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ČESKÁ ROZVOJOVÁ AGENTURA

2007 – MEZINÁRODNÍ KONFERENCE Alkalicky aktivované materiály – výzkum, výroba a využití

2007 - INTERNATIONAL CONFERENCE Alkali Activated Materials – Research, Production and Utilization

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TUNGSTEN MINE WASTE GEOPOLYMERIC BINDER VERSUS ORDINARY PORTLAND CEMENT BASED CONCRETE. ABRASION AND ACID RESISTANCE

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Abstract. This paper reports results of a research project related to the development of geopolymeric binder using mineral waste mud from the Portuguese tungsten mine Panasqueira. Abrasion and acid resistance of two ordinary Portland cement (OPC) strength class concrete mixtures (C20/25 and C30/37) and several tungsten mine waste mud (TMWM) geopolymeric binder mixtures was evaluated. Acid resistance was performed by submitting samples to solutions of sulphuric acid, nitric acid and chloridric acid, results of weight loss are reported. Abrasion resistance was assessed by the mass loss of cubic specimens when submitted to 1000 rotations with the Los Angeles apparatus test machine. This study indicates that TMWM geopolymeric binders possess higher acid and abrasion resistance than OPC based concrete mixtures.

Keywords. *Geopolymeric binder, tungsten mine waste mud, abrasion, acid, resistance*

1 Introduction

Studies of alkali-activated cements have a long history in the former Soviet Union Scandinavia, and Eastern Europe [1]. 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" [2]. The polymerisation process involves a chemical reaction under higly alkaline conditions on Al-Si minerals yelding polymeric Si-O-Al-O bonds with empirical formula $Mn\,[-(Si-O_2)z - Al - O]n.\ wH_2O$, where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium [3]. 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

CO_2 emissions [4]. The 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.

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. 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 amounting for several million tonnes and still being added almost 100 tonnes per day. Previous studies concerning the alkali-activation of TMWM together with a small percentage of calcium hydroxide suggests that a geopolymeric binder with extremely high early age strength can be produced [5]-[7].

Acid and abrasion resistance are properties required for structural materials for use in some aggressive environments. Traditional fly ash and metakaolin geopolymeric based binders are known to possess higher acid resistance than (OPC) concrete due to his low calcium compounds, as for the abrasion resistance there’s very little research publish about the performance of geopolymeric binders. Therefore the objective of the present work is to investigate if TMWM geopolymeric binders have superior acid and abrasion resistance than current OPC concrete binders.

2 Experimental program

2.1 Materials

2.1.1 TMWM geopolymeric binder

The mine waste mud consists mainly of muscovite and quartz. TMWM used in this study was subject to a thermal treatment at 950º C during 2 hours, mineralogical composition and thermal conditions were described elsewhere [8]. For those thermal conditions XRD patterns indicated that dehydroxylation did not result in a complete collapse of muscovite structure. 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 calcinations interval from 850 to 950ºC. The main muscovite peak ($2\theta=8,8^{\circ}$) persisted even after

Table 1. Chemical composition and specific surface.

Constituents (%)	Calcined 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

the sample had been heated at 950ºC although it decreased considerably. Peak area measurements revealed that about 12% of muscovite survived calcination at 950ºC. Molecular changes during dehydroxylation were also examined with infrared emission spectra (FTIR), confirming decrease in the absorption peaks at 3600-3700 (OH stretch).

The chemical composition and specific surface of the calcined mine waste mud is shown in Table 1, the figures 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. The SiO_2/Al_2O_3 atomic ratio is 5,5 higher than the one suggested by Davidovits of about 2 for making cement and concrete however,the final SiO_2/Al_2O_3 atomic ratio in the hardened binder depends mainly on the reactivity of Al-Si because not all the silica and alumina are reactive so one can not expect the same Si/Al ratio in the final hydration product as the one present in the original precursor material. Indeed most of the Al-Si materials cannot even supply sufficient Si in alkaline solution to start geopolymerization, this explains why they need extra silica provided in solution by waterglass, which influences the Si/Al ratio of the hardened binder. Mine waste Blaine fineness is low but is in the range of the most used slag based alkaline binders.

Table 3. Mix proportions and main properties of the OPC concrete binders.

Components	C20/25	C30/37
Cement II 32,5 (kg/m^3)	394	504
Fine river sand (kg/m^3)	632	417
Coarse aggregate (kg/m^3)	1032 (limestone)	1154 (granite)
W/C ratio	0,55	0,43
fcB$_{28d}$[a] (MPa)	25,6	37,8

[a] Average value of three specimens (150×150×150mm^3)

2.1.2 OPC concrete

Using the Faury concrete mix design method [9], a C20/25 and a C30/37 strength class OPC concrete mixtures were designed. The concrete mixes and their main properties are described in table 3. Concrete specimens were cast into cubic molds with 150mm high in order to be test in compression after 28 days curing, to confirm the concrete strength class. The concrete specimens for abrasion and acid resistance tests were cured immersed in water during 3 months. This curing period provides an almost as complete concrete hydration as old concretes in field practice and has been used by other authors [10]. After that time they were cut with an electric masonry saw to obtain 50×50×50 mm^3 cubic specimens.

2.2 TMWM mix proportioning and specimen preparation

In this investigation the TMWM mortars was a mixture of aggregates, waste mud, calcium hydroxide, alkaline silicate solution and water. The mass ratio of mine waste mud: activator was 1:1. Calcium hydroxide was used with a percentage substitution of 10%, because it was found that percentage lead 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. Previous investigations showed that this ratio lead to the highest compressive strength results in alkali-activated mine waste mud mortars [6]. 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 added to the activator. To produce a workable mix extra water has been added. 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%. Compressive strength data was obtained using 50×50×50 mm^3 cubic specimens. The fresh mortar were cast and allowed to set at room temperature for 24h before being removed from the moulds and kept at room temperature until tested in compression. 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% superplasticiser by mass of binder lime and mine waste mud were named respectively SC/SP and LS/SP.

2.3 Test procedures

2.3.1 Abrasion resistance

The abrasion resistance was evaluated using the Los Angeles abrasion apparatus, which consists of a metal cylinder, where eight 50×50×50 mm^3 cubic specimens have been placed together with eight steel spheres. The cylinder is then submitted to 1000 full rotations, being that after every 100 full rotations the specimens are weighed to detect the weight change.

2.3.2 Acid resistance

The resistance to acid attack was tested by immersion of the TMWM and OPC concrete 50×50×50 mm^3 specimens in 5% of sulphuric, chloridric and nitric acid solutions during 28 days. To keep a constat pH acid solutions were replace after 14 days. After 28 days the specimens were oven-dry to achieve constant weight and detachable particles were removed. The acid resistance was assessed by the differences in weight of dry specimens before and after acid attack.

3 Results and discussion

3.1 Abrasion resistance

The photographs of TMWM and OPC binder specimens submitted to abrasion test are shown in Fig. 1.

TMWM binder specimens show a low level of weight loss while in OPC specimens a severe weight loss was observed. For TMWM binders the higher abrasion resistance was achieved in paste specimens (Fig. 2).

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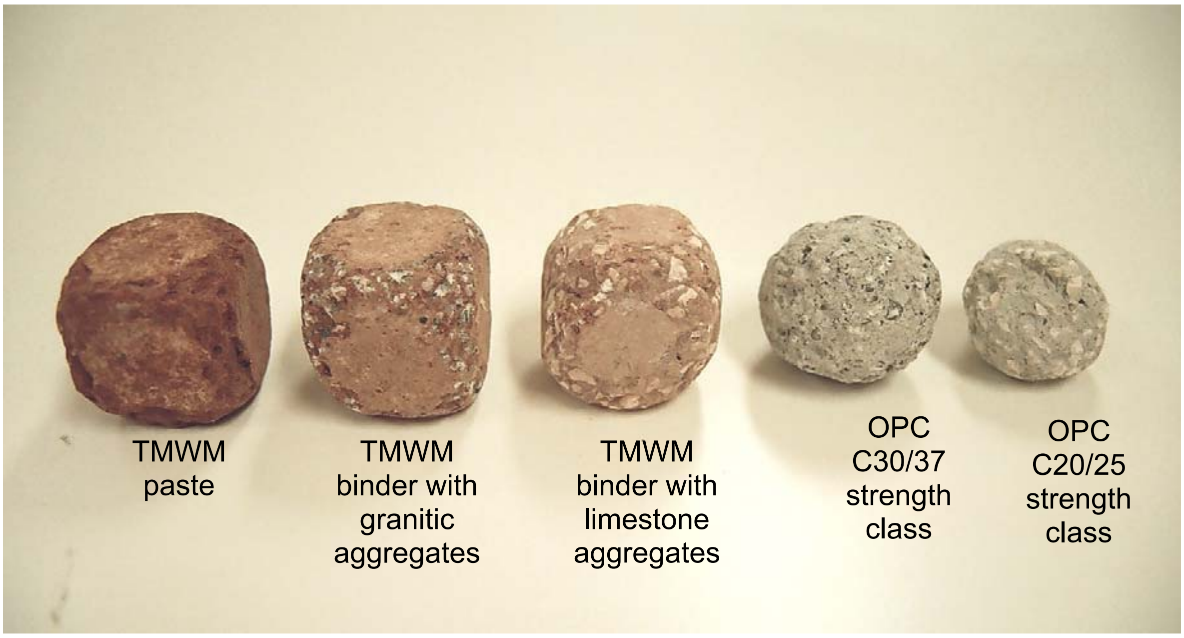

Fig. 1. TMWM and OPC binder specimens after 1000 full rotations in the Los Angeles apparatus.

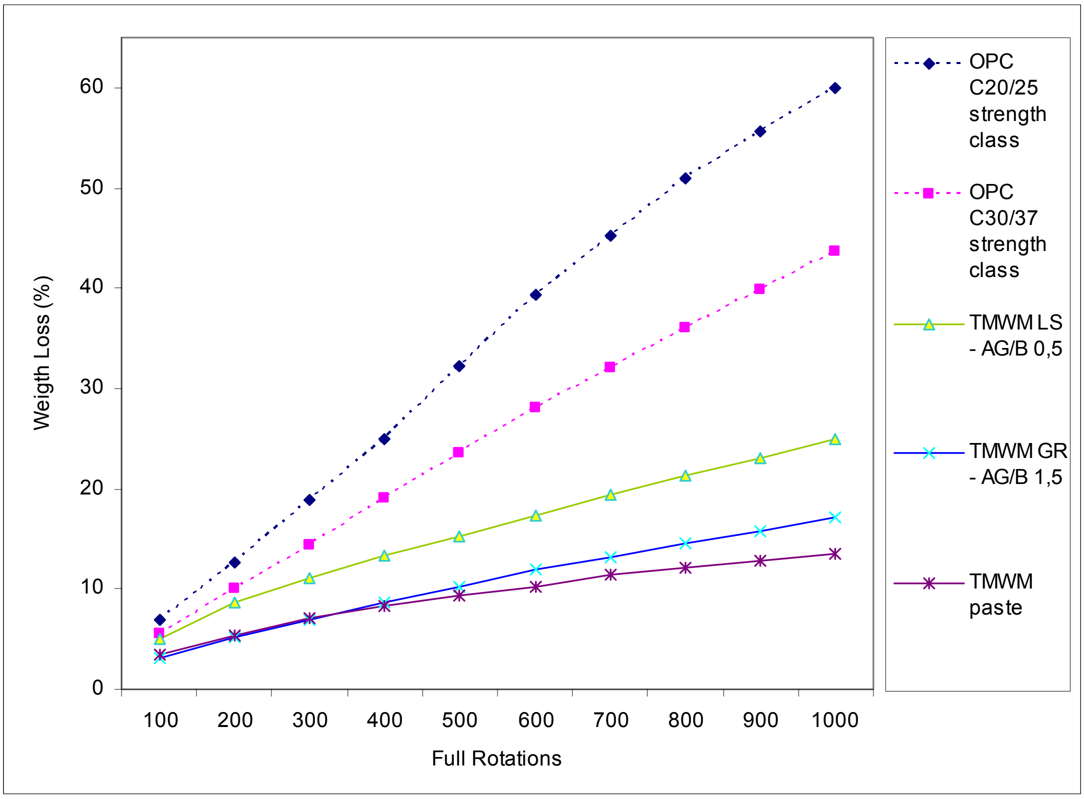

Fig. 2. Abrasion resistance with the Los Angeles test for OPC and TMWM binders using 50mm cubic specimens.

This result is related to the fact that TMWM 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. Nevertheless, other authors reported that for OPC binders, abrasion resistance is influenced by aggregate resistance [11]. Fig. 3 shows compressive strength and abrasion weight loss results for TMWM mortars and OPC concrete specimens.

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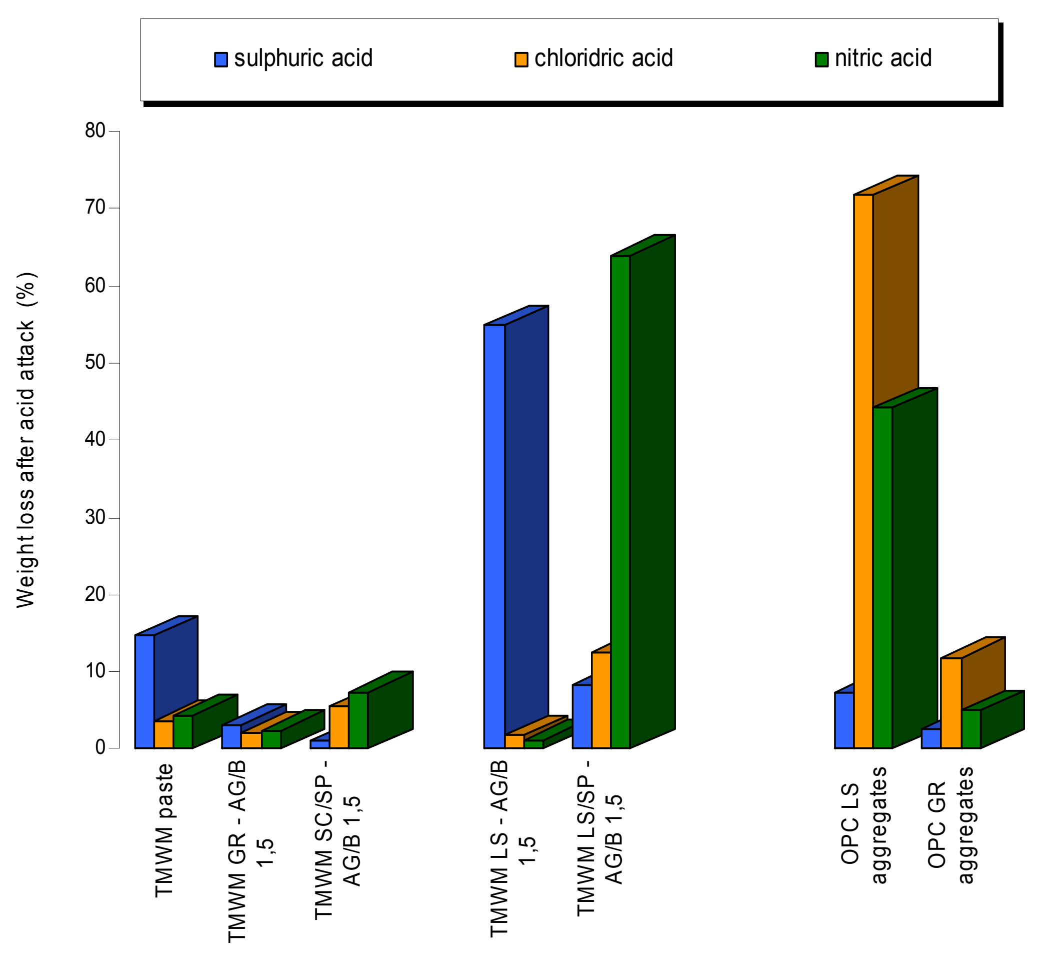

Fig. 3. Weight loss after acid attack.

3.2 Acid resistance

Acid resistance of OPC and TMWM binders as weight loss are shown in Fig. 3. Results are dependent not only from the type of acid but also from the type of aggregate. For TMWM binders, the mixtures GR e SC/SP have low weight loss results for the exposure to the several acids. As for the mixtures LS e LS/SP their weight loss behaviour is influenced by the type of acid. Specimens immersed in chloridric acid have low weight loss performance independent of aggregate type, as for specimens submitted to nitric and sulphuric acid attack are influenced by the presence of limestone aggregates.

With the exception of the mixture LS, all the other TMWM specimens immersed in sulphuric acid had low weight loss. As for the OPC specimens, their weight loss is due to the reaction between calcium hydroxide present at the surface of the specimens and the acid. In TMWM geopolymeric binders weight loss is due to the detachement of little particles leading to an increase in porosity and allowing the acid solution to enter inside the specimen and removing calcium compounds. For the mixture SC/SP, the weight loss is even lower and maybe due to the fact that the acid solution is unable to go inside the specimen because of their low porosity. This type of acid reacts with calcium compounds leading to the formation of calcium chloride which has a extremely low solubility (46,1%) [12], explaining the behaviour of the exposed limestone aggregates in the sawn OPC concrete specimens, and also the highest weight loss in OPC concrete specimens with granitic aggregates. For the remaining TMWM specimens it can be said that the low degree of acid attack is maybe related to unreacted sodium taking into account that the highest weight loss occurs to the mixture LS/SP. A similar behaviour takes place for the attack with nitric acid, since that acid reacts with calcium compounds forming calcium nitrate which has a solubility (56%) even higher than the one of calcium chloride, explaining the destruction of limestone aggregates in OPC specimens. For TMWM geopolymeric specimens the weigth loss is very low with the exception of the mixture LS/VS where a voluminous reaction had take place, being the mixture with the higher unreacted sodium in the matrix, the leaching of free sodium had certainly contribute to increase the porosity allowing the ingress of acid solution inside the specimen where it reacted with limestone aggregates.

4 Conclusions

The following conclusions can be drawn from this study:

Abrasion resistance for TMWM geopolymeric binders is higher than the one presented by current OPC binders. TMWM geopolymeric binders without limestone aggregates show good acid resistance higher than the one presented by OPC concrete. One believes that performance is due to the fact that TMWM binders has very low water absorption (less than 4%) and also to their low content in calcium generating less soluble compounds.

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