

## Innovative solutions for the use of high sulfate content materials as aggregates for concrete

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### ABSTRACT

Within the framework of the future railway link between Lyon (France) and Turin (Italy), it is proposed to use the highest part as possible of tunnel excavated materials as concrete aggregates. This objective will permit to prevent the excavation of new quarries, to limit the transport by road of excavated materials, and to avoid their definitive storage. Nevertheless, these excavated materials contain higher amounts of sulphates than those recommended by standards. The studies carried out leads to consider that several solutions can be proposed as washing materials before use, choosing appropriate cement, or using the excavated materials as a source of sulphates to control cement hydration.

**Keywords.** Sulphates, aggregates, cement, ettringite, innovative solution

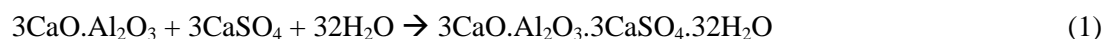
### INTRODUCTION

For the future railway link between Lyon (France) and Turin (Italy), Lyon Turin Ferroviaire (LTF), subsidiary of Réseau Ferré de France (RFF) and Rete Ferroviaria Italiana (RFI), wishes to use the highest part as possible of the 16 millions of m<sup>3</sup> of materials from tunnel excavation as concrete aggregates for the construction of some parts of the 57 km length base tunnel. This objective will permit to prevent the excavation of new quarries, promoting efficient and sustainable management of natural resources, to limit the transport by road of excavated materials, reducing greenhouse gas emission, and to avoid storage of materials in definitive deposit, reducing environmental impact.

However, some of these aggregates have sulphate (gypsum and anhydrite) contents higher than those recommended by current standards. In these conditions, sulphate species can react with hydrated cement compounds with, depending of environmental conditions, formation of

ettringite (or thaumasite if particular conditions are present) which leads to important damages of concrete structures.

The formation of ettringite results in reaction of sulphates with calcium aluminate compound and can lead to swelling of concrete with severe damages for the structure:



To prevent all damages caused by the sulphates, European standards limit their content (Table 1).

**Table 1. Sulphate limit contents for concrete compounds**

Internal origin of sulphate	Standard	Content of sulphate
Mixing water	(EN 1008,2003)	$\text{SO}_4^{2-} \leq 2\,000 \text{ mg/L}$
Cement	(EN 197-1,2001)	$\text{SO}_3 \leq 4.0\text{wt\%}$
Aggregate	(EN 12620+A1, 2008)	$\text{SO}_3 \leq 0.2\text{wt\%}$

As mentioned early, a part of the excavated materials intended to be use as concrete aggregates have a high sulphate content of 3.47% of  $\text{SO}_3$  in mass (60% anhydrite and 40% gypsum) and so they are not usable considering the European standard. Within such conditions, an experimental study has been defined to determine the rate of sulphate release in aqueous solutions of the excavated materials in order to propose some solutions to use the excavated materials as sand in concrete without degradation due to sulphate reaction. The two main ways, investigated as possible solutions, were the choice of an adapted cement and the use of excavated materials as a source of sulphates to control cement hydration.

## EXPERIMENTAL STUDY

### Release of sulphates from excavated materials

In order to know the solubility of sulphate ions from excavated materials, the materials were introduced in a closed vessel with 2 L of aqueous solution. The mass of materials was calculated from total sulphur content in order to have always sub-saturation in the solution. Then, the vessel is placed in an incubator on a roller agitator and the amounts of sulphates releases in the solution were analysed as a function of time. Three temperatures (20, 35, and 50°C) and three pH (7, 12.5, and 13.5) were investigated for different particle size fractions (0/0.315 mm, 0.315/1 mm, and 1/4 mm) of the excavated materials.

### Behaviours of mortars made with excavated materials

Different mortar compositions were studied using six cements and two sands. The three CEM I cements are composed at least 95% of clinker and have various  $\text{C}_3\text{A}$  contents and the the CEM I 52.5N PM ES was used with fly ash (75/25%), the CEM III/B and CEM III/C cements are composed of clinker and blast-furnace slag. The CSS cement is an over sulphated cement composed of clinker, blast-furnace slag and anhydrite. The chemical

compositions of cements, the mineralogical composition of the clinker and constituents of cements are given in Table 2. The first sand was recomposed using standard siliceous sand (fraction 0/2 mm) enriched in sulphate (60% of anhydrite and 40% of gypsum) to have the same sulphate content that in the excavated materials, i.e. 3.47% in mass of SO<sub>3</sub>. The second sand used is the fraction 0/4 mm of the excavated materials.

For all mixtures, the mixture proportions of the mortars were as following: cementitious material = 1; sand = 3 and water/cementitious material = 0.5. The fresh mixes of mortar, made following EN 196-1 standard (2006), were cast in 4\*4\*16 cm<sup>3</sup> moulds, compacted, and kept at 20+/-2 °C and 100% RH. After 24h, samples were removed from the moulds and the first swelling measurement was made as a reference with a precision of 0.002 mm. For each formulation, three mortar samples were placed in water at 20+/-2°C and their swellings were measured as a function of time.

**Table 2. Chemical composition of cements, mineralogical composition of the clinker and constituents of cement**

Chemical composition of cements (% by weight)						
Cement type	CEM I	CEM I PM <sup>1</sup>	CEM I PM-ES <sup>2</sup>	CEM III/B	CEM III/C	CSS
SiO <sub>2</sub>	19.30	20.33	21.55	31.00	32.55	29.93
Al <sub>2</sub> O <sub>3</sub>	5.70	3.14	3.63	8.98	8.94	10.81
TiO <sub>2</sub>	0.35	0.17	0.20	0.55	0.55	0.75
Fe <sub>2</sub> O <sub>3</sub>	4.09	4.44	3.88	1.86	0.93	0.50
CaO	62.48	63.14	63.20	48.75	46.39	39.26
MgO	0.90	0.75	0.86	5.99	6.26	7.31
Na <sub>2</sub> O	0.40	0.08	0.12	0.37	0.51	0.23
K <sub>2</sub> O	0.65	0.48	0.49	0.68	0.46	0.44
SO <sub>3</sub>	3.11	1.07	1.91	1.42	1.38	5.55
MnO	0.08	0.04	0.04	0.30	0.20	0.44
P <sub>2</sub> O <sub>5</sub>	0.60	-	-	0.18	0.07	0.04
Mineralogical composition of the clinker (% by weight)						
C <sub>3</sub> S	56.1	73.3	60.3	65.8	60	60.3
C <sub>2</sub> S	13.4	6.3	17.2	5.8	2.4	17.2
C <sub>3</sub> A	10.4	0.9	2.7	8.0	8.4	2.7
C <sub>4</sub> AF	10.0	14.9	14.1	13.6	11	14.1
Constituents of cements (% by weight)						
Clinker	98	98	98	28	15	5
Blast-furnace slag	0	0	0	70	84	80
Other	2	2	2	2	3	15

<sup>1</sup>PM: High resistant in marine environment <sup>2</sup>PM-ES: High resistant in high sulphate environment

## Hydration control of cement by excavated materials

Different mortar compositions were studied using two cements and two sands. Two cement types CEM I and CEM III/B were reconstituted from clinker, blast furnace slag, and gypsum. The chemical compositions of the clinker and the blast furnace slag are given in table 3. The first sand was a normalized silica sand (0/2 mm) and the second one was the fraction 0/4 mm of the excavated material. For all the mixtures, the composition of the mortars was as follows: water/cement = 0.49 and sand/cement = 2.07. The sand was moistened to 4% just prior to fabrication and, if necessary, an adjuvant was added to obtain a spreading of the mixture of 200 mm. Clinker, slag, gypsum and sand were first homogenised and the water was added for 30 seconds. Then for 6.5 min, the mixture was mixed. The mortar was then placed in a 4\*4\*16 cm<sup>3</sup> mould and vibrated. The specimens were demoulded after a moist cure (100% RH) of 24 hours and the first measurement of swelling, as a reference, was performed.

**Table 3. Chemical composition of clinker and blast furnace slag (wt%)**

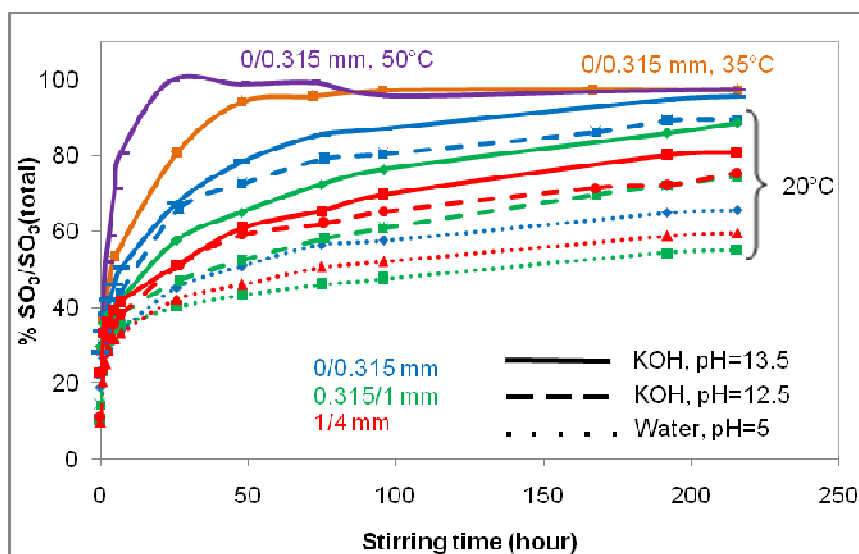
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Mn <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SrO
Clinker	19.31	6.34	0.33	4.27	65.29	0.97	0.26	0.63	0.10	0.38	0.16
BFS	35.64	11.24	0.64	0.33	42.42	7.75	0.30	0.42	0.37	0.02	0.06

## RESULTS AND DISCUSSION

### Release of sulphates from excavated materials

This study focused on the kinetic of sulphate release as a function of particle size fraction, temperature, and pH. Fast releases of sulphates in the various solutions are observed (Fig. 1). For example, at 20°C, in a KOH solution at pH=13.5 and after 7 hours of stirring, 50%, 42%, and 41% of sulphates are released respectively for 0/0.315 mm, 0.315/1 mm, and 1/4 mm fractions against 33%, 35%, and 33% in water at pH=7. Increasing the temperature also induces an acceleration of kinetics of sulphates release. Sulphate released contents are 67%, 81%, and 99% respectively at 20, 35, and 50°C for 0/0.315 mm fraction after 24 hours of stirring.

As pH of a concrete is very alkaline (12.5-13), the sulphates can be released in aqueous pore solution, and they can react with hydrated cement compounds to induce damages for the structure. Considering these conditions a first solution for a safe use of excavated materials can be proposed: the washing of the excavated materials in water for about 7 hours. This solution can be improved by using alkaline water and increasing temperature. Due to fast sulphate release, the two other solutions can be the use of excavated materials without washing (i) but with an appropriate cement avoiding swelling or (ii) as a source of sulphates to control cement hydration and particularly of calcium aluminates C<sub>3</sub>A. These two possibilities are presented in this paper.



**Figure 1. Kinetics of sulphate release in various aqueous solutions from excavated materials**

### Choice of suitable cement for the use of excavated materials

As observed in Figure 2, the expansions of mortar samples casted with standard sand enriched in sulphates or excavated materials and stored in water at 20°C are different depending on the cement used. The CEM I 52.5 N cement, with 10.4% of  $C_3A$ , leads to the highest expansion (0.22% at 190 days). Atahan (Atahan, 2011) observed a similar behaviour for mortars composed for CEM I 52.5N cement with 7.59% of  $C_3A$  and sand with a content of water soluble sulphates of 1.96% with a swelling close to 0.25% after 5 months.

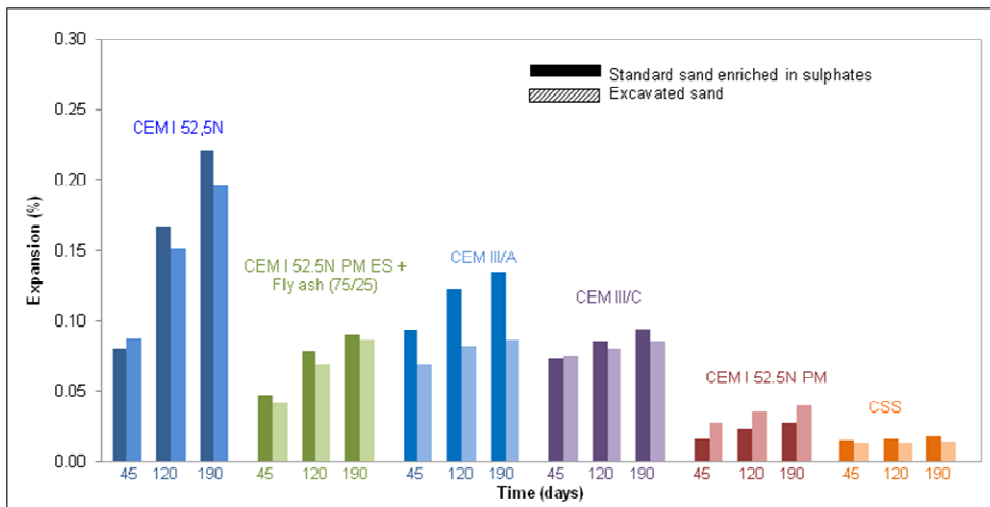
In contrast, the CEM I 52.5 N PM cement, with 0.9% of  $C_3A$ , has only an expansion of 0.03% at 190 days. This confirms the direct relationship between  $C_3A$  content and the risk of damage due to internal sulphate attack.

The blast-furnace slag cements, CEM III/A and CEM III/C cements, known as sulphate resistant, present an expansion at 190 days of respectively 0.14% and 0.09% and the most part of expansion comes in the first 7 days for which the expansions are respectively 0.06% and 0.05%. Compared with the CEM I 52.5 N cement, the addition of blast furnace slag in the cement reduces the expansion of mortar samples. When the blast furnace slag content increases, the expansion decreases, for example at 190 days from 0.22% for CEM I 52.5 N to 0.14% for CEM III/A, and to 0.09% for CEM III/C.

The mortars cast with CEM I 52.5 N PM ES cement and fly ash (75/25), show an expansion lower than for mortars cast with CEM I 52.5 N cement and blast-furnace slag cements, with a swelling of 0.09% at 190 days. The effect of blast-furnace slag and fly ash additions in the cements on the resistance against sulphate attack is also observed by (Atahan, 2011).

The over sulphated cement CSS, has the lowest expansion, which reaches less than 0.02% at 190 days. This cement contains already a great amount of sulphates and so, those provided by the sand do not have real impact.

The same swelling for the mortars made with sand enriched in sulphates and excavated sand induces that the sulphates, in the form of gypsum and anhydrite, from the excavated materials, have a similar behaviour that those introduced in the standard sand. Concerning the safe use of excavated materials, it can be highlighted with this study that the choice of CEM I with low  $C_3A$  or CSS as cement permits to limit drastically the swelling of cementitious materials.

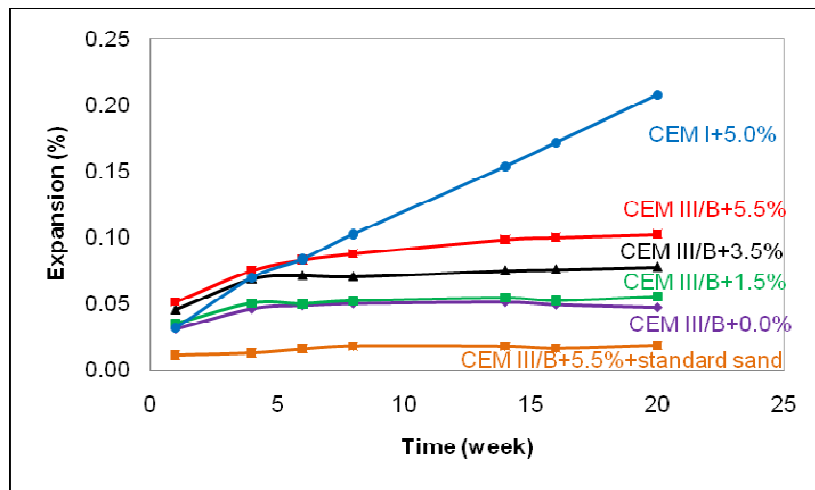


**Figure 2. Expansion after 45, 120 and 190 days (in water at 20°C) for mortar samples cast with standard sand enriched in sulphates and with excavated sand**

### Control of cement hydration using sulphates from excavated materials

As shown in Figure 3, the effect of blast furnace slag is again found by comparing the results of mortars cast with CEM I + 5.0% of gypsum and those with CEM III/B + 5.5% gypsum. After 20 weeks, the swelling decreased from 0.2% to 0.1%. Reducing the content of gypsum in the cement reduces the swelling of the material. At 20 weeks, the mortar specimens exhibit an expansion of 0.10, 0.08, and 0.05% respectively with 5.5%, 3.5%, and 0.0% of gypsum added to the mixture.

The mortars containing only clinker, slag and excavated materials (CEM III/B + 0%) show a very low expansion of 0.05% after 20 weeks. This study highlights that the use of sulphates leached from the excavated material is a solution to regulate the cement hydration and then to cancel any further damage due to sulphates.

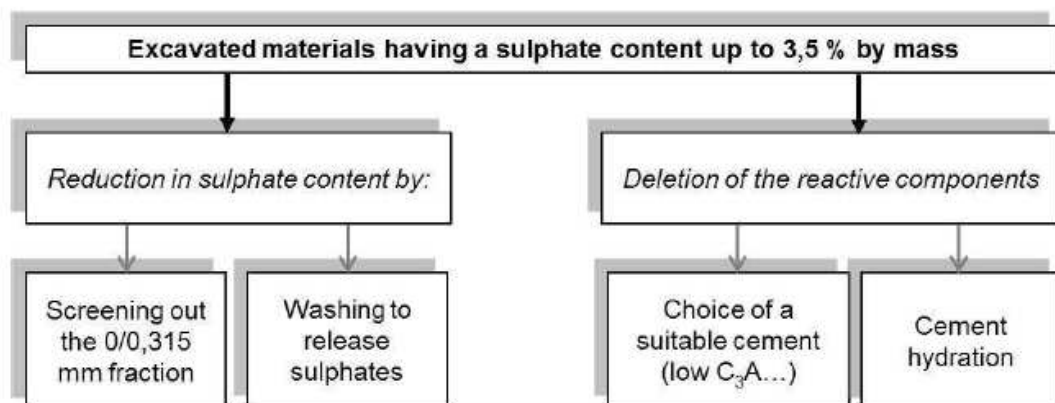


**Figure 3. Swelling of mortar samples stored in water at 20°C**

## CONCLUSION

Kinetic of sulphate release from the LTF tunnel excavated materials is fast and depends on the temperature and the pH of the solution. Increasing the temperature or the pH of the solution increases the kinetics of release. This research project is pointing out that several solutions can be proposed to reduce the internal sulphate reaction risk and then to valorise these excavated materials with sulphate content up to 3,5% by mass. These solutions consist on (Figure 4):

- the reduction in sulphate content by screening out the finest part of the materials in which there is the higher sulphate content, or washing the excavated materials in water solutions before use in order to release the sulphate;
- the deletion of the reactive components by choosing a suitable cement in order to cancel the risk of internal sulphate reaction, or using the sulphate leached from the excavated materials to regulate the cement hydration.



**Figure 4. Solutions to valorize in concrete excavated materials with high sulphate contents**

Complementary studies should be carried out in order to confirm these first results, in particular industrial tests in order to find out the best solution, to fix a realistic upper value of sulphate content, to check the workability of the concrete, and to monitor the durability of the concrete in situ.

Another important point is to consider these results, not only for the use of the specific material studied here, but also for the re-use of concretes from the demolition of buildings and often contaminated with gypsum.

### **ACKNOWLEDGEMENTS**

The authors are thankful to LTF for its financial support. The studies were conducted in collaboration with LTF, represented by N. Monin and a consulting engineer, J. Burdin; two cement suppliers: HOLCIM, represented by T. Mercenier, G. Van Rompaey, J-G. Hammerschlag, and P. Vuillemin, and VICAT, represented by M. Pasquier and L. Bessette. A research laboratory, LERM, represented by J-P. Commene was also involved in the study.

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