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Bond Strength Between Concrete Substrate And Repair Materials. Comparisons Between Tungsten Mine Waste Geopolymeric Binder Versus Current Commercial Repair Products.

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Abstract

An experimental preliminary investigation was conducted to evaluate bond strength between Ordinary Portland Cement concrete substrate and three repair materials. Tungsten mine waste geopolymeric binder and two commercial repair products were used as repair materials. This study indicates that tungsten mine waste geopolymeric binders possess much higher bond strength than current commercial repair products. Results also shows that commercial repair products gain no bond whatsoever to sawn concrete specimens. Scanning electron micrographs reveal that tungsten mine waste geopolymeric binders chemically bond to the concrete substrate. Cost comparisons between tungsten mine waste geopolymeric binder and current commercial repair products are also made showing that geopolymeric ones are by far the most cost efficient solution.

Keywords: geopolymeric binder paste, tungsten mine waste, repair products, bond strength

Introduction

Studies of alkali-activated cements have a long history in the former Soviet Union Scandinavia, and Eastern Europe (Roy,1999). Davidovits (1991,1999,2002) created the term "geopolymer", to characterise new materials with the ability to transform, polycondense and adopt a shape rapidly at low temperatures like "polymers". The polymerisation process involves a chemical reaction under highly alkaline conditions on Al-Si minerals yelding polymeric Si-O-Al-O bonds with empirical formula Mn [- (Si - O_2)z – Al - O]n. wH2O, where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium (K^+) or sodium (Na^+). This author reported several advantages of geopolymeric cementitious systems over Portland cement. Namely environmental benefits given that

Figure 1 Panasqueira tungsten mine.

geopolymeric based concrete has a much longer service life than Portland cement based concrete, to greater metals waste encapsulation capacity and lower (CO_2 emissions, 0,18 tonnes of CO_2 per tonne of cement). Geopolymerisation requires a precursor that contains significant quantities of silicon and aluminium held in an amorphous phase such as ashes from power stations or mining and quarrying wastes.

In Portugal mining and quarrying activities generated 17 Mt of mineral wastes in 2001 which represents 58% of total industrial waste. Additionally in order to respect the "Habitats"(1992) and "Birds" European Directives (1979), Portugal has a protected area equivalent to 7% of it total land area, a value that will soon increase to 22% due to Portugal´s recent proposal, under the Natura 2000 Network. This means significant efforts must be made by the scientific community to find alternative uses for mining and quarrying wastes in order to preserve Portuguese protected areas and their natural biodiversity.

Panasqueira is an underground mine situated in central Portugal on the southern edge of the Serra da Estrela mountain range, a natural park, near the Serra do Açor, a protected landscape, and also near the Zezere river (see Figure 1). Tungsten and tin have been mined in the Panasqueira area since the 1890s. During the mining process two types of mine waste are generated, coarse aggregates derived from rock blastings and waste mud conveyed by pipelines into lagoons, currently amounting for several million tonnes which are still being added almost 100 tonnes per day.

Previous research by Pacheco-Torgal et. al. (2005a) show that in Portugal the production of geopolymeric concrete types will be much more expensive than traditional Portland cement concrete due to the cost of the alkaline activators used in the first ones, however this differential will be reduced in a near future when Portland cement cost increase under the European Emissions Trading Scheme. An alternative to using geopolymeric based binders will be to replace high cost materials such as concrete repair products.

Good adhesion is one of the most important properties of concrete repair materials (Austin et al. 1999; Momayez et al. 2005). The objective of the present work is therefore to make some preliminary investigations about bond strength between Ordinary Portland Cement concrete substrate and three repair materials, tungsten mine waste geopolymeric binder and two current commercial repair products.

Experimental Program

Materials

Concrete Substrate

Using the Faury concrete mix design method (Faury, 1958; Lourenço and Coutinho,1986) two strength concrete classes were designed. The concrete mixes and their main properties are described in table 1. Concrete specimens were cured immersed in water during 3 months. This curing period provides an almost complete concrete hydration as old concretes in field practice and has been used by Hassan et al.(2001).

Current Commercial Repair Products

Two commercially available repair materials labelled R1 and R2 were used in this study. These repair materials are supplied as pre-packed blend of graded aggregates with a maximum size 2mm, cement, silica fume, fibers 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. Further data of the repair materials supplied by the manufacturer are as follows:

Material R1 - A water/powder ratio of 0,16 is recommended for use.
fc_{28d} = 45MPa, ft_{28d} = 9Mpa
Material R2 - A water/powder ratio of 0,14 is recommended for use.
fc_{28d} = 49MPa, ft_{1d} = 3Mpa, ft_{7d} = 6Mpa, ft_{28d} = 8Mpa

Table 1 Mix proportions and main properties of the concrete substrates.

Components	B1(C20/25)	B2(30/37)
Cement II 32,5 (Kg/m^3)	394	504
Fine river sand	632	417
Coarse aggregate	1032	1154
W/C ratio	0,55	0,43
fc_{28d}^{a} (MPa)	25,6	37,8
ft_{28d}^{b} (Mpa)	6,7	8,7

[a]Average value of three specimens (150×150×150mm^3)
[b]Average value of six specimens (40×40×160mm^3

Table 2 Chemical composition of mine waste mud (%).

SiO_2	$Al_2 O_3$	$Fe_2 O_3$	$K_2 O$	$Na_2 O$	Mg O	$S O_4$	$Ti O_2$	As	Other minor oxides
53,48	16,66	12,33	7,65	0,62	1,27	3,10	1,39	1,28	2,22

Tungsten Mine Waste Geopolymeric Binder Paste

The geopolymeric binder paste used in this investigation as repair product was made using tungsten mine waste mud previously subject to a thermal treatment at 950º C during 2 hours, in order to achieve the dehydroxylated state. Its mineralogical composition and thermal conditions were described by Pacheco-Torgal et al.(2005b, 2005c). The chemical composition of the mine waste mud is shown in table 2.

The geopolymeric binder paste used was a mixture of mine waste mud, calcium hydroxide and alkaline silicate solution. The mass ratio of mine waste mud: activator was 1:1. Calcium hydroxide was used with a percentage substitution of 10%, because this percentage led to the highest compressive strengths. An activator with sodium hydroxide (24M) and sodium silicate solution (Na_2O=8,6%, SiO_2=27,8%, Al_2O_3=0,4% and water=63,2%) was used with a mass ratio of 1:2,5. Pacheco-Torgal et al. (2005d, 2005e) have recently shown that these conditions lead to the highest compressive strength results in alkali-activated mine waste mud binders. Distilled water was used to 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 being added to the activator which according to Teixeira-Pinto et al. (2002) is the mixing option that leads to the best results. Compressive and tensile strength of geopolymeric based binder are as follow:

Fc_{1d} = 20MPa, fc_{7d} = 23MPa, fc_{14d} = 26,3MPa, fc_{28d} = 30,5MPa
ft_{1d} = 5,0Mpa, ft_{7d} = 6,4Mpa, ft_{14d} = 8Mpa, ft_{28d} = 8Mpa

Specimen Preparation, Strength Testing And Microanalysis

Concrete specimens were broken and in the middle and then repair products were used to bond the two halves. Figure 2 (a) and (b) shows the specimen preparation. The specimens were named after the strength class concrete substrate and the repair material. Specimens using C20/25 concrete repaired with commercial products were named respectively, B1+R1 and B1+R2. Similarly when mine waste mud geopolymer based binder was used to bond the two halves they were named, B1+GP. Some specimens have been cut with an electric sawn. Interfacial bond strength was indirectly measured with the flexural strength test (see Figure 2 (c)). This test although is not suitable to analyse bond strength allows quick and preliminary results about bond strength and have already been used by Yang et al (2000). Specimens with $40\times40\times160mm^3$ were used according to EN 1015-11. Tensile strength for each mixture was obtained from an average of 3 specimens.

For examination by scanning electron microscopy (SEM), specimens were embedded into a low viscosity epoxy resin, cut and polished. After the lapping stage an additional epoxy impregnation was performed, and the samples were relapped in order to ensure full resin impregnation and a good quality polish. The samples were then carbon-coated. A Hitachi S2700 scanning electron microscope was used equipped with a solid backscattered detector.

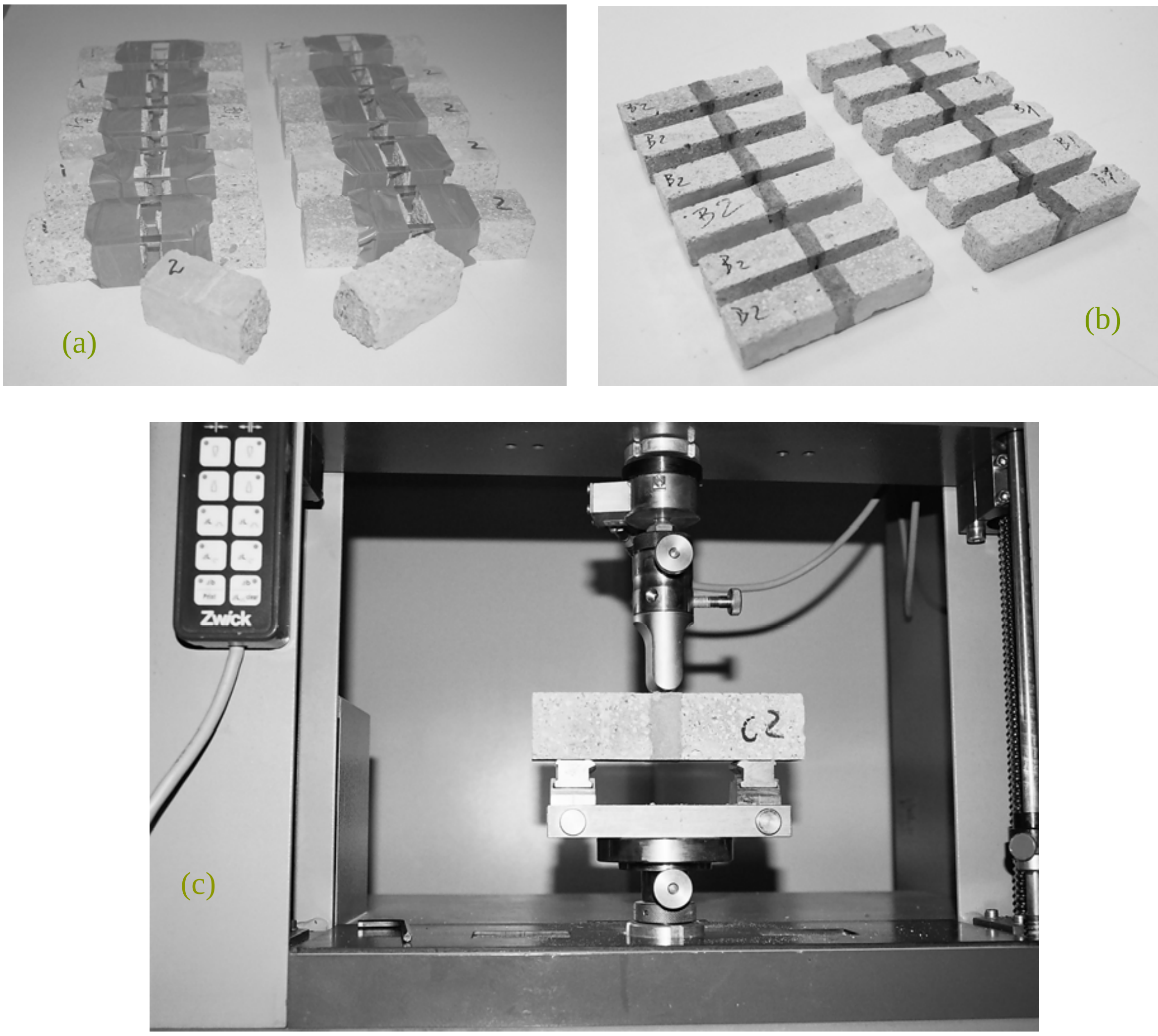

Figure 2 Specimen preparation: (a) concrete substrate specimens are broken in two halves and then prepared to receive the bonding product, (b) concrete specimens bond with mine waste geopolymeric paste, (c) flexural strength test

Results And Discussion

Results on the effect of the several repair solutions on interfacial bond strength and the failure mode are shown respectively on Figure 3. and on Figure 4. It can be seen that specimens repaired with tungsten mine waste mud geopolymeric binder present the higher bond strength even at early ages. Specimens repaired with geopolymer binder with 4 days curing have a higher flexural strength than specimens repaired with current commercial current products even after 14 days curing. The strength performance of such products is very dependent on the curing time and that constitutes a serious setback when early bond strength is required. The failure mode for specimens repaired with current commercial repair products R1 and R2 are identical and occurs in the interface section (see Figure 3 (a) and (c)). As for specimens repaired with geopolymeric binder failure occurs in the concrete substrate section and in the repaired section(see Figure 3 (b)). When specimens with sawn concrete halves were used current commercial repair products didn't show any bond capacity whatsoever. As for specimens using sawn halves and repaired with geopolymer binder they show a very high flexural strength and binder failure occurs in the concrete substrate section only (see Figure 3 (d)).

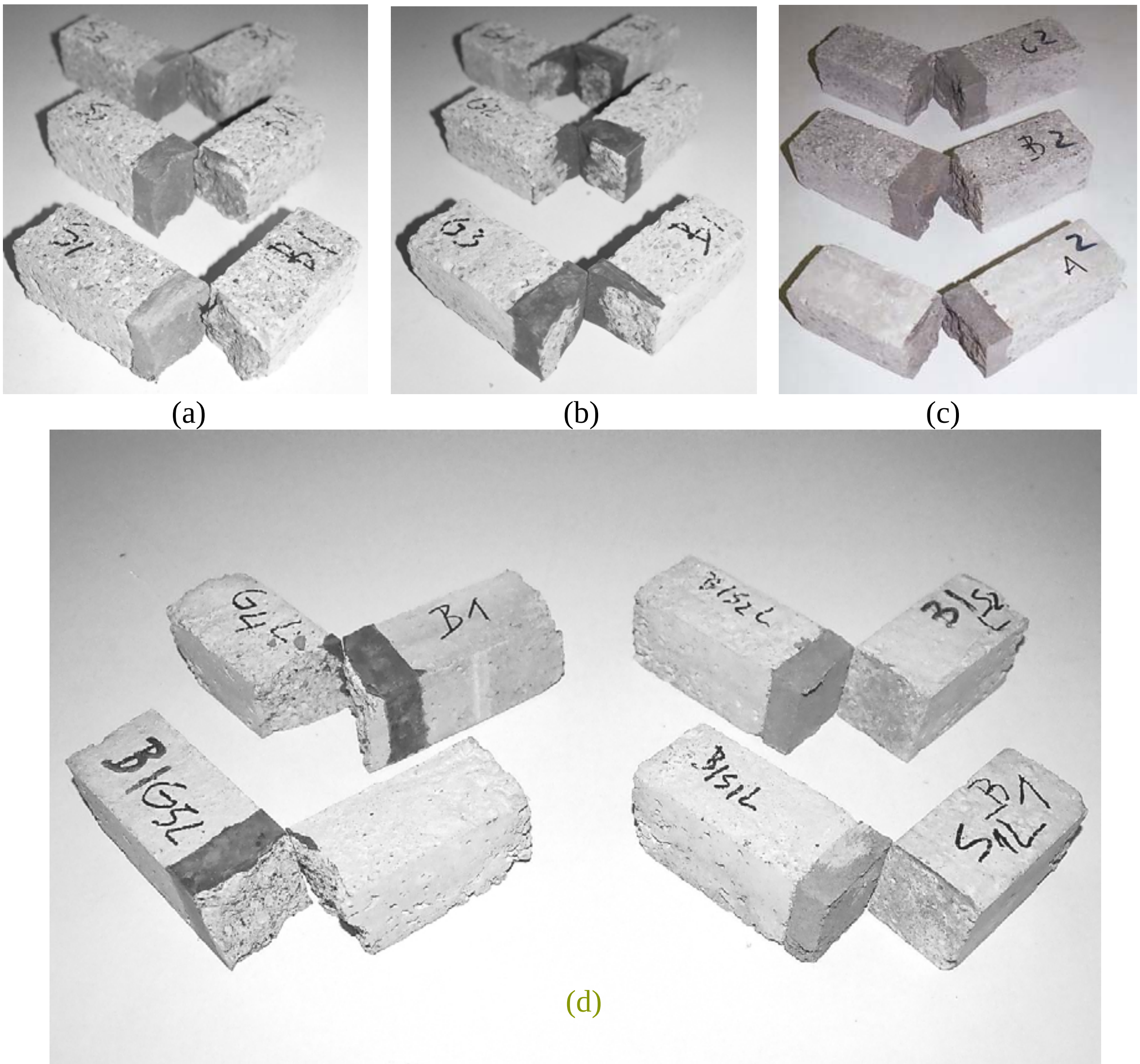

Figure 3 Concrete specimens after flexural test: (a)Broken halves repaired with R1, (b)Broken halves repaired with GP, (c)Broken halves repaired with R2, (d) Sawn halves repaired with GP and R2.

The explanation to that behaviour relies on the fact that sawn surfaces have higher contact area of cement paste which is rich in calcium hydroxide phase and will react to geopolymeric based binder due to the need of positive ions such as Ca^{++} to be present in the framework cavities to balance the negative charge of Al^{3+} ions. Therefore concrete substrate 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 (see Fig. 5).

Economic Analysis

In order to evaluate the economic profitability of the different repair solutions, comparisons between their materials cost were made. In table 3 the cost of prime materials used to prepare the repair mortars are reported. It must be noted that these values are relative to Portuguese market prices in the year 2005. The cost of repair mortars are reported in table 4.

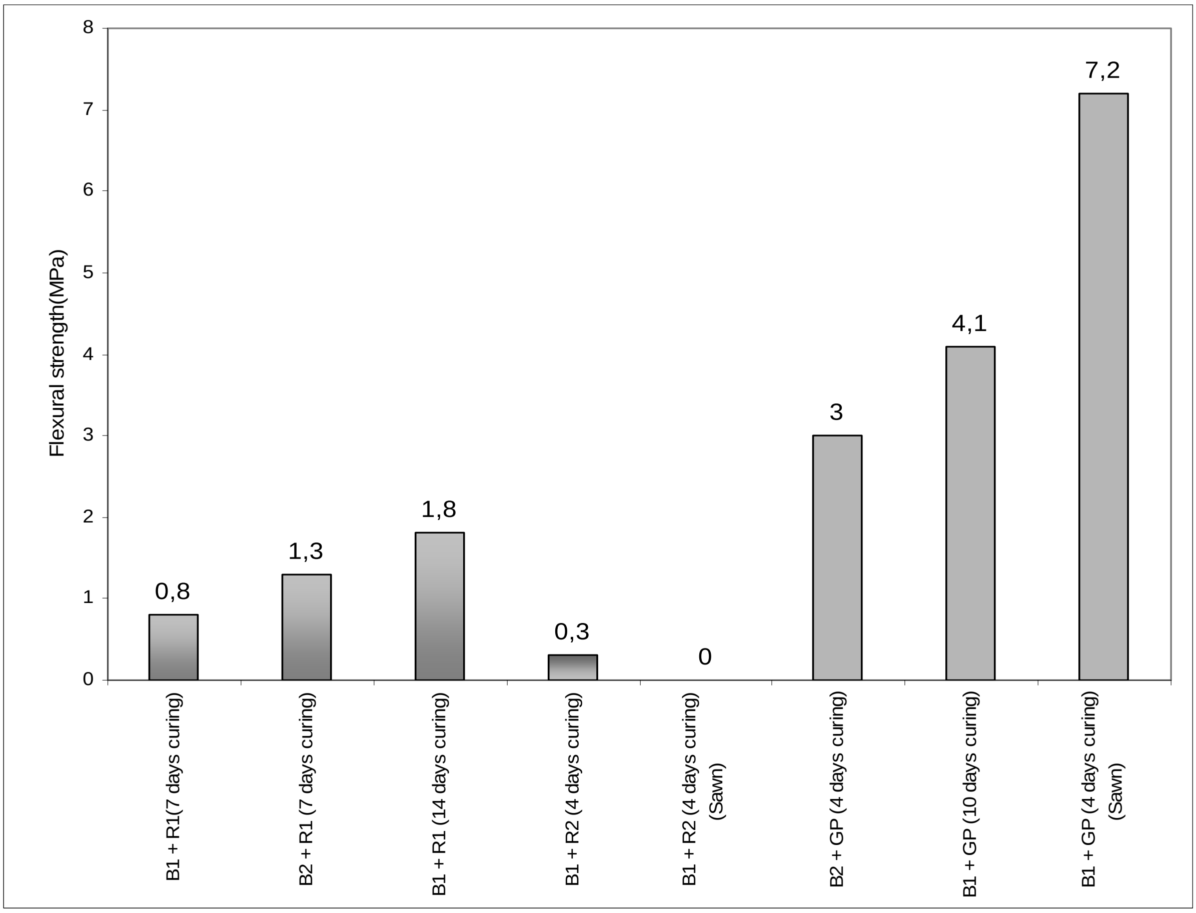

Figure 4 Flexural strength.

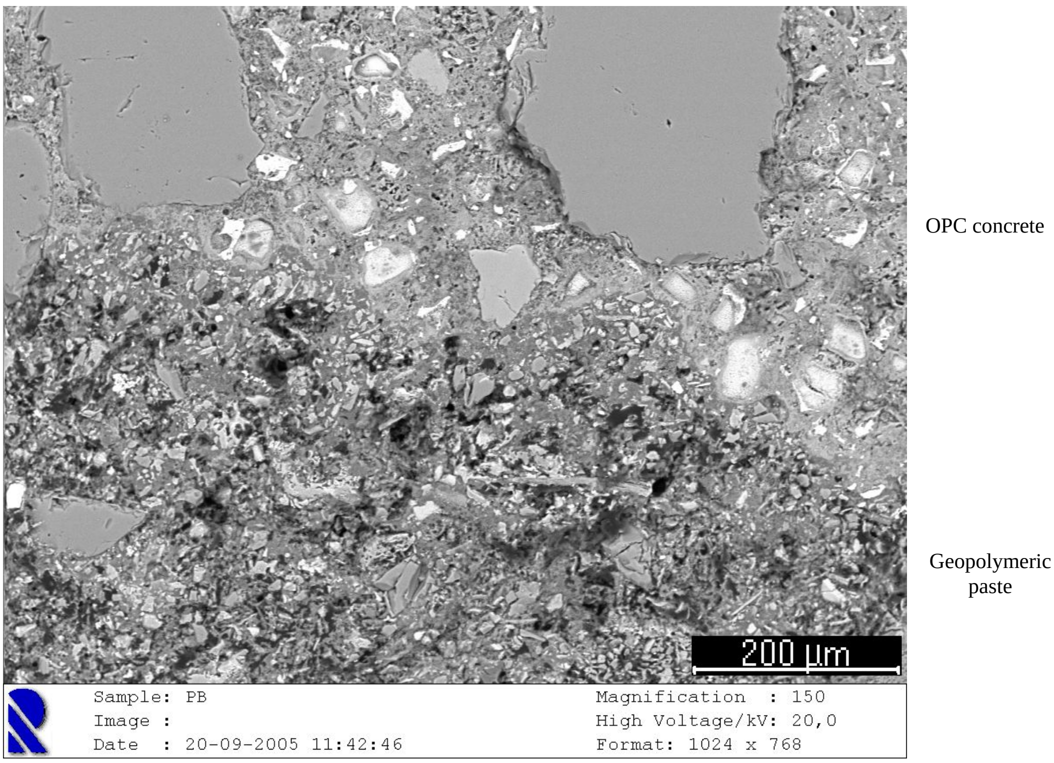

Figure 5 SEM micrographs of interfacial transition zone between concrete substrate and geopolymeric paste

Table 3 Cost of prime materials used to prepare the repair mortars.

Prime materials	Waterglass	Sodium hydroxide flakes	TMWM[a]	Calcium hydroxide	Repair material R1	Repair material R2
Cost (€/ton.)	428	728	25	100	910	1646

[a]Includes calcination and grinding operations cost

Table 4 Cost of repair mortars.

Mixture	Cost (€/ m^3)
Geop. TMWM	271
Repair material R1	1820
Repair material R2	3292

Even if current commercial repair materials had the same mechanical performance of geopolymeric binder the cheapest one (R1) is still 6,7 times higher than geopolymeric repair binders. When comparing the cost to flexural strength ratio the differences are even higher (see Fig. 6). Current commercial repair material R1 is a very expensive solution at least at early ages. Repairing concrete substrate with tungsten mine waste geopolymeric binder is 11 times cheaper independently of repaired concrete type.
Moreover, in addition to materials cost, environmental costs related to future introduction of taxes on quarrying and mining wastes disposal and on primary construction raw materials must also be taken into account.

Conclusions

The following conclusions can be drawn from this preliminary study:

a) Tungsten mine waste geopolymeric binder possess much higher bond strength than current commercial repair products. That advantage is higher at early ages.
b) Commercial repair products gain no bond to sawn concrete specimens as for geopolymeric type they achieved the highest strength with that kind of substrate surface.
c) Scanning electron micrographs reveal that tungsten mine waste geopolymeric binder chemically bond to the concrete substrate.
d) Cost comparisons between tungsten mine waste geopolymeric binder and current commercial repair products show that geopolymeric ones are by far the most cost efficient solution.

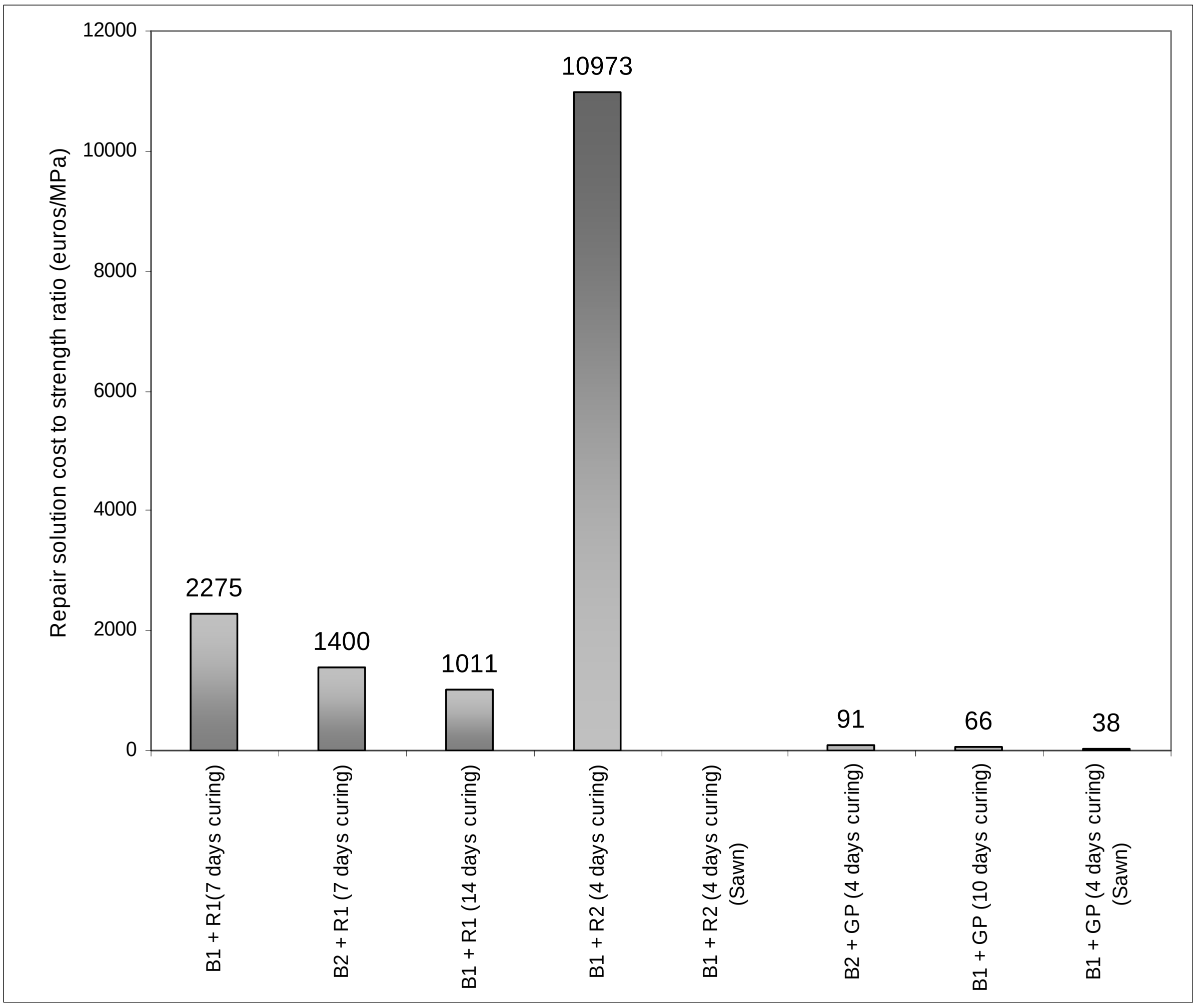

Figure 6 Cost to strength ratio.

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