# Mitigation of Internal Expansive Reaction: the role of Tungsten Mine Sludge

S. Sousa[1, a], A. Santos Silva[2,b], A. Velosa[3,c], A. Gameiro[2,d], F. Rocha[4,e]

[1]Department of Geosciences, University of Aveiro, Aveiro, Portugal

[2]Materials Department, National Laboratory of Civil Engineering, Lisboa, Portugal

[3]Department of Civil Engineering, Geobiotec, University of Aveiro, Portugal

[4]Department of Geosciences, University of Aveiro, Aveiro, Portugal

[a]sofiasousa@ua.pt, [b]ssilva@lnec.pt, [c]avelosa@civil.ua.pt, [d]agameiro@lnec.pt, [e]Tavares.rocha@ua.pt

**Keywords:** alkali-silica reaction, delayed ettringite formation, mitigation, tungsten mine sludge

**Abstract.** The concrete degradation caused by internal expansive reaction (IER) is a problem that affects many structures in the world. These reactions, which include the alkali-silica reaction (ASR) and the internal sulphatic reaction (ISR) related with delayed ettringite formation, are very dangerous, due the expansive behavior of products formed, that cause the cracking of concrete. So it is urgent to find preventive methods to avoid or mitigate the onset of these reactions in new structures. This work aims to show the applicability of sludge from a tungsten mine in the mitigation of the IER. To evaluate the effect of sludge in the mitigation of ASR and ISR, mortar and concrete mixes were produced with 30% (%in mass) of cement replacement. The results obtained so far allow stating that tungsten mine sludge as Portland cement replacement could be effective in the ASR and ISR mitigation.

## Introduction

Concrete performance and durability is disturbed by internal damages that may have been caused by the alkali-aggregate reaction or delayed ettringite formation (DEF). The most common alkali-aggregate reaction is the alkali-silica reaction (ASR). ASR occurs when certain types of silica minerals present in aggregates reacts with the alkali and hydroxyl ions in cement paste. The reaction forms an alkali-silica gel that in presence of water swells and expands causing the cracking of concrete [1, 2]. The internal sulfatic reaction due to DEF occurs in concretes that have experimented heat curing (temperature >65ºC) and exposed to frequent humidity [3, 4]. DEF is considered an internal type of sulfate attack, since the sulphates come from the concrete constituents.

To prevent the risks of ASR and ISR pozzolanic wastes or cementitious by-products are normally used as additions or in cement replacement in mortars and concretes [5, 6].

In Portugal, there exits large quantities of mining wastes, namely, tungsten mine sludge (TMS) that can be reused in the cement industry as a pozzolanic material. The reuse of this material contributes to a decrease in the $CO_2$ emissions from Portland cement production, contributing to minimize the environmental problems due its disposal and reduce the use of non-renewable resources.

This works aims to present the applicability of TMS in the prevention or mitigation of the ASR and the ISR reactions in concrete.

## Experimental

### Materials and experimental procedure

TMS was subject to calcination (950ºC at 2h) in order to enhance its pozzolanic activity [7], and afterwards crushed in a ball mill and then sieved to pass 75µm. TMS was used as a partial cement replacement. The chemical composition of the employed cements and the TMS was obtained by fluorescence X-ray spectroscopy, being presented in table 1.

**Table 1.** Chemical composition of the potland cements and the TMS used in this study

| Chemical analysis (weight %) | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | MnO | $SO_3$ | $TiO_2$ | $P_2O_5$ | $K_2O$ | $Na_2O$ | $Na_2O_{eq}$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TMS | 62,57 | 18,62 | 9,99 | 0,63 | 2,15 | 0,13 | --- | 0,86 | 0,24 | 4,01 | 0,45 | 3,09 | 0,34 |
| CEM I-A | 18,81 | 5,15 | 3,18 | 63,7 | 1,5 | --- | 2,69 | --- | --- | 1,02 | 0,19 | 0,86 | 3,18 |
| CEM I-B | 19,74 | 4,14 | 2,69 | 63,54 | 2,42 | --- | 3,11 | --- | --- | 0,64 | 0,08 | 0,5 | 3,13 |

Mortar and concrete prism tests were used to evaluate the effectiveness of TMS in ASR and DEF expansion. Mortar and concrete mixes (Table 2) were performed according to ASTM C 1260, RILEM AAR-3, RILEM AAR-4 and MLPC nº66 test-methods [8, 9].
The microstructure and the microanalytical analysis (SEM/EDS) of the mortar and concrete samples were studied at different testing ages on a scanning electron microscope JEOL JSM-4600 fitted with an OXFORD energy dispersive X-ray analyzer.

**Table 2.** Mortar and concrete mixes used

<table>
<tr><th colspan="2" rowspan="2">Test Methods</th><th rowspan="2">Aggregate type</th><th rowspan="2">w/b ratio</th><th colspan="2">Composition (% of addition)</th></tr>
<tr><th>REF</th><th>TMS</th></tr>
<tr><td rowspan="3">ASR</td><td>ASTM C1260</td><td rowspan="3">Reactive siliceous gravel</td><td>0,47</td><td rowspan="4">0</td><td rowspan="4">30</td></tr>
<tr><td>RILEM AAR-3</td><td rowspan="3">0,45</td></tr>
<tr><td>RILEM AAR-4</td></tr>
<tr><td>DEF</td><td>MLPC nº66</td><td>Non reactive siliceous gravel</td></tr>
</table>

## Results and discussion

### ASR expansion tests and SEM/EDS examinations

Figures 1 and 2 show the expansive behaviour of mortar and concrete mixes.
The expansion results obtained according ASTM C 1260 test (Fig. 1) show that 30% of TMS has no significant expansion regarding the REF expansive behavior. According the threshold limits of ASTM C 1260 it can be suggest that the 30% of TMS has a positive effect in ASR mitigation.

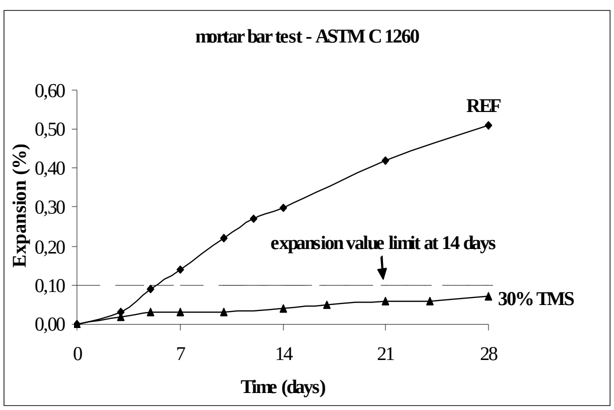



**Figure 1.** Expansion of mortars in the ultra-accelerated ASTM C 1260 test

Concrete ASR tests are still ongoing; the results available (Fig.2) seems confirm that 30% of TMS have a positive effect in ASR inhibition.

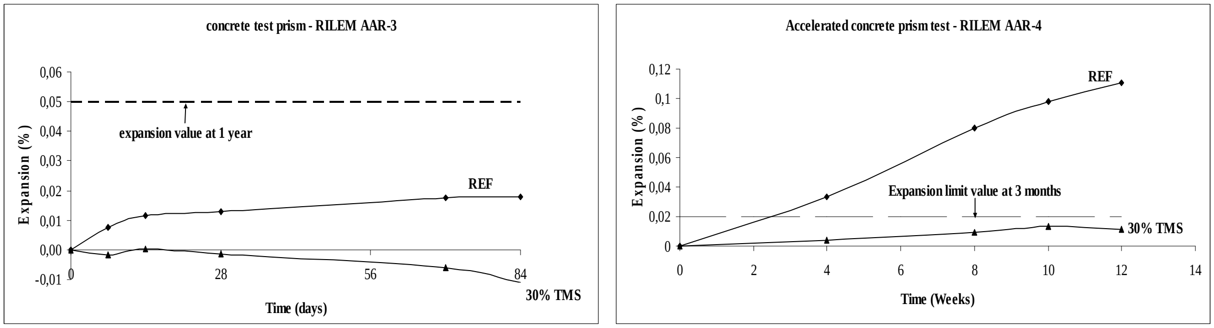
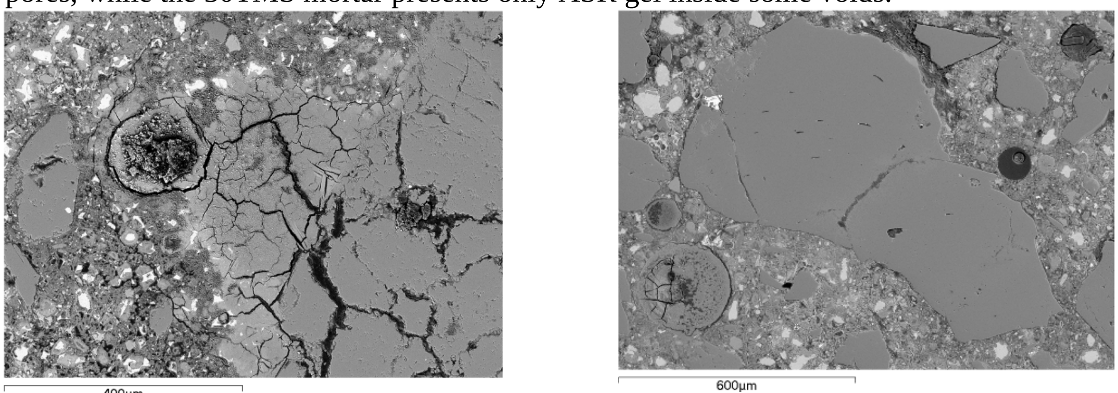



**Figure 2.** Expansion of concrete mixes in RILEM AAR-3 and RILEM AAR-4 tests

The SEM/EDS analysis of mortars after 28 days of testing, show (Fig. 3) a huge difference regarding ASR gel occurrence. REF mortar presents ASR gel in aggregate/paste interfaces and in the pores, while the 30TMS mortar presents only ASR gel inside some voids.




a) b)

**Figure 3.** SEM/EDS images of mortar mixes at 28 days of testing according to ASTM C 1260 showing the occurrence of ASR gel; a) REF; b)30TMS

One of the main ASR or DEF inhibition mechanisms due to the addition of pozzolanic materials is the reduction of the Ca/Si ratio in CSH gel that increases the alkali fixation [10], and also the aluminum when materials rich in this element are used [11].
In order to evaluate the effect in the CSH composition of 30% of TMS, several EDS microanalysis were performed on the mortar mixes after 28 days of testing according to ASTM C 1260.
The results of Ca/Si ratio in CSH gel (Fig.4a) show that the incorporation of 30% TMS effectively decreases this ratio. This may be explained due to the pozzolanic effect of TMS that reduces the calcium content of CSH gel. The evolution of the $Na_2O_{eq}$ on the CSH (Fig.4a) shows a higher value on the 30%TMS mix, which indicate a higher ability to fix the alkali ions in the CSH. This is in agreegment with some authors, that state that is the main mechanism of mineral admixtures in ASR inhibition [12,13,14,15]. Besides, a good correlation between expansion and Ca/Si ratio decrease is observed (Fig. 4b).

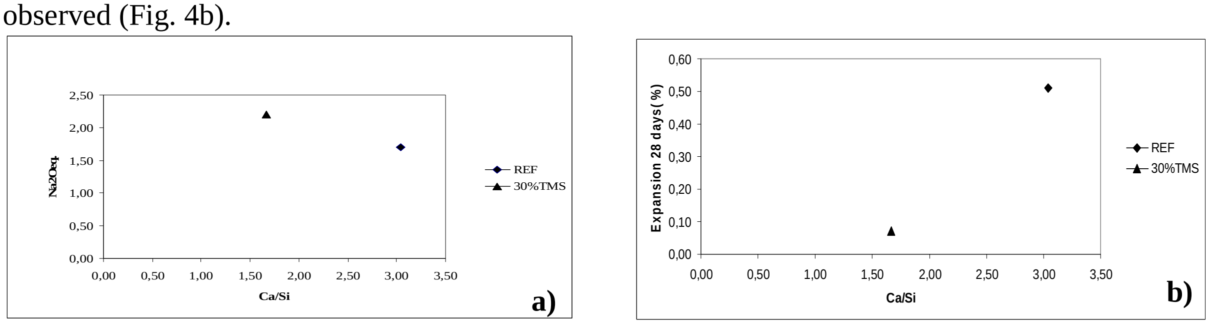



**Figure 4.** EDS analysis of the CSH gel in mortars at 28 days of testing in ASTM C 1260: a) $Na_2Oeq$ vs Ca/Si ratio; b) Expansion vs Ca/Si ratio.

**DEF expansion test and SEM/EDS examinations**

Figure 5 presents the expansive behaviour of concrete mixes tested according to MLPC nº66 method. The results obtained at 8 months show no significant expansion occurs in the 30TMS mix, which seems that 30% TMS has capacity to inhibit the DEF expansion. This effect could be due to the alkalinity and aluminum reduction in the pore solution due to pozzolanic reaction [16].

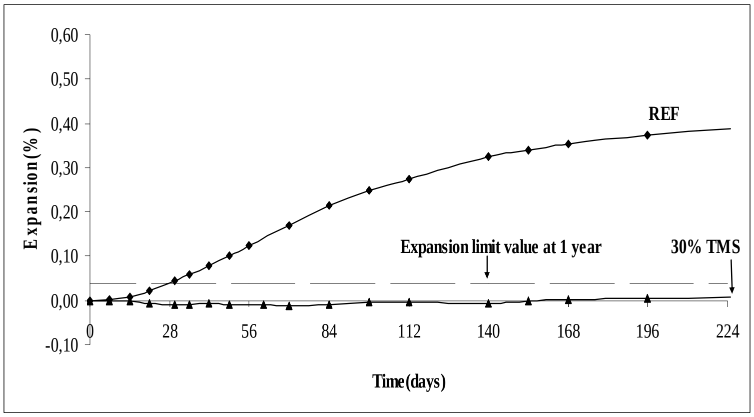



**Figure 5.** Expansion of concrete mortar in MLPC nº66 test

The SEM/EDS analysis of the 30TMS shows that the sulfates are mainly mobilized in the calcium monosulfoaluminate instead of in the ettringite formation (Fig. 6). These features can be explained due to the sulfates adsorption by the CSH gel and due the reactive $Al_2O_3$ present in the TMS [17].

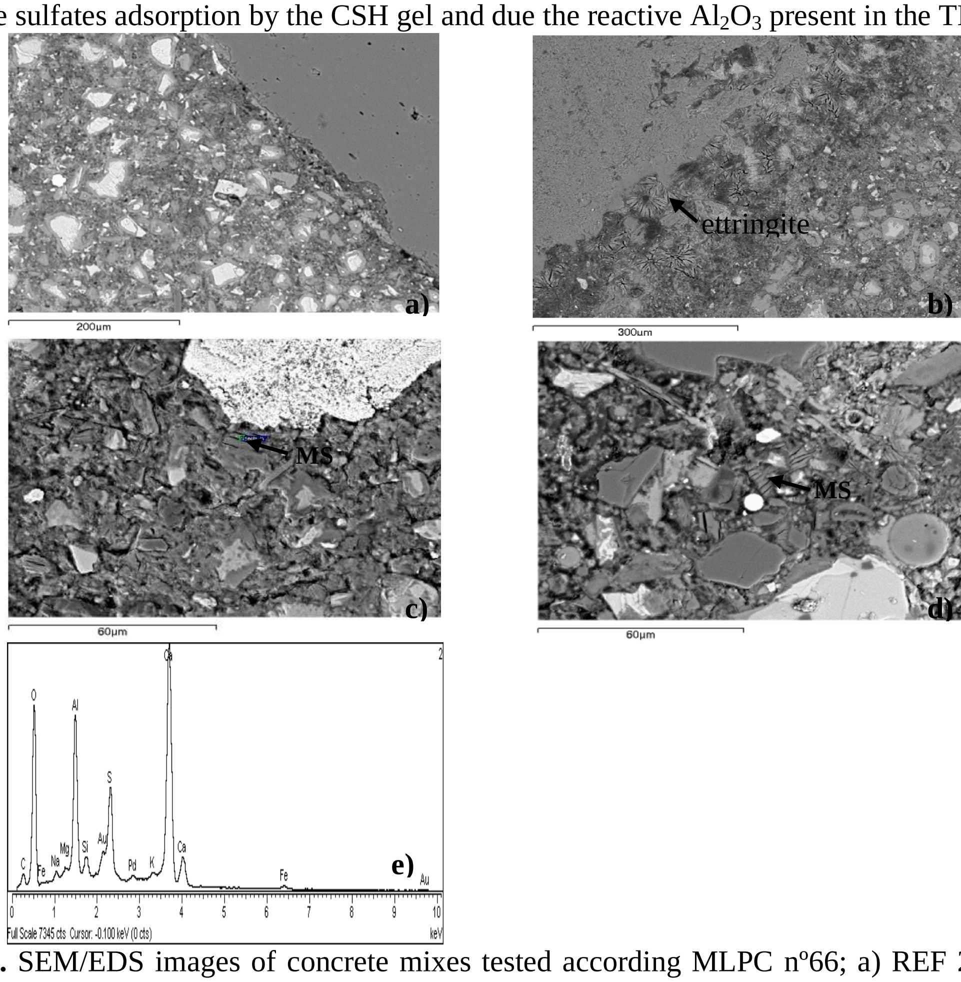



**Figure 6.** SEM/EDS images of concrete mixes tested according MLPC nº66; a) REF 28 days; b) REF 180 days; c) 30TMS 28 days; d) 30TMS 90 days; e) Eds spectra of calcium monosulfoaluminate (MS)

**Compressive strength**

Figure 6 presents the compressive strength evaluation of concretes tested according to MLPC nº 66 method. The compressive strength tests were performed according to the specification LNEC E 226 [17]. The results obtained show that the 30% TMS decreases the mechanical strength in comparison with the REF mix, however the 30TMS mix shows that there is a positive evolution in this property with time.

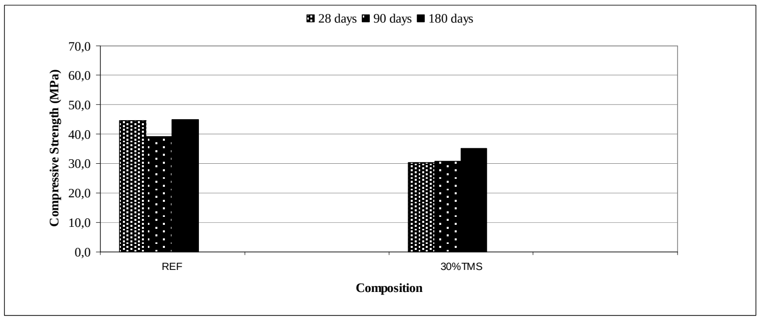



**Figure 7.** Compressive strength evolution of concretes tested according MLPC nº66

## Conclusions

The results obtained in this study shows that tungsten mine sludge can be used as partial cement replacement in preventing internal expansive reactions. The level of replacement employed (30% by mass) seems to be sufficient to suppress the ASR and DEF expansion. The inhibition mechanism of the tungsten mine sludge seems to be related with its pozzolanic activity that leads to the alkalinity reduction as well the alkali and aluminum fixation in the CSH of the cement paste.

## Acknowledgments

The authors wish to acknowledge the Foundation for Science and Technology (FCT) for the financial support under project EXREACT (PTDC/CTM/65243/2006), IMPROVE (Improving the performance of aggregates for the inhibition of alkali-aggregate reactions in concrete, PTDC/ECM/115486/2009) and project DURATINET (Durable Transport Infrastructures in the Atlantic Area Network) for Transnational Programme Atlantic Area 2007-2003, co-financed by FEDER.

## References

[1] Cyr, M., Rivard, P., Labreque, F., Reduction of ASR-expansion using powders ground from various sources of reactive aggregates, Cement and Concrete Composites 31(2009) 438-446.

[2] Hou, X., Struble, L., J., Kirkpatrick, R., J., Formation of ASR gel and the roles of C-S-H and portlandite, Cement and Concrete Research 34 (2004) 1683-1696.

[3] Taylor, H., F., W., Famy, C., Scrivener, K., L., Delayed ettringite formation, Cement and Concrete Research 31 (2001) 683-693.

[4] Pavoine, A., Divet, L., Fenouillet, S., A concrete performance test for delayed ettringite formation: Part II validation, Cement and Concrete Research 36 (2006) 2144-2151.

[5] Cyr, M., Rivard, P., Labreque, F., Reduction of ASR-expansion using powders ground from various sources of reactive aggregates, Cement and Concrete Composites, 31 (2009) 438-446.

[6] Ramlochan, T., Zacarias, P., Thomas, M. D. A., Hooton, R.D., The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature. Part I: Expansive behaviour, Cement and Concrete Research, 33 (2003) 807-814.

[7] Torgal, F. Pacheco, Desenvolvimento de ligantes obtidos por activação alcalina de lamas residuais das minas da Panasqueira (in Portuguese). PhD Thesis, Engenharia Civil, Departamento de Engenharia Civil e Arquitectura da Universidade da Beira Interior, (2006)

[8] ASTM C 2001, "Standard test method for potential alkali reactivity of aggregates (mortar-bar method)", ASTM International, West Conshohocken, United States, p. 5

[9] RILEM Recommendations: B-TC-106-3-Detection of potential alkali-reactivity of aggregates-Method for aggregate combinations using concrete prisms, Materials and Structures, vol.33, p.290-293.

[10] Hong, S.Y: and Glasser, F.P., Alkali sorption by C-S-H and C-S-A-H gels. Part II. Role of alumina; Cement and Concrete Research, 32 (2002) 1101-1111.

[11] Santos Silva, A., Degradação do betão por reacções álcalis-sílica. Utilização de cinzas volantes e metacaulino para a sua prevenção (in Portuguese). PhD Thesis, LNEC/Universidade do Minho, (2005).

[12] Hong, S.Y: and Glasser, F.P., Alkali binding in cement pastes. Part I. the C-S-H phase; Cement and Concrete Research, 29(1999) 1893-1903

[13]Hong, S.Y: and Glasser, F.P., Alkali sorption by C-S-H and C-S-A-H gels. Part II. Role of alumina; Cement and Concrete Research, 32, (2002) 1101-1111.

[14] Shehata, M. H. and Thomas, M.D.A., Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali-silica reaction in concrete", Cement and Concrete Research, 32(2002) 341-349.

[15] Ke- rui, Y., Cai-Wen, Z., Zhi-gang, L., Cong, N., A study on alkali-fixation ability of C-S-H gel, Proceedings of the 12th International Conference on Alkali-Aggregate Reaction in Concrete, Beijing, China (2004) 221-225

[16] Ramlochan, T., Zacarias, P., Thomas, M. D. A., Hooton, R.D., The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature. Part II: Microstructural and microchemical investigations, Concrete Research, 34 (2004) 1341-1356.

[17] LNEC E 26, 1968, Betão. Ensaio de compressão, Especificação LNEC, Lisboa