

Alkali Activated Geopolymeric Binder Using Tungsten Mine Waste: Preliminary Investigation.

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ABSTRACT

This paper reports preliminary results of a PhD research project related to the development of an alkali-activated geopolymeric binder using mineral waste mud from the Portuguese tungsten mine Panasqueira which is still operating. Mineralogical analysis indicates that the waste mud is composed mainly of muscovite and quartz with a high content of iron and alkali metals. Results of the dehydroxylation process are presented by x-ray diffraction and infrared emission spectroscopy patterns of quenched waste powder and also from compressive strength of alkali-activated mortar specimens, showing a significant potential as a geopolymeric source precursor.

Considerations about Portuguese industrial waste production are made showing a high level ratio of CO₂ emissions mostly from cement industry, a nation-wide lack of fly ash and blast furnace slag to be used as cementitious by-products and huge amounts of quarrying and mining wastes and also the need to preserve its large and protected natural areas leading to the use of aluminosilicate minerals as the only reasonable alternative to the development of alkali-activated friendly environmental binders.

Materials raw cost comparisons between Portland cement based concretes and alkali-activated geopolymeric based concretes are also made showing that Portland cement based ones are by far the most economic ones but not for very long due to the expected increase in Portland cement cost under the recent implementation of CO₂ emissions trading scheme (ETS).

1. Introduction

Current estimates of world cement manufacture are 1700 Mt (millions tonnes)/year accounting for 5% of global CO₂ emissions [1]. With a production of 185 Mt of Portland cement and considering global Western Europe CO₂ emission in the year 2000 of 3500 Mt, European cement industry accounts for 4,6% of CO₂ global emissions [2,3]. Portland cement CO₂ emissions, results from calcination of limestone (CaCO₃) and from combustion of fossil fuels, including the fuels required to generate the electricity power plant. To make Portland cement clinker limestone is heated with a source of silica in a kiln at temperatures well over 1350° C according to the reaction [1]:



The production of one tonne of cement generates 0,55 tonnes of chemical CO₂ and requires an additional 0,39 tonnes of CO₂ in fuel emissions, accounting for a total of 0,94 tonnes of CO₂. Nowadays cement industry uses a variety of additives either fly ash (PFC) or blast furnace slag (BFC). Cement replacement with additives are responsible for less CO₂ emissions than plain Portland cement, Gielen reports CO₂ process and energy related emission of 0,67 tonnes for PFC (25% replacement) and 0,35 tonnes for BFC (65%

replacement) [3]. A clear example comes from Lafarge, the world's largest cement manufacturer, since 1990 cement production have cut net emissions by 11,8%, from 0,767 to 0,685 tonnes of CO₂ per tonne of cement [4]. According to Worrell estimated global potential for CO₂ emission reduction through blended cements could varied between 22-29% [5].

In 1978, Davidovits created the term "geopolymer", to characterise new materials with the ability to transform, polycondense and adopt a shape rapidly at low temperatures like "polymers" [6]. Davidovits reported several advantages of geopolymeric cementitious systems over Portland cement mainly environmental, due to the fact that geopolymeric based concrete has a much longer service life than Portland cement based ones, to the metals waste encapsulation capacity and to lower CO₂ emissions, 0,18 tonnes of CO₂ per tonne of cement [7]. Geopolymerisation involves a chemical reaction between various alumino-silicate oxides with silicates under highly alkaline conditions, yielding polymeric Si – O – Al – O bonds indicating that only Si – Al materials might become sources of geopolymerisation. They require 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.

Kyoto Protocol requires developed countries, as whole to reduce their emissions of greenhouse gas to 5,2% below their levels in the base-year level (1990). For EU-15 the Kyoto Protocol sets the target of an 8% emissions reduction. Within this overall target differentiated emissions limitation have been agreed for each EU-15 member. For Portugal Kyoto commitments implies a reduction of greenhouse gas emissions to 27% above base-year level until 2012. However in 2001 emissions were 36%, above Portuguese individual greenhouse gas reduction targets and according to greenhouse gas emissions trends for EU-15 members in 2002, Portugal emissions reach 41% above 2010 target emissions.

Portuguese cement industry which produces 10 Mt every year is responsible for almost 10% of global emissions, twice the European and world averages. Portugal generates every year just about 0,25 Mt of fly ash from power stations and 0,15 Mt of blast furnace slag which represents only 4% of Portland cement production. The current alternative in Portuguese ready-mixed concrete market is to buy ashes in Spain (which produces 7Mt per year 15% of its Portland cement production) but that's not a very sustainable one.

Therefore reduction in CO₂ emissions can not be achieved using high cement replacement additives. Instead and due to his favourable geologic conditions Portugal mining and quarrying industry had generated around the years several millions tonnes of aluminosilicate wastes which can now be reuse to produce geopolymeric friendly environmental binders.

2. Environmental Issues About Mining And Quarrying Wastes

For the past fifteen years many countries have carried out surveys about mining and quarrying waste materials. The main reasons for undertaking such surveys are the need to conserve scarce natural resources, reduce environmental pollution and to conserve energy [8]. Not very long ago the failure cases of Aznalcollar mine in Spain (April, 1998) which

Table 1 - Metal production versus generated mine waste [9]

Metal	Iron	Aluminium	Nickel	Lead	Copper	Tungsten	Zinc
Extracted metal (%)	40	30	2,5	2,5	1	0,25	0,05
Excavated rock (Mt)	25 503	869	387	1077	11 026	125	1267

affected 2656 ha of Donana Nature Park with pyrite sludge, Baia Mare mine (January, 2000) and Baia Borsa mine (March, 2000) in Romania clearly showed that in a short term and environmentally speaking mine wastes represent a clear and present danger as important as greenhouse gas emissions[10,11].

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. The main industries depending on these materials employs more than 4 million people and produce goods with a value around € 700 billion [12].

About 2,25 billion tonnes of waste has been generated in Western Europe between 1998 and 2001 and 550 million in Eastern new member countries. Mining and quarrying waste represent 15% of total waste in Western Europe and 31% in Eastern Europe[13]. Table 1 shows the enormous amount of waste generated during metal extraction.

In Portugal mining and quarrying activities generated 17 Mt in 2001 which represents 58% of total industrial waste. Fig. 1 shows that mining and quarrying wastes generated in Portugal are well above the average waste production sector both in Western Europe and in Eastern Europe new member countries. Besides it must be take into account that under "Habitats" and "Birds" European Directives [14,15], Portugal has a percentage of protected area over the total land area of 7% and that value will soon increase considerably to 22% due to Portuguese recent proposal, under the Natura 2000 Network, which compares in a favourable manner to Europe average protected area of 8,4%. Therefore significant efforts must be made by scientific community to find alternative uses for mining and quarrying wastes in order to preserve Portuguese protected areas and its natural biodiversity.

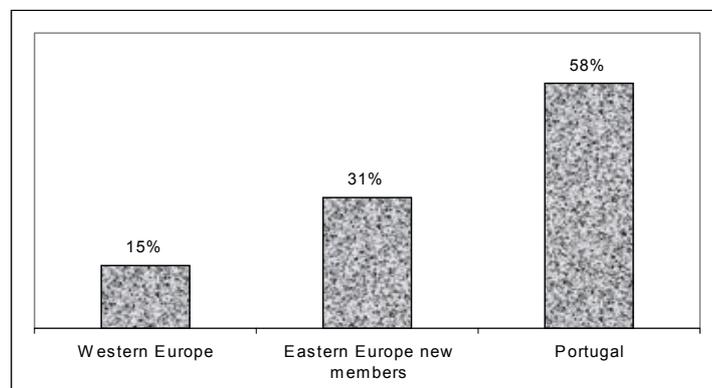


Fig.1 - Percentage of mining and quarrying wastes versus total waste

3. Panasqueira Tungsten Mine

Panasqueira is an underground mine utilising room and pillar mining methods situated in central Portugal on the southern edge of the Sierra da Estrela mountain range, a natural park, near the Sierra do Açor, a protected landscape, and also near the Zezere river. Tungsten and tin have been mined in the Panasqueira area since the 1890s. In the mid 1980s, Panasqueira's had over 1,000 employees in its underground mining and plant operations that processed 600 000 tonnes of ore per annum to produce in excess of 2,000 tonnes of tungsten oxide (WO_3) just about of 0,3 % of excavated rock.

During the mining process two types of mine waste are generated, coarse aggregates derived from rock blastings which is in fact a by-product used in minor quantities by the road pavement industry using hot bituminous mixtures since 1970s, (research in the field of cold open mixtures with those aggregates had been carried out recently [16]) and waste mud conveyed by pipelines into lagoons amounting for several million tonnes and still generating almost 100 tonnes per day. Fig.2 shows the environmental impact of Panasqueira mine wastes.



Fig. 2 - Panasqueira tungsten mine. Coarse aggregate deposits and waste mud lagoons.

4 - Experimental Research

4.1 - Mineralogical and chemical composition

Mineralogical composition of mine waste mud deduced from XRD study using a Rigaku Geigerflex diffractometer, was muscovite and quartz which were identified by their characteristic patterns as follows: muscovite (card 46 - 1409) and quartz (card 46 - 1045).

Table 2- Chemical composition (%)

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

Chemical composition of waste mud was obtained by atomic absorption using a spectrophotometer. The figures in table 2, clearly show that mine waste mud consists essentially of silica and alumina, contaminated with arsenic and sulfur and with a high content of iron and potassium oxide which according to Xu et al. [17] is one of the factors having a significant correlation with compressive strength of geopolymers based minerals. The SiO₂/Al₂O₃ atomic ratio is 5,5 higher than the one suggested by Davidovits of about 2 for making cement and concrete however Teixeira-Pinto [18] using alkali-activated metakaolin based mixtures found that some mixtures with calcium hydroxide and an atomic ratio of SiO₂/Al₂O₃= 5,1 lead to higher compressive strength performances.

4.2 - Thermal treatment

The waste was thermally treated to achieve the dehydroxylated state. The calcination took place in a static calciner previously heated to calcination temperature using powder samples with a mass of 2,5 Kg placed in a container with a maximum of 5 cm high. Phase transformations on calcination were monitored by XRD of waste powder quenched to room temperature to avoid crystallization of amorphous muscovite. The recorded patterns (Fig.3) indicate that dehydroxylation did not result in a collapse of muscovite structure. Calcination results in a formation of an amorphous phase causing an increase general background (BG) in XRD patterns (Table 3) and dominantly taking place in the calcinations interval from 850 to 950° C with a thermal behaviour similar to other phyllosilicate clay minerals [19]. The main muscovite peak (2θ=8,8°) 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.

At that temperature structural dehydroxylation process is complete according to other authors [20,21]

Table 3 – Calcination effects on XRD diffraction of mud 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

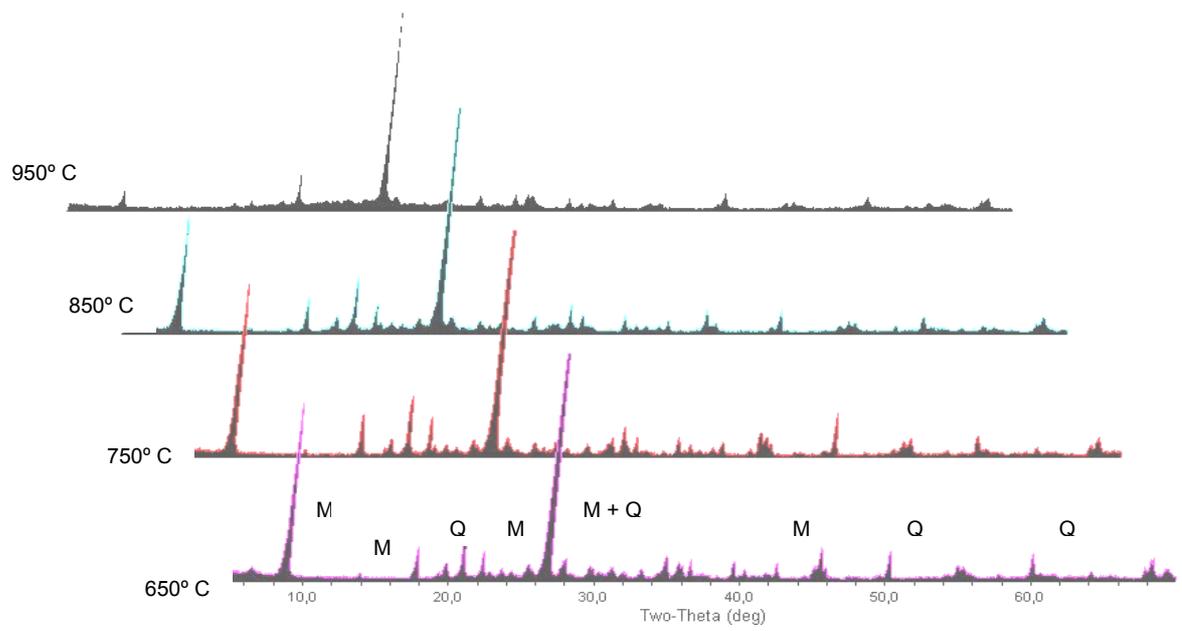


Fig. 3 - XRD patterns of mine waste treated at different temperatures (M-muscovite and Q- quartz)

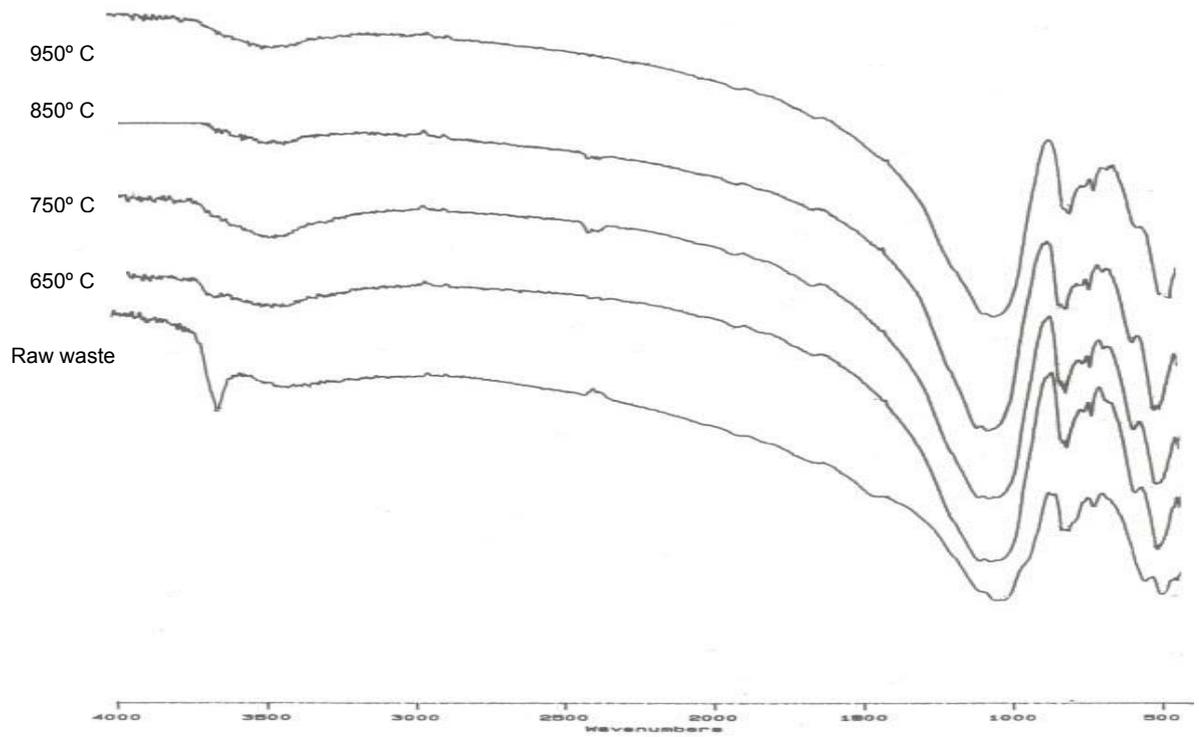


Fig. 4 -Infrared emission spectra of raw waste powder treated at different temperatures

Molecular changes during dehydroxylation were examined with infrared emission spectroscopy patterns using powdered KBr pellets and are shown in Fig.4.

The dehydroxylation process is confirmed by the diminishing absorption peaks at 3600-3700 (OH stretch) this is consistent with previous results of other researchers [22] however the peak does not disappear totally indicating only a partial transformation. The characteristic decrease in K-O bond strength typical of layer silicates in the stretching frequency range between 90-200 cm^{-1} was not been confirm because the spectrometer device could not show the wavenumber region below 400 cm^{-1} a far infrared wavenumber region only available to some infrared devices

4.3 Mechanical properties of alkali-activated waste mortar

Compressive strength of alkali-activated waste mortars was used to evaluate dehydroxylation degree, 50x50x50 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 ($\text{Na}_2\text{O}=8,6\%$, $\text{SiO}_2=27,8\%$, $\text{Al}_2\text{O}_3=0,4\%$ and water=63,2%) was used with a mass ratio of 1:2,5. This activator as been widely used by other researchers namely Hardjito et al. [23]. Distilled water was used to dissolve the sodium hydroxide flakes to avoid the effect of unknown contaminants in the mixing water. Waste and calcium hydroxide were mixed with a mass ratio of 5:1. According to Teixeira-Pinto the use of calcium hydroxide induce the geopolymerization reaction in a medium sodium hydroxide concentration and the lack of it can only be overcome with the use of high sodium hydroxide concentrations. Palomo [24] using calcium-hydroxide mixtures claims that when activation is carried out with 10M or higher concentrations, the main reaction product is still an aluminosilicate, with polimeric character similar to the one obtained without calcium hydroxide [24].

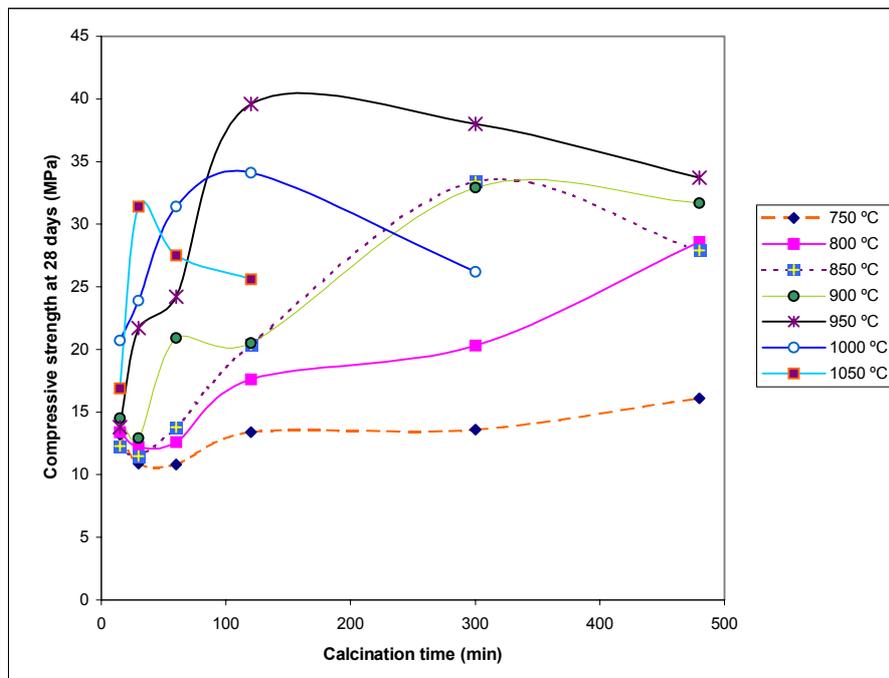


Fig. 5 - Compressive strength of alkali-activated waste mortars

Davidovits explains the importance of calcium hydroxide presence 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 [6].

The results of the compressive strength of mortars made with waste mud calcined during 30, 60, 120, 300 and 480 minutes and subject to the same grinding procedure are shown in Fig.5. Calcination temperature below 750° does not contribute to the compressive strength of alkali-activated waste mud based mortars which means has no effect whatsoever in the reactivity of the waste. Increasing calcination temperature to 800° C showed some reactivity although only after a long calcination time. Calcination at 850° C and 900° C lead to a very similar compressive strength after 5 hours of calcination but underperform against a calcination temperature at 950° C during 2 hours, which clearly shows a structural change in the calcined material. Calcination of waste powder at 950° C during 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 showed in table 3.

Furthermore increase 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. [21]. Results also indicate that there is an optimum time and calcination temperature related to energy efficiency. However those kind of considerations were valid only if dehydroxylation process in a static calciner were the best available technology which is not. Salvador studies about flash calcination led to the development of a flash calciner industrial 800 Kg/h production unit capable of reduce calcination time to a few seconds and with the additional advantage of no further grinding operations[25,26] .

4 - Economic considerations

The cost of geopolymeric based concrete is one of the major factors which still remains a severe disadvantage over Portland cement based concrete explaining why this new product is not yet a current alternative despite the fact of its “discovery” in 1978. Mainly due to differences in raw materials cost across the world there are not studies about that subject. It is of relevant importance to understand the cost of each raw material (aggregates, precursor, activator) on the cost of concrete, only the it is possible to investigate towards a cheaper geopolymeric based concrete.

Table 4 shows the composition and the compressive strength of four concrete mixtures, two geopolymeric based types (GA [19], and M9 [23]), and two Portland cement based types being one with 60% fly ash replacement (CV60[27]) and made with cement type 42,5 and the other with cement type 32,5 and without any additive.

Table 5 shows the cost of the four concrete mixtures expressed by cubic meter including the percentage cost of each raw material and in a strength ratio basis. Only the cost of materials were considered due to the fact that it represents the major part in concrete cost, assuming that concrete mixtures had the same workability.

It can be seen that geopolymeric concrete types are much more expensive than traditional Portland cement concrete by cubic meter. These results are not consistent with economic considerations made by Palomo about the cost of one cubic meter of alkaline activated fly ash concrete [26], maybe due to different cost of raw materials in Spain.

The cheapest geopolymeric concrete type (M9) cost per cubic meter is 74% above the expensive Portland cement based concrete type (CV60). The explanation for that relies on

the cost of alkaline solutions, 83% in GA concrete type and 71% in M9 concrete type, meaning that low cost alumino-silicate precursors are not an issue. Further geopolymeric concrete type M9 is 62% cheaper than GA type due mainly to less 56% in the amount of the activator and also to the use of a low concentration sodium hydroxide solution.

When comparing the cost to strength ratio traditional concrete are not so interesting, in that case the cheapest geopolymeric concrete type is just 8% above the cheapest Portland cement based concrete type and Portland cement based concrete type (PPC) is 28% above the cheapest geopolymeric concrete type.

However it must be noted that market demands for concrete strength are in general very low, Portuguese strength average is 35% in the range [15 – 25MPa], 55% in the range [25 – 35MPa], and only 10% above 35MPa [27], and European average is even worst respectively 51%, 33% and 9% indicating that concrete market demand is mostly for low to medium strength class concrete.

Fig.6 and Fig.7 show concrete cost evolution with future Portland cement cost increase due to the European Emissions Trading Scheme (ETS) [30]. When comparing costs by cubic meter only above a cement cost increase of more than 100%, Portland cement based concrete cost will be above the cheapest geopolymeric concrete type. However if comparisons were established in a strength ratio basis, a 50% cost increase in Portland cement means that geopolymeric based concrete types will become an economic alternative to traditional concrete.

Geopolymeric based concrete using Panasqueira mine waste mud will cost perform very similar or even under M9 geopolymeric concrete type cost which underlines is future competitiveness over traditional Portland cement based concrete

5. Conclusions

With a high level ratio of CO₂ emissions above international commitments under Quioto Protocol, in a great part due to cement industry, lacking enough amounts of traditional cementitious by-products such as fly ash and blast furnace slag, possessing huge amounts of quarrying and mining wastes and needing to preserve its large protected land and its natural biodiversity, Portugal is the right field to the use of environmental friendly binders, using mining and quarrying wastes.

Preliminary research about Panasqueira waste mud mineralogical and chemical composition as well as data from thermal treatment shows a relevant potential as a geopolymeric source precursor.

At the present moment concrete based on Portland cement is economically very competitive, however future increase cost due to (ETS) will reduce that advantage. Some scenarios related to CO₂ cost increase will not overpasses the range [23 – 38 €/ton CO₂] [31,32], meaning that CO₂ "tax" alone is not enough to reduce Portland cement competitiveness. However those analysis often forget that CO₂ reduction targets under Kyoto Protocol are just the first step into a CO₂ "free" economy. So major reduction targets can soon be expected. Furthermore, future introduction of taxes on quarrying and mining wastes disposal and on primary construction raw materials will boost economic feasibility of geopolymeric based binders, helping to signal structural economic changes towards a more sustainable development

Table 4 - Concrete type composition and compressive strength

Concrete type	Composition (Kg/m ³)							Compressive strength at 28 days (MPa)
	Aggregates	Sand	Portland cement	Fly ash	Metakaolin	Sodium silicate solution	Sodium hydroxide solution	
Geopolymeric Metakaolin based GA [18]	930	792	-	-	300	200	100 (15M)	57
Geopolymeric fly ash based M9 [23]	1756	-	-	476	-	120	48 (8M)	60
Plain Portland cement based C20/25	880	812	370 Type 32,5	-	-	-	-	25
Fly ash cement based CV 60 [27]	850	774	200 Type 42,5	300	-	-	-	35

Table 5 - Cost of concrete mixtures (only materials)

Concrete type	Total materials cost (€ /m ³) and percentage of total cost(%)							Total cost	
	Aggregates (7,7 € / ton)	Sand (7,1 € / ton)	Portland cement Type 32,5 (85€ / ton) Type 42,5 (139€ / ton)	Fly ash (20€ / ton)	Metakaolin (30€ / ton)	Sodium silicate solution (420 € / ton)	Sodium hydroxide flakes (714 € / ton)	(€ / m ³)	(€ / MPa)
GA	7 (5%)	6 (5%)	-	-	9 (7%)	84 (63%)	27 (20%)	133	2,3
M9	14 (17%)	-	-	10 (12%)	-	50 (61%)	8 (10%)	82	1,4
PPC	7 (16%)	6 (14%)	31 (70%)	-	-	-	-	44	1,8
CV 60	7 (15%)	6 (13%)	28 (59%)	6 (13%)	-	-	-	47	1,3

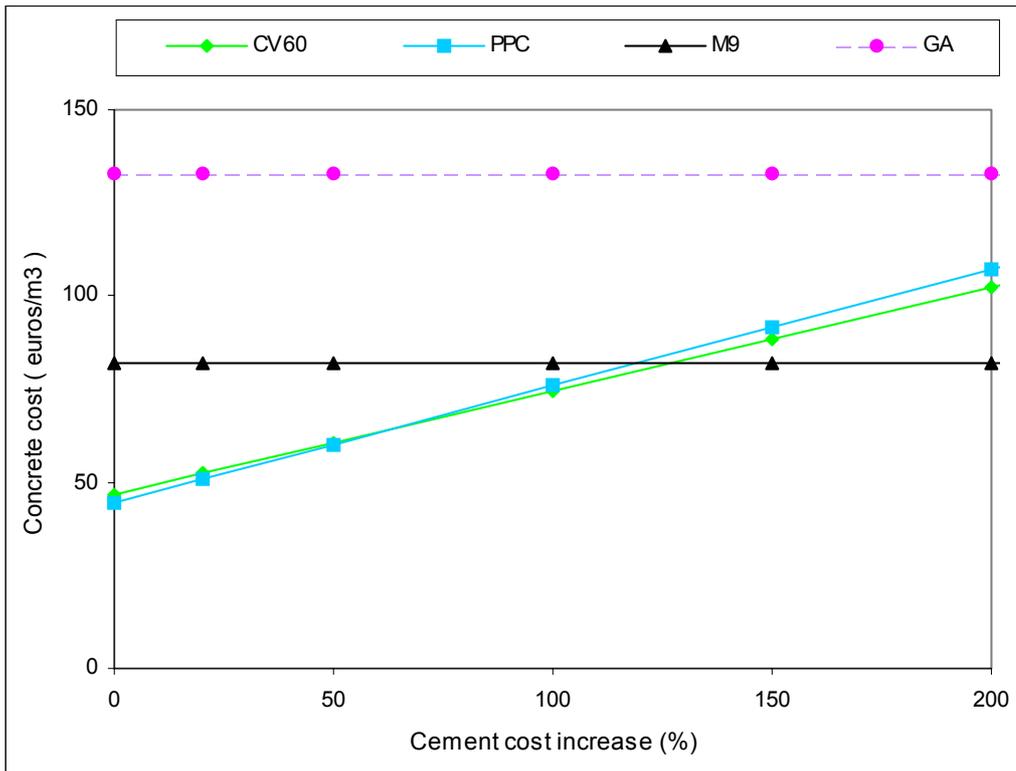


Fig. 6 - Concrete cost versus cement cost increase

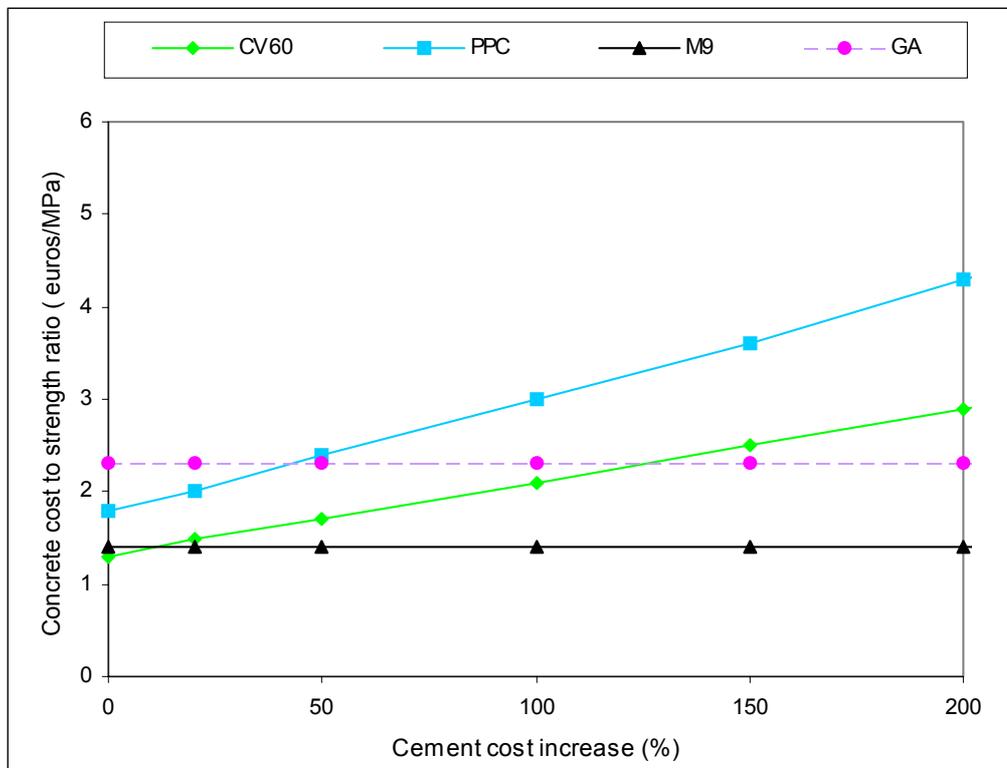


Fig. 7 - Concrete cost strength ratio versus cement cost increase

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