					
	VMR	VMA	VMR	VMA	VMR	VMA	VMR	VMA	VMR	VMA
Zinc	0.5	3.0	1.0	5.0	1.0	5.0	(*)	–	2	10
Arsenic	0.01	0.05	–	0.05	0.05	0.1	–	0.05	0.1	10
Lead	–	0.05	–	0.05	–	0.05	–	0.05	50	20
Copper	0.02	0.05	0.05	–	1.0	–	(**)	–	0.2	5.0
Manganese	0.05	–	0.1	–	1.0	–	0.02	0.05	0.2	1.0
Iron	0.1	0.3	1.0	2.0	1.0	–	0.05	0.2	5.0	–
Potassium	–	–	–	–	–	–	0.01	0.01	–	–
Sodium	–	–	–	–	–	–	0.02	0.15	–	–
Magnesium	–	–	–	–	–	–	0.03	0.05	–	–
Sulphates	150	250	150	–	150	250	0.03	0.25	575	–

VMR – Maximum recommended value
VMA – Maximum value
* – After standard treatment (0.1×10^{-3})
** – After standard treatment (0.1)
A1 – Physical treatment and disinfection
A2 – Physical and chemical treatment and disinfection
A3 – Physical and chemical treatment of control and disinfection

and how these species influence reaction mechanisms involved in the hardening of these new binders. So, further investigations are needed using aggregates with different sizes and different porosity levels.

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