Use of tungsten mine sludge waste in the mitigation of internal expansive reaction

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T 61

ABSTRACT

The degradation of concrete structures by the internal expansive reactions (IER), which include the alkali-silica reaction (ASR) and the internal sulphate reaction (ISR) related with the delayed ettringite formation (DEF), are two of the major problems that affect nowadays several concrete structures in the world. Therefore, it is essential to find preventive methods to inhibit the appearance of these reactions in new concrete structures.

This research work aims to investigate the effectiveness of tungsten sludge from a Portuguese mine in the inhibition of IER and is part of an extensive study to elucidate the role that the mineral additions have in the mechanism of inhibition of IER in concrete.

For this purpose several concrete mixes were produced by using tungsten sludge as a partial cement replacement.

The results of accelerated expansion tests and microestructural evolution of the concretes shows that the incorporation of 30% of tungsten sludge as cement replacement appears to be effective in the mitigation of ASR and ISR.

KEYWORDS

Alkali-silica reaction; internal sulphate reaction; mineral additions; mitigation; tungsten mine sludge

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INTRODUCTION

The degradation of concrete structures by the alkali-silica reaction (ASR) and the internal sulphate reaction (ISR) are a problem that affects an increasing number of concrete structures around the world.
The alkali-silica reaction (ASR) is the most frequent form of the alkali-aggregate reaction (AAR). It happens between the reactive silica present in some aggregates and the hydroxyl (OH^-) and alkaline (Na^+, K^+) ions in the cement paste. In the presence of enough water or high humidity, an alkali-silica gel is formed, and it can swell and cause cracking of the concrete [Cyr *et al* [2009]].
The internal sulphate reaction (ISR) occurs due to the ettringite formation in a cementitious material after hardening is substantially complete and with only sulphate ions from inside the concrete constituents [Taylor *et al* [2001]; Pavoine *et al* [2006]]. This form of sulphate attack is mainly concerned in concretes that have experienced high curing temperatures, e.g. precast products made by elevated-temperatures or mass concretes in which the temperature has risen excessively due to the heat of hydration, in the presence of water.
The main issues in the cement industry are related to the environmental impact caused by the extraction of raw materials and the CO_2 emissions in the ordinary Portland cement (OPC) production.
Is well know that the use of by-products like fly ash, silica fume or blast-furnace slags, can be used in the concrete, as pozzolanic materials, avoiding the consumption of non-renewable resources and the environmental problems due to the disposal of these wastes. The use of these materials as a partial cement replacement by mass can prevent the ASR [Cyr, M. *et al* [*2009*]] and ISR reactions [Ramlochan, T. *et al* [2003]].
In Portugal, there is a large volume of mining wastes, which over the years have been dumped in landfills. These wastes can be reused and incorporated in the concrete industry as pozzolanic materials, bringing numerous benefits. They can contribute for the reduction of CO_2 emissions from the OPC production, and can improve the durability of concrete structures, namely in the prevention of IER.
The mineral addition used in this study was tungsten sludge from a Portuguese mine. This material was previously subject to a heat treatment (950 ºC during 2 h), in order to increase its pozzolanic activity [Torgal, F. [2006]].
This work presents the potential mitigation effect that mine sludge may have on the inhibition of ASR and ISR reactions in concrete.

EXPERIMENTAL METHODS

Materials

Tungsten mine sludge (TMS) of Portuguese origin was used. After being sieved, the TMS was subjected to a calcination process (2 h at 950ºC) in order to increase its pozzolanic reactivity [Torgal, F.[2006]]. The chemical compositions, obtained by X-ray fluorescence spectroscopy, of the materials employed in this study are presented in Table1.

Table 1 Chemical composition of materials used in this study

	TMS	**CEM I - A**	**CEM I - B**
Chemical Analysis (%)			
SiO_2	62,57	18,81	19,74
Al_2O_3	18,62	5,15	4,14
Fe_2O_3	9,99	3,18	2,69
CaO	0,63	63,70	63,54
MgO	2,15	1,50	2,42
MnO	0,13	--	--
SO_3	--	2,69	3,11
TiO_2	0,86	--	--
P_2O_5	0,24	--	--
K_2O	4,01	1,02	0,64
Na_2O	0,45	0,19	0,08
Na_2O_{eq}	3,09	0,86	0,50
LOI	0,34	3,18	3,13

Expansion tests

To evaluate the effect of the TMS in the ASR inhibition, mortar and concrete prisms were cast using a reactive siliceous aggregate with a CEM I - A type according to the requirements of ASTM C 1260, RILEM AAR-3 and AAR-4 test methods [ASTM C 1260[2001], [RILEM B-TC-106-3]. The mortar and concrete mixes studied are presented in Table 2.

In the ASTM C 1260 experiments, 3 mortars bars with 25 x25 x 285 mm were kept in a container with a 1N sodium hydroxide solution at 80º C during 28 days. In this test the efficiency of a certain pozzolanic material is positive in the ASR mitigation if the expansion at 14 days is less than 0.10%.

In RILEM AAR-3 and RILEM AAR-4 tests, concrete prisms (7,50 x 7,50 x 28,50 cm) were produced with a binder content of 440Kg/m^3, a water/binder of 0,45 and stored in a satured chamber for 24h.

After curing the concrete prisms in the RILEM AAR-3 test method were kept during 1 year in a chamber at 38ºC and HR>95%, while in the AAR-4 method the duration of the test is 20 weeks at 60ºC and HR>95%, and measurements are taken periodically.

Table 2. Mortar and concrete mixes used in the ASR expansion tests

Test method	Aggregate type	w/b ratio	% of addition	
			Control	TMS
ASTM C 1260	Alkali-reactive siliceous gravel	0,47	0	30
RILEM AAR-3		0,45		
RILEM AAR-4				

In the ISR study, concrete cylinders (11cm x 22cm) were produced with a CEM I - B type and a non reactive siliceous aggregate. In the mixes (Table 3) it was used a binder content of 440 kg/m^3, with a water/binder of 0,45 and a fixed alkalis content of 5,50 kg/m^3 concrete. These mixes were tested according to the accelerated MLPC No. 66 test method [Pavoine and Divet, [2007], being the expansion and mass measurements of the specimens taken periodically.

Table 3. Concrete mixes for the ISR expansion test

Test	Aggregate type	W/b ratio	% of addition	
			Control	TMS
MLPC nº66	Non reactive siliceous gravel	0,45	0	30

SEM/EDS examinations

Microestructural and X-ray microanalytical examination (SEM/EDS) of the mortars and concretes were performed on a scanning electron microscope JEOL JSM-4600 fitted with an OXFORD energy dispersive X-ray analyser. Polished specimens were prepared from mortar and concrete specimens at 28 and 90 days of storage after each expansion test method. The samples, after drying, were vacuum impregnated with a low viscosity epoxy resin, then polished and sputtered with a gold-palladium film.

RESULTS AND DISCUSSION

ASR expansion tests and SEM/EDS observations

Figure 1 shows the expansion of the mortars with and without TMS tested according the ASTM C 1260 test method.
The results shows that, the control mortar (REF) exceed the expansion limit criteria of 0,10% at 14 days of testing. At 28 days the REF mortar expanded by more than 0,50%. With 30% TMS no appreciable expansion (i.e., no grater than 0,07%) was obtained, which can be understood as effective in inhibition of ASR.

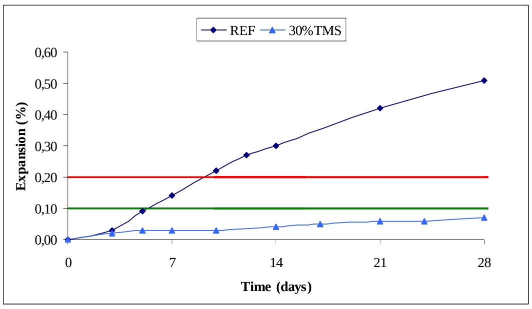

Figure 1 Expansion of mortars with cement (REF) and 30% TMS in ASTM C 1260 test method

To confirm the mortar behaviour of the 30% TMS, concrete mixes were tested according the RILEM AAR-3 and AAR-4 procedures [RILEM B TC-106-3]. According to the results obtained so far (Table 4) we can assume that the 30% TMS seems to be effective in the ASR mitigation.

Table 4 Results of the ASR expansion tests

Test Methods	Expansion (%)	
	Limit	Results
ASTM C 1260	Exp< 0,1 at 14 days	0,04 at 14 days
RILEM AAR-3	Exp> 0,04 at 1 year	0 at 28 days
RILEM AAR-4	Exp> 0,02 at 3 months	0 at 28 days

Figure 2 Shows the SEM/EDS observations on REF and 30% TMS mortars bars after 28 days of testing according ASTM C 1260.
The control mortar, REF, presents ASR gel in enough quantity, in aggregate/paste interfaces and filling the pores. These observations are in agreement with the results of expansion tests obtained.
The 30% TMS mortar also show ASR gel but only inside voids. It’s also visible that the TMS mortar is more microporous than the REF mortar, which can serve to accommodate the expansive products eventually formed.

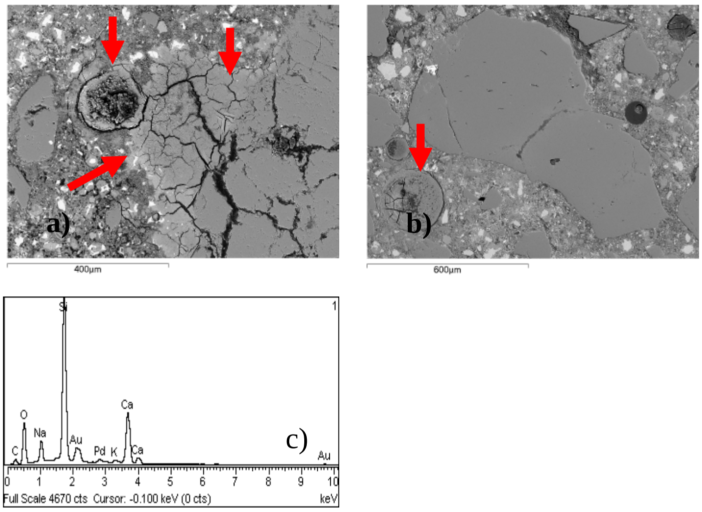

Figure 2 SEM/EDS images of ASR gel at 28 days in mortars tested according ASTM C 1260: a) Control; b) 30% TMS c) EDS spectrum of ASR gel

To evaluate the modification of the CSH gel by the incorporation of 30% TMS, EDS microanalysis were taken at CSH locations on the mortars tested after 28 days in ASTM C 1260 test method. For statistical accuracy, approximately 10-15 EDS microanalysis were done in each mortar.
It is known that the pozzolanic mineral additions in concrete can change the Ca/Si ratio in the CSH gel, decreasing it. Also, in the last few years the matter of alkali fixation in CSH gel has been thoroughly studied [Hong and Glasser [1999, 2002]];[Shehata and Thomas[2000,2002]]; [Ke-rui *et al* [2004], and appears to be related with the Ca/Si ratio, increasing with the decrease of this ratio.
It is also known that pozzolanic additions rich in aluminium, such as fly ash and metakaolin, may cause a greater variation of the chemical composition of the CSH gel, due to the incorporation of a higher quantity of aluminium [Santos Silva [2005]].
The evolution of the CSH atomic Ca/Si ratio (Figure 3) shows that the TMS mix presents compared to the REF mix, a decrease of this ratio. This may be due to ASR development, that predominates in the

REF mix, which is related with the increased solubility of silica aggregates in the reaction, while in the TMS mix the decrease is main related to the consumption of $Ca(OH)_2$ due to the pozzolanic reaction. The evolution of the Na_2Oeq content on the CSH (Figure 3) shows a higher value on TMS mix, which indicates a higher fixing capacity of the alkali ions by the CSH gels formed in this mix. This finding is in agreement with some papers, that showing this is one of the main inhibition mechanism of mineral admixtures in ASR [Hong and Glasser [1999, 2002]];[Shehata and Thomas[2000,2002]]; [Ke-rui *et al* [2004].

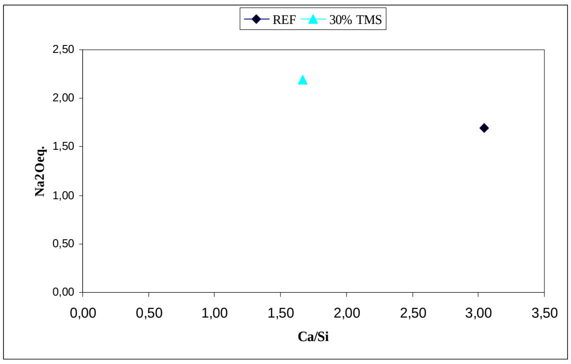

Figure 3 Existing Na_2Oeq vs. Ca/Si in the paste at mortar composition

Figure 4 shows the obtained correlation between de expansion value at 28 days and the CSH Ca/Si ratio on ASTM C 1260 mortar test. This results confirms the good inhibition characteristics of 30% TMS on ASR.

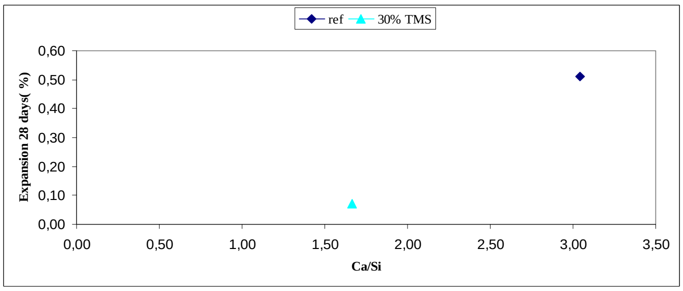

Figure 4 Expansion at 28 days vs. Ca/Si ratio of the CSH in the ASTM C 1260 test method.

ISR expansion tests and SEM/EDS observations

The ISR expansion tests are still on going, but so far no expansion was verified (Table 4). This behaviour may be due to the pozzolanic effect of the TMS, accomplished by a reduction of the alkalinity in the pore solution, as happens with other mineral additions with known positive effects on ISR mitigation [Ramlochan, T., *et al* [2004]].

Table 5 Results of the **MLPC No. 66 test method**

Expansion (%)	
MLPC nº66 limit at 1 year	Result at 84 days
0,04	0,00

The SEM/EDS observations (Figure 5) didn't show ettringite formation on the 30% TMS, but rather calcium monosulfoaluminate. This finding could be due to a decrease in sulphate paste content as a result of its caching by the CSH or also to an increase in reactive Al_2O_3 due to the addition replacement used.

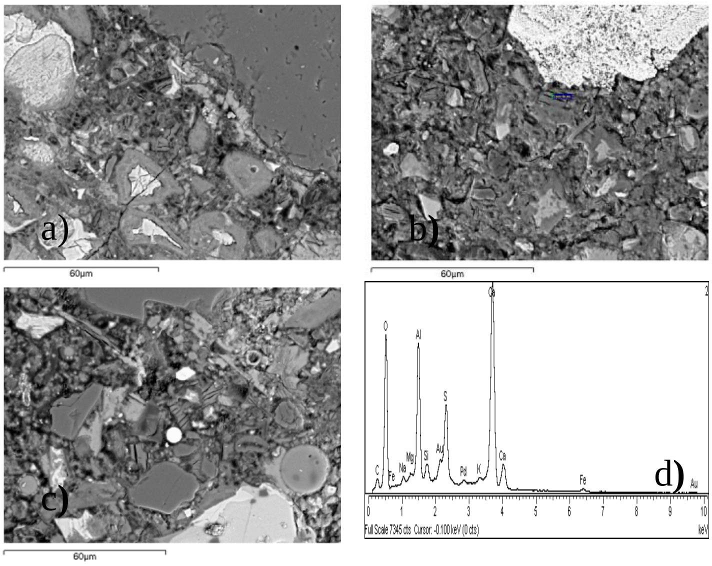

Figure 5 SEM/EDS images at 28 and 90 days of the concrete mixes tested on **MLPC No. 66 test method**: a) REF – 28d; b) 30% TMS – 28d; c) 30% TMS-90 d; d) Calcium monosulfoaluminate EDS spectra

CONCLUSION

The tungsten sludge from a Portuguese mine seems to be effective as an addition in concrete in order to mitigate the ASR and ISR reactions.

It appears that 30% (by mass) of cement replacement with sludge may be efficient in the mitigation of such reactions.

The inhibition mechanism of the sludge seems to be related to their ability to reduce the alkalinity of the paste, as a result of the consumption of calcium hydroxide and alkali ions.

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