

# Stabilization of soils containing sulfates by using alternative hydraulic binders

Laura Diaz Caselles, Julie Hot, Cédric Roosz, Martin Cyr

## ▶ To cite this version:

Laura Diaz Caselles, Julie Hot, Cédric Roosz, Martin Cyr. Stabilization of soils containing sulfates by using alternative hydraulic binders. Applied Geochemistry, 2020, 113, pp.104494. 10.1016/j.apgeochem.2019.104494 . hal-02520099

# HAL Id: hal-02520099 https://hal.insa-toulouse.fr/hal-02520099

Submitted on 21 Jul 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

## 1 Stabilization of soils containing sulfates by using alternative hydraulic binders

2 3 4

5

6

7

9

Laura Diaz Caselles\*, Julie Hot, Cédric Roosz, Martin Cyr

LMDC, INSA/UPS Génie Civil, 135 Avenue de Rangueil, 31077 Toulouse cedex 04 France. \*Corresponding author: diazcase@insa-toulouse.fr

## 8 Abstract

10 Excavation operations during construction produce several tons of soil, which frequently contain high 11 concentrations of sulfates (>0.5 wt%). In accordance with the requirements of the French decree for waste classification for disposal, a soil containing sulfates is classified as "inert and non-hazardous 12 13 waste" if the leachable sulfate concentration is lower than a mass fraction of 0.1%. To prevent sulfate 14 leaching from excavated soils, solutions for immobilizing sulfates are needed and the associated 15 stabilization mechanisms must be understood. On the other hand, the reuse of soils containing sulfates 16 for civil engineering purposes can lead to significant risks after their treatment with ordinary cementitious binders because of chemical reactions involving sulfates. These reactions can promote 17 the formation of massive ettringite crystals resulting in expansion, cracking and eventually catastrophic 18 19 damage of materials or structures. For these reasons, the stabilization of soils containing sulfates by 20 adding alternative hydraulic binders is studied in this paper. Several binders were used to treat a sulfate-spiked soil. It was observed that treatment with cementitious binders having high C<sub>3</sub>A content 21 led to volume expansions greater than 5%, while treatments with binders containing a high fraction of 22 ground granulated blast furnace slag (GGBS) showed volume expansions of less than 5% and about 23 89% of sulfates were immobilized in the solid matrices. These preliminary results suggest that GGBS 24 25 binders are effective for the treatment of soils containing sulfates. Moreover, numerical calculations using PHREEQC were compared with experimental results to improve the understanding of sulfate 26 immobilization mechanisms. 27

28

29 Keywords: Sulfates; Immobilization; Soils; Volume expansion; PHREEQC

- 30
- 31
- 32
- 33
- 34

#### 1 **1. Introduction**

In France, excavated soils are considered as waste and they are classified in different categories depending on their concentration of leachable characteristic constituents. In accordance with the French decree on waste classification for disposal (Legifrance, 2014), a soil containing sulfates is classified as "inert and non-hazardous waste" if the leachable sulfate concentration is lower than a mass fraction of 0.1%. To decrease sulfate leaching from excavated soils, solutions for immobilizing sulfates are needed and the associated stabilization mechanisms must be understood. On the other hand, the reuse of soils containing sulfates for civil engineering purposes can be considered.

In civil engineering, the mechanical properties of soil are improved by adding lime or cement. However, it has been reported that lime treatment of a soil containing sulfates represents a potential risk to the stability and durability of the material application because of expansive reactions induced in the treated soil. Several studies have highlighted that sulfate-rich soils treated with either ordinary Portland cement or lime lead to expansion of the material (Cabane, 2004; Celik and Nalbantoglu, 2013; Colas, 2012; Harris et al., 2006; Hunter, 1988; Kolani et al., 2012; Puppala et al., 2003; Talluri et al., 2013; Wang et al., 2003).

Moreover, it has been shown that soils containing clays with a mass fraction of at least 10% and 1% of sulfates produced significant swelling after treatment with lime (Dermatas, 1995; Hunter, 1988). In a high pH system (pH>12), an expansive mineral known as hydrated calcium sulfoaluminate or ettringite ( $3CaO\cdotAl_2O_3\cdot 3CaSO_4\cdot 32H_2O$ ) can precipitate when sulfate, alumina and calcium ions, and water are available to react. In treated soils, alumina ions could come from either the cement used in the treatment or from the dissolution of clays in the soil because of the increase of pH after the lime-treatment (Celik and Nalbantoglu, 2013; Dermatas, 1995; Hunter, 1988; Puppala et al., 2004).

23 It has also been reported that the swelling potential of sulfate-rich soils is decreased when they are 24 treated with binders other than lime (Celik and Nalbantoglu, 2013; Harris et al., 2006; Kota et al., 1996; Mahedi et al., 2018; Puppala et al., 2004, 2003; Talluri et al., 2013; Wang et al., 2003). Wang et al. 25 26 (2003) investigated the stabilization of sulfate-rich soils by partially replacing ordinary Portland cement 27 (OPC) by alternative materials such as ground granulated blast furnace slag (GGBS), class C fly ash 28 (CFA) and amorphous silica (AS). The authors showed that the replacement of OPC by GGBS decreased the amount of expansion in the soil and no expansion was detected when CFA and AS were 29 30 used. Similarly, Puppala et al. (2003) studied the effectiveness of the treatment of sulfate-rich soils 31 (2000 mg/kg to 5000 mg/kg of dry mass) with sulfate-resisting cement of types I/II and V. By adding 5% of such cements, they observed a decrease in the free swelling from 30% to less than 5%. 32

In the literature, preliminary work in this field focused primarily on the evaluation of the swelling phenomena in sulfate-contaminated soils. However, not much is known about the decrease in leachable sulfate concentration after treatment and the sulfate stabilization mechanisms. This work aims to (i) compare the capacity of several alternative binders to immobilize sulfates in a sulfate-spiked soil in natural pH conditions (pH 7) and (ii) understand the sulfate immobilization mechanisms by using a single step batch method. The stabilization technique was used to decrease the sulfate leaching from treated soils and the swelling phenomenon was studied for all the treatments. Stabilization groups together the chemical processes permitting the decrease in the potential risk of a hazardous waste due to the decrease in the toxicity and the water solubility of pollutants (Chen et al., 2009; Peysson, 2005).

7 In this study, four different binders were chosen to treat a sulfate-spiked soil: one Ordinary Portland 8 Cement (OPC), one alternative clinker mainly composed of ye'elimite  $C_4A_3\overline{S}$  and belite  $C_2S$ , one GGBS 9 CEM III/C cement and one experimental binder composed of 90% GGBS and 10% OPC. Leachable sulfate concentrations were determined by using ion chromatography by analyzing eluates extracted 10 from leaching tests carried out in accordance with the European standard NF EN 12457-2, which is 11 12 required by French law (Legifrance, 2014). Leachable heavy metals concentrations were also 13 determined by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Swelling 14 of untreated and binder-treated soils was evaluated by performing volume expansion tests on 15 compacted specimens. Additionally, mechanical properties were evaluated by determining the indirect 16 tensile strength. Finally, sulfate stabilization mechanisms were studied using Scanning Electron 17 Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) and X-ray diffraction (XRD) by analyzing 18 mineral phases that could contain sulfates. In order to better understand the underlying sulfate 19 stabilization mechanisms, experimental results were compared with numerical calculations obtained from a geochemical model using the PHREEQC code (Parkhurst and Appelo, 1999). 20

- 21 **2.** Materials and methods
- 22 2.1. Materials

#### 23 2.1.1. Sulfate-spiked soil

24 Since a natural sulfate-rich soil was not available, it was chosen to artificially contaminate a soil from 25 the Paris region. This soil was classified as a "silt" using the Unified Soil Classification System (USCS). Its chemical composition is presented in Table 1. It had a total organic carbon (TOC) content of about 26 2450 mg/kg of dry mass  $\pm$  6% and no heavy metal contamination was detected. In order to study the 27 sulfate stabilization, the soil was spiked with 1.8% of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) powder in order to obtain 28 29 a mass fraction of 1% of sulfates (SO<sub>4</sub><sup>2-</sup>) (10000 mg/kg of dry mass of soil). The sulfate dosage of 1% 30 is reported as the level where sulfate-rich soils usually present swelling phenomena after cement treatment (Centre de recherches routières, 2004). In addition, gypsum was selected as the sulfate 31 source because sulfates are generally found in this form in the soils of France (Société Française de 32 33 Chimie, 2016; Wild et al., 1999). Moreover, gypsum is reported to be the major source of sulfate that 34 produces swelling in soils treated with lime (Burkart et al., 1999). This mineral has the highest water solubility among the common sulfate minerals found in soils (2.4 g/l at 25 °C) (Alexander et al., 2013;
 Escadeillas and Hornain, 2008; Eswaran and Gong, 1991; Klimchouk, 1996).

## 3 2.1.2. Binders

Four cementitious binders, with the ability to chemically consume sulfates during their hydration processes, were tested to stabilize sulfates contained in the soil. The chemical compositions of each of the anhydrous binders are summarized in Table 1. The binders tested were:

- One Ordinary Portland cement (OPC), CEM I 52.5 N CE CP2 NF, with a C<sub>3</sub>A content of 8.6%. In
   this study, it is referred to as "CEM I". It was expected that this binder would consume a large
   amount of sulfates due to the reaction between the aluminate phases (C<sub>3</sub>A) and the gypsum
   contained in the soil to form ettringite. In this system, ettringite is not a suitable phase because it
   can lead to volume changes. It should be noted that the main hydration products of this binder are
   portlandite (CH) and calcium silicate hydrate (C-S-H) gel.
- One sulfoaluminate clinker mainly composed of ye'elemite (Ca<sub>2</sub>Al<sub>6</sub>O<sub>12</sub>SO<sub>4</sub> or C<sub>4</sub>A<sub>3</sub>S̄ in cement notation) and belite (Ca<sub>2</sub>SiO<sub>4</sub> or C<sub>2</sub>S in cement notation). It is referred to as "Clinker Y". It should be noted that the SO<sub>3</sub> concentration in this binder is about 8 wt%, which is about half of the SO<sub>3</sub> content found in classic calcium sulfoaluminate binders (Glasser and Zhang, 2001). It was expected that this binder would also consume a large amount of sulfates because its main hydration product is ettringite, which is formed until sulfates are consumed and, then, monosulfate is precipitated (Midgley and Bhaskara Rao, 1978; Winnefeld and Lothenbach, 2010).
- One ground granulated blast furnace slag (GGBS) CEM III/C cement (according to EN 197-1),
   composed of 82% GGBS, 15% Portland clinker and 3% of secondary constituents. The designation
   of this binder is CEM III/C 32.5 N–LH/SR PM and it is referred to as "CEM III/C". This binder was
   chosen to verify the effect of the proportion of slag and Portland clinker on the immobilization of
   sulfates. The main hydration products in this type of binders (slag blended with Portland clinker)
   include C-S-H phases, C-A-S-H (when alumina replaces some silica), hydrotalcite (M<sub>5</sub>AH<sub>13</sub>),
   ettringite and AFm phases such as C<sub>4</sub>AH<sub>13</sub> (Chen and Brouwers, 2007; Kolani et al., 2012).
- One experimental binder composed of 90% GGBS and 10% OPC, with the OPC designation
   CEM I 52.5 N R CE CP2 NF. In this study, it is referred to as "90%GGBS+10%OPC". The addition
   of Portland cement to GGBS is required to increase the pH and enable the hydration reaction of
   GGBS and, thus, the precipitation of cementitious phases (Hewlett, 2004). In this binder, the main
   hydration products are C-S-H, C-A-S-H, hydrotalcite, ettringite and AFm phases.
- Table 1 Chemical compositions of the soil and each of the anhydrous binders (% by weight). The GGBS and
   OPC binders presented in this table were used to fabricate the experimental binder "90%GGBS+10%OPC".

| Oxide/phase                    | Oxide/phase Soil | CEM I | Clinker Y | CEM III/C | Experimental binder |       |
|--------------------------------|------------------|-------|-----------|-----------|---------------------|-------|
| composition                    |                  |       |           |           | GGBS                | OPC   |
| CaO                            | 13.23            | 64.48 | 45.10     | 46.09     | 43.80               | 64.04 |
| SiO <sub>2</sub>               | 57.70            | 20.22 | 10.56     | 31.29     | 37.41               | 21.87 |
| Al <sub>2</sub> O <sub>3</sub> | 7.20             | 5.23  | 23.47     | 10.46     | 10.20               | 3.96  |
| Fe <sub>2</sub> O <sub>3</sub> | 2.86             | 3.32  | 9.71      | 0.91      | 0.60                | 3.08  |
| MgO                            | 1.06             | 0.80  | 1.00      | 5.84      | 6.40                | 1.25  |
| Mn <sub>2</sub> O <sub>3</sub> | 0.11             | 0.00  | 0.01      | 0.00      | 0.20                | 0.03  |
| Na <sub>2</sub> O              | 0.74             | 0.28  | 0.17      | 0.53      | 0.21                | 0.15  |
| K <sub>2</sub> O               | 1.59             | 0.76  | 0.27      | 0.65      | 0.28                | 0.74  |
| TiO <sub>2</sub>               | 0.64             | 0.00  | 1.29      | 0.00      | 0.70                | 0.17  |
| P2O5                           | 0.21             | 0.00  | 0.11      | 0.00      | 0.10                | 0.10  |
| SO <sub>3</sub>                | 0.05*            | 3.02  | 8.07      | 2.52      | 0.10                | 3.35  |
| CI-                            | -                | 0.07  | 0.01      | 0.30      | -                   | -     |
| C <sub>3</sub> A               | -                | 8.60  | -         | 8.40      | -                   | 8.00  |
| C <sub>3</sub> S               | -                | 61.00 | -         | 63.00     | -                   | -     |
| C <sub>2</sub> S               | -                | -     | 20.30     | -         | -                   | -     |
| C4AF                           | -                | 11.10 | -         | 10.50     | -                   | -     |
| $C_4A_3\bar{S}$                | -                | -     | 54.30     | -         | -                   | -     |
| C <sub>3</sub> MS <sub>2</sub> | -                | -     | 4.50      | -         | -                   | -     |
| C₃FT                           | -                | -     | 9.30      | -         | -                   | -     |
| CS                             | -                | -     | 0.40      | -         | -                   | -     |
| LOI (loss on ignition)         | 14.60            | 1.80  | 0.23      | 1.40      | 0                   | 1.26  |

1 \*SO<sub>3</sub> concentration in the natural soil. This soil was additionally spiked with 1.8% gypsum to obtain 1% of sulfates 2 (SO<sub>4</sub><sup>2-</sup>).

#### 3 2.1.3. Sample preparation and curing

All of the samples were fabricated in accordance with the French standard NF P94-100. The aim of this standard is to evaluate the mechanical performance of a soil treated with either lime or hydraulic binders. Before sample fabrication, the soil was dried at 40 °C and reduced to a particle size below 5 mm. Then, it was mixed dry with a mass fraction of 1.8% of gypsum in the form of powder in order to obtain a mass fraction of 1% of sulfates (1% SO<sub>4</sub><sup>2-</sup>).

9 The sulfate-spiked soil without binder was used as the reference or control formulation (F1). For the other mixtures (F2, F3, F4 and F5), the sulfate-spiked soil was mixed dry with the binders using a 10 11 dosage of 10% of dry mass of soil. This binder dosage level was selected to ensure sufficient 12 mechanical properties for all of the treatments. Before compaction of the samples, the water content of 13 all the formulations was determined in accordance with the European standard NF EN 13286-2. This 14 standard specifies a method for determining the relationship between the water content and the dry 15 density of untreated or treated soils with hydraulic binders using Proctor compaction. Compaction was carried out by using cylindrical test molds (50 mm in height and 50 mm in diameter) at 96% of the 16 maximum dry density. All of the samples were protected in hermetically sealed bags in order to 17 18 preserve the water content and were stored in a room at 20 °C until tests were conducted. The five 19 formulations tested are described in Table 2.

#### 1 **Table 2** – Designations and compositions of all the formulations studied (% of dry mass of soil).

| Designation/Formulation | Composition  | Water* to solid ratio<br>(E/S) |
|-------------------------|--|--------------------------------|
| F1 (untreated soil)     | Silt + 1% SO4 <sup>2-</sup>                          | 0.17                           |
| F2                      | Silt + 1% SO4 <sup>2-</sup> + 10% CEM I              | 0.15                           |
| F3                      | Silt + 1% SO4 <sup>2-</sup> + 10% Clinker Y          | 0.15                           |
| F4                      | Silt + 1% SO4 <sup>2-</sup> + 10% CEM III/C          | 0.17                           |
| F5                      | Silt + 1% SO4 <sup>2-</sup> + 10% (90% GGBS+10% OPC) | 0.17                           |

2 \* Water content determined in accordance with the European standard NF EN 13286-2

## 3 2.2. Test methods

#### 4 2.2.1. Leaching tests

5 In this study, leaching tests were carried out in accordance with the European standard 6 NF EN 12457-2 as required by French law (Legifrance, 2014). This standard allows the 7 characterization and evaluation of leachable constituents of waste materials in a single step batch 8 procedure at natural pH condition (pH 7). This method is useful to compare the capacity of several 9 binder treatments to immobilize sulfates in a soil using distilled water as the leachant solution. Thus, 10 the influence of leachant pH on the leachability of constituents from the sulfate-spiked soil is not 11 covered in this study.

In order to perform the NF EN 12457-2 test, samples were cured for 28 days as described in 12 section 2.1.3. Samples were crushed to a particle size below 4 mm and placed in 1 L polypropylene 13 14 bottles containing distilled water with a liquid to solid ratio (L/S) of 10 L/kg. All bottles were shaken for 15 24 h in an end-over-end tumbler at 7 rpm. The solid residue was separated by filtration using a vacuum device and 0.45 µm membrane filters. After filtration, the conductivity and pH were measured in each 16 of the eluates and then stabilized using a 2 v% nitric acid (HNO<sub>3</sub>) solution. All of the resulting solutions 17 18 were stored at 4 °C until the chemical analyses were performed. A minimum of two specimens were 19 used for each formulation. Arithmetic average results are presented with a confidence interval of 95%.

Sulfate immobilization was evaluated by measuring the leachable sulfate concentration using ion chromatography (Dionex Ion Chromatography System (ICS-3000)). Before analyses, all solutions were diluted by a factor of 100 using ultrapure water (18 M $\Omega$ .cm). Additionally, the conductivity, pH and heavy metal concentrations were measured in the leachate solutions. Heavy metal concentrations were determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Optima 7000 DV machine). In this case, all solutions were diluted by factors of 10, 25 or 100 using ultrapure water (18 M $\Omega$ .cm) with 2 v% HNO<sub>3</sub>.

27 2.2.2. Evaluation of swelling and mechanical properties

1 Swelling phenomena and mechanical properties of all mixtures were evaluated in accordance with 2 the French standard NF P 94-100. This standard proposes the immersion of all treated soil samples in water at 40 °C for 7 days. The aim of this immersion is to accelerate the hydration process and to verify 3 4 whether the treatment leads to expansion of the material (Wang et al., 2003). Before the immersion 5 period, this standard recommends a specific curing time for treated soils. When soil is treated with lime, the curing period is 3 days  $\pm$  4 h. For soil treatment with other binders, the minimum curing time 6 7 recommended is 4 h  $\pm$  15 min and the maximum curing time is 7 days. Therefore, in this study, the 8 minimum and maximum curing times were tested on all binders. Preliminary testing showed that a 4-h 9 curing appeared to be insufficient to meet the requirements for splitting tests (results not presented 10 here). For this reason, a curing of 7 days was chosen for both volume expansion and splitting tests.

11 For volume expansion tests, initial geometrical measurements of all samples were taken after 12 7 days of curing using a digital sliding caliper and final volumes were measured at the end of the 13 immersion by applying Archimedes' principle. Specimens used to evaluate mechanical properties followed a preparation procedure similar to that for volume expansion tests. At the end of the immersion 14 15 period, the indirect tensile strength was assessed by carrying out splitting tests in accordance with European standard NF EN 13286-42, which proposes diametral compression tests on compacted soil 16 specimens. For both volume expansion and splitting tests, three specimens were used per formulation. 17 Arithmetic average results are presented with a confidence interval of 95%. 18

19 This standard takes two criteria into account to assess the performance of a soil treated with 20 hydraulic binders: (1) volume expansion, and (2) indirect tensile strength. These criteria and their 21 guideline values are presented in Table 3.

Table 3 – Criteria and guideline values to evaluate the performance of a soil treated with hydraulic binders
 according to the French standard NF P 94-100.

| Borformanaa of the treated acil | Parameter (after immersion for 7 days) |  |  |  |
|---------------------------------|--|--|--|--|
| Ferrormance of the treated-soli | Volume expansion (Gv) in %             | Indirect tensile strength (Rit) in MPa |  |  |
| Suitable                        | ≤ 5                                    | ≥ 0.2                                  |  |  |
| Doubtful                        | 5 < Gv ≤ 10                            | 0.1 ≤ Rit < 0.2                        |  |  |
| Unsuitable                      | > 10                                   | < 0.1                                  |  |  |

24 2.2.3. Mineralogical and microstructural characterizations

In order to understand the sulfate-stabilization mechanisms, mineralogical and microstructural analyses were carried out on treated soil samples using Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS). SEM observations were made on carbon-coated fracture surfaces and on polished sections, previously mounted in resin. Two different scanning electron microscopes were used, a JEOL JSM-6380LV and a JEOL JSM 7800, equipped with Rontec XFLASH 3001 and SDD X-Max 80mm2 EDS detectors, respectively. Images were obtained with both secondary (SE) and back-scattered (BSE) electrons with magnifications between 100x and 10000x. SEM observations coupled with EDS mapping and EDS punctual analyses were also carried
 out in order to identify correlations between various chemical elements and sulfate.

Additionally, X-ray diffraction (XRD) analyses were performed in order to identify mineral phases that could contain sulfates. A Bruker D8 diffractometer with the Bragg-Brentano configuration and copper radiation source (Cu K $\alpha$ ,  $\lambda$ =1.54 Å) was used. The anode voltage was 40 kV and the electric current intensity was 40 mA. XRD analyses were carried out on powder previously crushed to a particle size below 40 µm.

#### 8 2.3. Modeling

9 Experimental results were compared to numerical calculations in order to better understand the 10 sulfate stabilization mechanisms. Simulations were carried out using the PHREEQC code version 3.0 11 (Parkhurst and Appelo, 1999). In this code, mineral-solution equilibria are calculated considering the 12 extended Debye-Hückel activity coefficient model and using the Debye-Hückel B-dot relation (C. 13 Helgeson, 1969). The thermodynamic properties used in this work came from the Thermoddem database (Blanc et al., 2012). Hydrogarnet phase (C<sub>3</sub>(A,F)S<sub>0.84</sub>H<sub>4.32</sub>), which is a typical cementitious 14 phase in the studied system, was added to this database using the Gibbs free energy of formation 15 16 presented by Lothenbach et al. (2019).

In the geochemical model, the initial solution was defined using an *L/S*=10 L/kg, a temperature of *T*=25 °C and a *pH* of 7.0. According to chemical analyses (Table 1) and XRD analyses, the soil was defined as a combination of four main constituents represented in the form of quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), illite (K<sub>0.85</sub>Al<sub>2.85</sub>Si<sub>3.15</sub>O<sub>10</sub>(OH)<sub>2</sub>) and magnetite (Fe<sub>2</sub>O<sub>3</sub>) in molar proportions (mol%) of 72.8%, 21.2%, 4.4%% and 1.6%, respectively. Sulfate was introduced into the model using 10.4 mmol of gypsum (a constant sulfate concentration of 1% was used for all of the simulations). Finally, the binder was defined by its elemental chemical composition expressed in moles.

## 24 **3. Results**

#### 25 3.1. Leaching tests

Leachable sulfate and heavy metal concentrations, conductivity, and pH of eluates extracted from leaching tests for each of the formulations are presented in Table 4. Concentrations exceeding the thresholds are in bold. Leachate concentrations are expressed in mg/kg of dry mass of solid (soil and binder) and are compared to the "inert and non-hazardous waste" thresholds established by French law (Legifrance, 2014) in order to verify that no significant heavy metal concentrations were released after binder treatment. Leachate concentrations of all formulations are schematically represented in Figure 1. In this figure, the radial axes represent the concentrations measured for each element

- 1 normalized by their thresholds, which are established by French law and represented by the red dotted
- 2 line. Outside this line, thresholds are not respected.

3 Table 4 - pH, conductivity values and leachable sulfate, chloride, fluoride and heavy metal concentrations of all

4 formulations. Leachate concentrations are expressed in mg/kg of dry mass. Bold values indicate the 5 concentrations exceeding the thresholds established by French law (Legifrance, 2014).

Inert and non-Chemical species Units hazardous waste F1 F2 F3 F4 F5 Threshold 12.4 pН 7.5 11.7 11.3 11.4 \_ 1662 Conductivity μS/cm 3425 747 653 1050 Sulfates (SO42-) mg/kg 1000 9174 138 759 986 785 Arsenic (As) mg/kg 0.5 <0.2 <0.2 <0.2 <0.2 <0.2 20 0.5 0.2 0.2 0.3 Barium (Ba) mg/kg 0.6 Cadmium (Cd) < 0.002 < 0.002 < 0.002 < 0.002 mg/kg 0.04 < 0.002 Chromium (Cr) mg/kg 0.5 < 0.1 8.0 2.3 < 0.1 < 0.1 2 Copper (Cu) mg/kg <0.2 0.4 <0.2 <0.2 <0.2 Mercury (Hg) 0.01 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 mg/kg Molybdenum (Mo) mg/kg 0.5 0.1 0.1 0.3 < 0.01 0.2 Nickel (Ni) mg/kg 0.4 < 0.1 0.3 < 0.1 < 0.1 0.1 Lead (Pb) 0.5 <0.1 < 0.1 < 0.1 mg/kg <0.1 < 0.1 Antimony (Sb) mg/kg 0.06 < 0.002 < 0.002 < 0.002 < 0.002 < 0.002 Selenium (Se) < 0.01 < 0.01 < 0.01 mg/kg 0.1 <0.01 < 0.01 Zinc (Zn) mg/kg 4 <0.2 <0.2 <0.2 <0.2 <0.2 Chlorides (Cl-) 800 18.6 27.1 3.7 50.4 156.7 mg/kg Fluorides (F-) mg/kg 10 3.3 6.9 2.0 2.2 2.1



F4

Se

Pb

N

CI-

Sb

As

Ba

Cd







| F1: Untreated soil |
|--------------------|
| F2: CEM I          |
| F3: Clinker Y      |
| F4: CEM III/C      |
| =5: 90%GGBS+10%OPC |
|                    |

 Inert and non-hazardous waste threshold Figure 1 - Ratio between leachate concentrations of each formulation and the "inert and non-hazardous waste"
 limit for each element normalized by their thresholds (red dotted line). A logarithmic scale is used.

3 As mentioned previously, the initial sulfate concentration in the soil was 10000 mg/kg of dry mass. 4 When leaching tests were carried out in the untreated sulfate-spiked soil (formulation F1), it was found that the leachable sulfate concentration was approximately 10 times higher than the guideline value for 5 6 "inert and non-hazardous waste" (1000 mg/kg of dry mass) established by French law (Legifrance, 7 2014). As shown in Table 4 and Figure 1, for the untreated soil, the leachable sulfate concentration 8 was about 9174 mg/kg of dry mass ± 16%. In contrast, treatment of the sulfate-spiked soil with CEM I 9 binder (formulation F2) showed a noteworthy decrease in leachable sulfate concentration, which was 10 below the guideline value. In this case, the sulfate concentration released in solution was about 11 138 mg/kg of dry mass ± 9%. Similarly, treatment of sulfate-spiked soil with the sulfoaluminate binder 12 "Clinker Y" (formulation F3) significantly decreased the leachable sulfate concentration. In this treatment, a sulfate concentration of 759 mg/kg of dry mass ± 12% was detected in solution. However, 13 14 in both formulations F2 and F3, chromium (Cr) was also detected in solution with a higher concentration than the limit for "inert and non-hazardous waste" (0.5 mg/kg of dry mass). Therefore, the use of these 15 16 two binders in the treatment of the sulfate-spiked soil represents a disadvantage due to the high concentration of Cr released in solution. 17

On the other hand, sulfate-spiked soil treated with GGBS-binders (formulations F4 and F5), showed the decrease in leachable sulfate concentration and leachable heavy metal concentrations were well within the established limits. For the formulation F4 (CEM III/C), the sulfate concentration released in solution was 986 mg/kg of dry mass  $\pm 21\%$  and for formulation F5 (90%GGBS+10%OPC), the leachable sulfate concentration was 785 mg/kg of dry mass  $\pm 8\%$ .

It should be noted that, for all formulations, leachable chlorides (Cl<sup>-</sup>) and fluorides (F<sup>-</sup>) concentrations
were below the "inert and non-hazardous waste" thresholds established by French law, with less than
800 mg/kg of dry mass for Cl<sup>-</sup> and less than 10 mg/kg of dry mass for F<sup>-</sup>.

## 26 3.2. Evaluation of swelling phenomena and mechanical properties

Figure 2 shows the indirect tensile strength and the volume expansion results for each formulation. For formulation F1 (untreated soil), splitting tests were not performed because of insufficient mechanical strength. Therefore, an indirect tensile strength of 0 MPa is indicated in Figure 2(a).



1

Figure 2 – Evaluation of mechanical properties and swelling for all formulations. The red dotted lines represent
 the guideline established by French standard NF P 94-100. (a) Indirect tensile strength is expressed in MPa. (b)
 Volume expansion is expressed in percentage.

5 It can be observed that formulation F1 (untreated soil) had a volume expansion of  $7.1\% \pm 1.1\%$ , which is greater than the maximum guideline value of 5%. The soil expansion is probably due to the 6 presence of swelling clays. On the other hand, soil treatment with CEM I (formulation F2) presented an 7 indirect tensile strength of 0.26 MPa  $\pm$  0.01 MPa, which is higher than the minimum guideline value of 8 9 0.20 MPa. However, the volume expansion value was higher than 5%, classifying this treatment as 10 "doubtful" (cf. Table 3). Treatment of the sulfate-spiked soil with the "Clinker Y" binder (formulation F3) was also classified as "doubtful" because the indirect tensile strength reached approximately 11 0.19 MPa  $\pm$  0.002 MPa, which was lower than the accepted guideline value (0.2 MPa). In addition, the 12 volume expansion was close to the limit value of 5% ( $4.2\% \pm 0.6\%$ ). 13

Treatment of the sulfate-spiked soil with binders containing high slag levels, such as CEM III/C and "90%GGBS+10%OPC" (formulations F4 and F5, respectively) resulted in a significant decrease in the swelling and maintained an indirect tensile strength above 0.20 MPa. For formulations F4 and F5, the volume expansion reached  $2.0\% \pm 0.6\%$  and  $1.4\% \pm 0.2\%$ , respectively; and the indirect tensile strengths were about 0.23 MPa  $\pm$  0.03 MPa and 0.22 MPa  $\pm$  0.06 MPa, respectively. As such, both treatments F4 and F5 were classified as "suitable".

## 20 3.3. Microstructural characterization: general observations

SEM observations were carried out on fracture sections of all the formulations and the images obtained are presented in Figure 3. SEM images of formulation F1 (untreated soil) are presented in Figure 3(a) and Figure 3(b). As shown, gypsum was the sulfate specie observed and its chemical composition was verified by punctual EDS analyses, having a CaO to SO<sub>3</sub> molar ratio of 1. SEM images of fracture surfaces of formulations F2 and F3 are shown in Figure 3(c) and Figure 3(d), respectively. In both formulations, ettringite crystals were easily identified. For soil treated with CEM I binder (F2), ettringite was observed at higher magnifications than for soil treated with "Clinker Y" binder (F3). Conversely, for formulations containing high GGBS levels (F4 and F5), no expansive phases were observed on the fracture surfaces. As presented in Figure 3(e) and Figure 3(f), the SEM images of F4 and F5 formulations showed a microstructure consisting of an agglomeration of phases, without the typical morphology of sulfate-bearing minerals such as ettringite or gypsum.



8

Figure 3 – SEM images obtained from untreated and treated soils. (a), (b) Formulation F1 (untreated soil) showing sulfate in the form of gypsum. (c) Formulation F2 (CEM I) showing ettringite crystals. (d) Formulation F3 (Clinker Y) showing ettringite precipitates. (e) Formulation F4 (CEM III/C) showing agglomeration of phases (f) Formulation F5 (90GGBS+10OPC) showing agglomeration of phases without typical morphology of sulfatebearing crystal.

## 14 3.4. Focus on formulation F5: experimental and numerical results

15 Particular attention was paid to the experimental binder composed of 90% GGBS and 10% OPC 16 (formulation F5) due to its capacity to immobilize sulfates (89% of sulfates immobilized in the solid) without releasing heavy metals into solution. Additionally, this treatment did not show significant volume
expansions, as was seen in Figure 2. In order to better understand the sulfate stabilization mechanisms
in this formulation, it was decided to extend the microstructural analyses and to compare experimental
data with numerical calculations.

## 5 *3.4.1. Microstructural characterization: formulation F5*

6 As explained in section 3.3, the identification of mineral phases containing sulfates was difficult and no typical morphology of sulfate-bearing crystals such us ettringite and gypsum was observed on the 7 8 fracture surfaces of formulation F5 (cf. Figure 3(f)). Therefore, SEM observations coupled with EDS 9 mapping and EDS punctual analyses were carried out on polished sections of this formulation. One of the EDS mapping analyses is shown in Figure 4(a). EDS mapping analyses provided information about 10 the distribution of sulfates in this sample and revealed that sulfates were always associated with 11 12 calcium. In order to verify the composition of the species containing sulfates, EDS punctual analyses 13 were performed in these zones. Ettringite was the dominant phase identified in the zones presenting 14 high concentrations of sulfates (SO<sub>3</sub> to CaO molar ratio of 0.50 and an Al<sub>2</sub>O<sub>3</sub> to CaO molar ratio of 15 0.17).

16 SEM/EDS analyses were completed by carrying out XRD analyses in the soil before and after 17 treatment. XRD patterns obtained from formulation F5 were then compared to XRD patterns obtained from untreated sulfate-spiked soil (F1). XRD analyses are presented in Figure 4(b). The pattern for 18 untreated soil (F1) revealed a large peak between 20 11° and 12°, which is characteristic of the 19 20 presence of gypsum. The XRD pattern of formulation F5 showed the decrease in intensity of gypsum peaks and revealed the appearance of new peaks between 20 9° and 10° and 15° and 16°, which are 21 characteristic of the ettringite phase. However, residual gypsum in formulation F5 revealed that gypsum 22 was not completely dissolved by the (probably insufficient amount of) water provided to the system 23 24 during the fabrication of the samples.



**Figure 4** – Identification of ettringite in formulation F5 at 28 days of curing. **(a)** At left, BSE image of polished section indicating the zones where ettringite phase was found. At right, EDS elemental mapping showing the zonation of sulfur, calcium, aluminum, sodium, silicon and magnesium elements. **(b)** Selected range of the XRD pattern obtained from formulation F1 (untreated soil) and formulation F5 showing the reduction of intensity of the gypsum peak (G) and the appearance of ettringite peaks (E) in formulation F5.

## 7 3.4.2. Experimental vs. modeling results: formulation F5

In order to better understand sulfate stabilization mechanisms, numerical modeling was performed for formulation F5 and experimental and numerical results were compared. Thus, the influence of the proportion of GGBS+OPC binder on sulfate immobilization in the sulfate-spiked soil was evaluated by varying the dosage of the binder from 0% to 20% (in percentage by mass) as presented in Table 5. Assuming congruent dissolution in the model, this experimental binder was defined by its elemental chemical composition expressed in moles (cf. Table 1).

The results of batch-reaction calculations were compared to leachable sulfate and leachable major element concentrations, which were experimentally determined after leaching tests at 28 days of curing. Consequently, the kinetics of chemical reactions were not taken into account in this model, which represents only the state of equilibrium reached by the system. For some minerals defining the soil constituents, such as quartz and iron(III) oxide (magnetite), the dissolution was not permitted due to their very slow kinetics of dissolution at 20 °C in alkaline conditions (Brady and Walther, 1990; Dove
and Crerar, 1990; Schwertmann, 1991).

3 Since few thermodynamic data exist for GGBS binder, several calculations were made by assuming 4 its hydration at four different degrees: 10%, 20% 30% and 40%. As reported in the literature, the 5 hydration of GGBS and OPC mixes is more complex than that of Portland cement. GGBS reacts more slowly with water and not all the GGBS binders react in the same way (Hewlett, 2004). It is largely 6 recognized that the rate of hardening of GGBS binders is slower than that of Portland cement during 7 8 the first 28 days of curing (Hewlett, 2004). Lothenbach et al. (2012) showed that, over one month, 9 approximately 70% of the slag had reacted in a system containing about 60% slag and a water to binder (W/B) ratio of 1.1. Taylor et al. (2010) reported that, over two years, approximately 68% of the slag had 10 reacted in a Portland-slag system containing about 50% slag and an W/B ratio of 0.4. It seems that 11 higher hydration degrees are estimated in systems containing large amounts of available water. Taylor 12 et al. (2010) showed that the degree of slag hydration in a slag-blended system also depended on the 13 14 proportion of slag provided. This means that, over the same time period, a system containing high 15 proportions of slag presents lower rates of slag reaction compared with systems containing lower slag 16 amounts. Taylor et al. (2010) estimated that, over two years of reaction, only 36% of slag had reacted 17 in a formulation containing 90% GGBS and 10% OPC.

In the current investigation, it is, therefore, important to consider the hydration degree of the GGBS
 as a significant factor influencing the immobilization of sulfates in formulation F5.

Table 5 – Formulations used to verify the sulfate stabilization mechanisms in formulation F5 (90%
 GGBS+10%OPC) (% of dry mass of soil).

| Designation | Composition                                    |
|-------------|--|
| F5-20       | Silt + 1% SO4 <sup>-2</sup> + 20% 90GGBS+10OPC |
| F5-15       | Silt + 1% SO4 <sup>-2</sup> + 15% 90GGBS+10OPC |
| F5-12       | Silt + 1% SO4 <sup>-2</sup> + 12% 90GGBS+10OPC |
| F5-10       | Silt + 1% SO4 <sup>-2</sup> + 10% 90GGBS+10OPC |
| F5-8        | Silt + 1% SO4 <sup>-2</sup> + 8% 90GGBS+10OPC  |
| F5-7        | Silt + 1% SO4 <sup>-2</sup> + 7% 90GGBS+10OPC  |
| F5-5        | Silt + 1% SO4 <sup>-2</sup> + 5% 90GGBS+10OPC  |
| F5-2        | Silt + 1% SO4 <sup>-2</sup> + 2% 90GGBS+10OPC  |

Experimental and numerical data of pH values, sulfate, calcium, aluminum, silicon and magnesium concentrations in solution are plotted in Figure 5, where element concentrations are given in mM (mmol/L). All the data were plotted as a function of the binder dosage (ranging from 0% to 20%). Experimental data are represented by black circles while model calculations are given by lines. Solution concentrations are also completed by the molar quantities of solid phases involved in the modeled reactions (Figure 6). These quantities are divided into two groups here for ease of reading: silicon dominant phases (M-S-H, C-S-H and illite) are shown in Figure 6(a) and aluminous dominant phases
 (ettringite, hydrogarnet and gibbsite) in Figure 6(b).

3 As shown in Figure 5(a), experimental and numerical data were in good agreement for the sulfate 4 concentrations in solution. Experimental data and simulations showed that sulfate concentration in 5 solution decreased when the content of "GGBS+OPC" binder increased. Experimentally, the sulfate concentration in solution remained relatively stable for formulations containing more than 7% of binder. 6 This behavior can be explained by the ettringite stability as shown in Figure 6(b). In addition, simulations 7 8 showed that the GGBS hydration level seemed to have an impact on the slope of the curve representing 9 the sulfate concentration in solution. Depending on the GGBS hydration level considered, a modification on the sulfate concentration in solution was observed. However, the GGBS hydration level 10 11 no longer affected the sulfate concentrations calculated beyond 15% of binder dosage. The best agreement between experimental and numerical data was obtained when a GGBS hydration level of 12 30% was assumed. 13

14 The results obtained for other leached elements are shown from Figure 5(b) to Figure 5(c). As for 15 sulfates, the most important changes are observed for formulations containing less than 10% of binder. Calcium, silicon and magnesium concentrations calculated in solution are mostly controlled by C-S-H 16 17 and M-S-H as shown in Figure 5(b), Figure 5(d), Figure 5(e) and Figure 6(a). On the other hand, 18 aluminum concentrations in solution presented a more complex behavior due to the competition 19 between aluminous phases (cf. Figure 5(c)). For formulations ranging from 0% to 10% of binder, 20 aluminum presented a first evolution mainly dominated by ettringite formation as shown in Figure 6(b). 21 Experimental data for formulations with high binder dosage (>10%) showed that a maximum

aluminum concentration was reached between 10% and 15% of binder dosage and then remained relatively stable. This behavior was not well modeled in the calculation results. The authors think that the difference found between numerical and experimental results in aluminum behavior could be explained by the aluminum mineral phases used in the model. In fact, it was verified that a decrease of 1% in the aluminum content present in the illite (used in the model to represent the soil), decreased the aluminum concentrations in solution by about 50%, without modifying the trend of the curve shown in Figure 5(c).

The pH values measured and calculated in solutions are shown in Figure 5(f). The first value measured in the system without binder (untreated soil) was close to 7.4. After the addition of the binder to the soil, pH increased significantly in the solution (pH 11-12). It seems that the proportion of binder in the treatment had a little effect on the variation of pH in the solution since it stayed relatively constant between pH values 11 and 12. This evolution was well reproduced by the model (but was slightly lower than experimental values) and was mainly controlled by the C-S-H composition.



Figure 5 – Comparison between numerical and experimental data obtained from formulation F5 (90%GGBS+10%OPC). All the data are plotted as a function of the binder dosage. Black circles: experimental data. Line with larger dots: 40% GGBS hydration level. Solid line: 30% GGBS hydration level. Line with smaller dots: 20% and 10% GBBS hydration. (a) Leachable sulfate concentration, (b) leachable calcium concentration, (c) leachable aluminum concentration, (d) leachable silicon concentration, (e) leachable magnesium concentration (using a logarithmic scale), (f) pH values.





Figure 6 – Molar quantities of major phases calculated from the geochemical simulation of formulation F5 (90%GGBS+10%OPC) assuming a GGBS hydration level of 30%. All the data are plotted as a function of the binder dosage. (a) Illite, C-S-H and M-S-H phases, (b) Ettringite, gibbsite and hydrogramet.

#### 1 4. Discussion

#### 2 4.1. Sulfate stabilization with CEM I and Clinker Y binders

3 Results presented in this paper confirm that treatment of sulfate-contaminated soils with cementitious binders is useful to decrease sulfate leaching. As presented previously, untreated sulfate-4 5 spiked soil released of about 90% of sulfates in solution. It was verified that the treatment with ordinary 6 Portland cement (formulation F2) and Clinker Y (formulation F3) showed a large decrease in sulfate 7 concentration in solution after leaching tests. For formulation F2, it was calculated that a mass fraction 8 of about 99% of sulfates were fixed in the solid. For formulation F3, the percentage of sulfates fixed in 9 the solid was 92%. As explained in the literature, these binders provided aluminum to the system and also increased the pH (Hunter, 1988), which led to the instability of gypsum contained in the soil and 10 11 to the precipitation of ettringite as shown in Figure 3 and Table 4. Ettringite is reported to be the most 12 stable phase under these conditions permitting the decrease in leachable sulfate concentration (Brown 13 and Bothe, 1993; Cody et al., 2004; Feng et al., 2016; Warren and Reardon, 1994).

14 Nevertheless, the stabilization of sulfates in soils by these two binders (CEM I and Clinker Y) is limited because of: (i) the release of chromium and (ii) the significant swelling measured. In fact, 15 16 chemical analyses of eluates after leaching tests showed that both formulations F2 and F3 released 17 chromium (Cr) at concentrations that were higher than the established "inert and non-hazardous waste" 18 threshold (0.5 mg/kg of dry mass of soil) (cf. Table 4 and Figure 1). Previous studies have investigated 19 the presence of chromium in cements (Eštoková et al., 2012; Sinyoung et al., 2011; Sorrentino, 2011). 20 Sinyoung et al. (2011) conducted leaching tests in cement clinkers and found that chromium exceeded 21 the allowable leachable concentration established by the United States Environmental Protection Agency (US EPA). Estoková et al. (2012) indicated that the concentration of soluble chromium in 22 23 binders was proportional to the OPC clinker content. That explains why some types of cements, such as CEM III or CEM V, have a low chromium content; in these cases, chromium content decreases with 24 OPC content. In addition, it has been shown that slag can reduce Cr(VI) to Cr(III) due to the reducing 25 properties of this material. As reported in the literature, Cr(III) is less soluble than Cr(VI), therefore, slag 26 27 binders decrease the leachable Cr concentration (Allan and Kukacka, 1995; Kindness et al., 1994).

28 In terms of swelling, both formulations F2 and F3 had larger volume expansions than the 29 expansions measured in formulations F4 and F5. Swelling phenomena in F2 and F3 formulations can 30 be attributed to the presence of ettringite crystals in the matrices, as shown in in Figure 3 (ettringite 31 was observed at higher magnifications in F2 than for F3). The marked expansion in formulation F2 32 (CEM I-treatment) was expected due to the large aluminate content in the form of C<sub>3</sub>A (8.6%), which 33 reacted with gypsum to form ettringite. These results support previous findings in the literature where 34 noteworthy swelling was reported on sulfate-contaminated soils treated with OPC or lime (Dermatas, 35 1995; Puppala et al., 2004, 2003; Wang et al., 2003). Moreover, volume expansion on formulation F2

1 was greater than that measured for formulation F3 (6.5% and 4.2%, respectively) (cf. Figure 2). The 2 authors think that this can be explained by the difference in the type of ettringite formed. Mehta, (1983) reported that differences in the crystal habit and size of ettringite can affect the expansion behavior of 3 4 the material. Mehta, (1983) proposed two types of ettringite crystals. Ettringite crystals of type 1 has 5 large lath-like crystals ranging from 10 µm to 100 µm and several micrometers thick and it is usually 6 formed during the hydration of supersulfated cements such as the sulfoaluminate clinker used in the present formulation F3. This type of ettringite is not expansive. Conversely, ettringite of type 2, 7 8 presenting small rod-like crystals (1 µm to 2 µm long) is considered as expansive because of large 9 amounts of these crystals have been found in deteriorated concretes under sulfate attacks. Additionally, 10 some observations have shown that microcrystalline ettringite is capable of adsorbing large amounts 11 of water on the surface, causing volume changes (Mehta, 1973). Type 2 ettringite is assumed to be the 12 ettringite observed in formulation F2.

13 In contrast, significant volume expansion was not expected on samples treated with the "Clinker Y" binder (formulation F3) because the main hydration product of sulfoaluminate clinkers is ettringite, 14 15 which usually precipitates during the consumption of the calcium sulfate after 1 to 2 days of hydration (Winnefeld and Lothenbach, 2010). However, we think that, in this treatment, the volume expansions 16 17 can be explained by a delay in hydration due to the unavailability of water at the beginning of the hydration process. It should be noted that the water to solid ratio (W/S) of formulation F3 was about 18 19 0.15, meaning that not enough water was available to hydrate the binder during the first few days of 20 curing. As explained previously, volume expansion tests were conducted at 7 days of curing and 21 samples were immersed in water at 40 °C for 7 days. Under these conditions, the additional water 22 provided to the system could lead to the precipitation of secondary ettringite and consequently the 23 expansion of the samples.

#### 24 4.2. Sulfate stabilization with GGBS binders

As presented in Table 4 and Figure 1, treatments of sulfate-spiked soil with GGBS binders 25 26 (formulations F4 and F5) showed a large decrease in sulfate concentration in solution after leaching 27 tests. It was calculated that of about 89% of sulfates were immobilized in the solid. Reduced species of sulfur present in GGBS as sulfides and native sulfur (Allan and Kukacka, 1995; Chaouche et al., 28 29 2017) could play an important role to decrease the leachable sulfate concentration in F4 and F5 30 treatments. However, it should be noted that the amount of sulfur provided to the treatment by the 31 addition of GGBS binder is about 0.009% wt, which seems very low to significantly decrease the leachable sulfate concentration. Additionally, leachable heavy metal concentrations were well within 32 the established limits. For F4 and F5, pH values in solution were lower than pH measured in 33 34 formulations F2 and F3. This condition could have decreased the release of anionic heavy metals such 35 as chromate, which is strongly pH dependent (Alloway, 2013; Bourg and Loch, 1995; Leisinger et al., 36 2014). As mentioned previously, GGBS has reducing properties due to reduced sulfur species. It has been shown that Cr(VI) can be reduced to Cr(III) when GGBS is added to OPC mixtures. Thus,
 leachable Cr concentration decreases after leaching tests (Allan and Kukacka, 1995; Kindness et al.,
 1994).

SEM/EDS and XRD analyses showed that sulfates were partially consumed by the formation of 4 5 ettringite phase (cf. Figure 4). These experimental observations were confirmed by modeling. 6 Numerical calculations showed that ettringite was the most stable phase at the equilibrium of the 7 system. In this study, the precipitation of ettringite was defined as one of the mechanisms dominating 8 the immobilization of sulfates in the GGBS-treated soil. It should be noted that, in the geochemical 9 model, a hydration level of 30% for the GGBS binder was assumed, which enabled good agreement 10 between numerical and experimental results. The low hydration level of GGBS binder at 28 days can 11 explain the difficulty in experimentally identifying the phases containing sulfates in formulation F5 and 12 also other possible mechanisms of sulfate stabilization. Wild et al., (1993) studied the stabilization of sulfates in sulfate-rich clays treated with GGBS-lime binders. They proposed that the amorphous phase 13 14 C-A-S-S-H was initially formed, which seems to be a precursor of ettringite formation. Similarly, Wild et al. (1999) suggested that, in lime-slag systems, gypsum is consumed but part of the products formed 15 during the reaction are not crystalline. This can be another explanation of the difficulty in identifying 16 17 sulfate-bearing phases in the GGBS formulations F4 and F5.

18 Unlike treatments F2 and F3, formulations F4 and F5 did not reveal ettringite formation to be a 19 source of large volume expansions. GGBS-treated soils had volume expansions lower than 5%, which 20 demonstrated the ability of GGBS binders to stabilize sulfates without producing significant swelling. 21 This finding reinforces previous studies reporting the usefulness of binders other than lime or OPC in 22 the treatment of sulfate-rich soils (Celik and Nalbantoglu, 2013; Kogbara and Al-Tabbaa, 2011; Puppala et al., 2003; Tasong et al., 1999; Wild and Tasong, 1999; Wild et al., 1998). Celik and Nalbantoglu 23 24 (2013) found that soils containing sulfates at a concentration of about 10000 mg/kg of dry mass that 25 were treated with only lime showed swelling of about 8% with respect to the initial volume of the sample. However, when GGBS was added, the swelling was reduced to 1%. Similarly, Wild and Tasong, (1999) 26 27 showed a significant reduction in expansion when clays containing sulfates where stabilized by using 83% GGBS and 17% lime. They measured little expansion (< 2%) in the samples during the first 7 days 28 29 of moist curing. Wild et al. (1999) explained that, in a GGBS-lime soil system, the proportion of GGBS 30 influenced the magnitude of expansion. Higher GGBS content led to low expansions (< 5%) in sulfate-31 rich soils. The reduction of expansion in this type of system can be explained by the consumption of 32 lime, which usually precipitate in the form of portlandite in clinker-rich binders, by the GGBS to be 33 activated (Wild et al., 1999). In this case, GGBS reaction became the dominant reaction and the amount 34 of lime is considered insufficient to enable the precipitation of large amounts of expansive phases (Wild et al., 1999). As mentioned previously, Wild et al. (1999) explained that, in a sulfate-rich soil treated 35 36 with mixtures with low lime and high slag content, gypsum is consumed and no crystalline ettringite can

be formed. The authors of the present article think that the low hydration rate of the GGBS binder used
in formulation F5 led to small volume changes over the 7 days of immersion test.

3 Treatment of sulfate-rich soils with GGBS binders appears to be useful for the stabilization of 4 sulfates. However, there are several factors that require further investigation. The influence of leachant 5 pH on the leachability of sulfates from sulfate-spiked soil is not determined by EN 12457-2 procedure. In order to understand the sulfate immobilization as a function of leachant pH other procedures could 6 7 be used such as the method presented by the European standard EN 14429. On the other hand, 8 leaching tests are usually applied to treated soils at short-term hydration (28 days). However, in the 9 case of soils treated with GGBS binders, this curing can underestimate the capacity of such binders to 10 stabilize sulfates due to the low rate of hydration. It is suggested that a higher immobilization of sulfates 11 (or other pollutants) could be observed in soils treated with GGBS binders if leaching tests were carried 12 out at long-term. Further investigation can be also addressed to the evaluation of long-term durability of GGBS-treatments as mentioned by Wild et al. (1999). 13

14 Finally, as mentioned previously, in this study, leaching tests were carried out in accordance with 15 the European standard NF EN 12457-2 as required by French law (Legifrance, 2014). This leaching 16 method is presented in the literature as a dynamic test that simulates the worst case of leaching behaviors, mainly because of the L/S (10 L/kg) and the particle size used (below 4 mm) (Vitkova et al., 17 18 2011). It should be noted that NF EN 12457-2 procedure does not require the characterization of the 19 particle size below 4 mm. As reported in the literature, this condition led to discrepancies between several results from an identical waste source (Lackovic et al., 1997; Vitkova et al., 2011; Zandi et al., 20 21 2008). Zandi et al. (2008) explained that concentrations in eluates are underestimated when the dust 22 fraction (<0.5 mm) is discarded from the leaching tests. Conversely, results are overestimated if only 23 the finer fraction is considered because larger proportion of fine grain fraction leads to larger concentrations of elements in leachates. Therefore, further experimental investigations are needed to 24 25 estimate the disparity between results coming from similar wastes by performing this leaching test. Characterization of particle size below 4 mm is highly recommended in order to increase the reliability 26 27 of this leaching test.

#### 28 **5.** Conclusions

Sulfate immobilization mechanisms were studied in four different formulations. Treatments of sulfate-spiked soil with ordinary Portland cement of type CEM I and with an alternative clinker mainly composed of ye'elimite and belite resulted in a high immobilization of sulfate (>80 %) in the solid. However, chromium (Cr) was released into solution in excess of the limit established by French law (0.5 mg/kg of dry mass of soil). Moreover, neither of the treatments was appropriate because volume expansions exceeded the guideline value (5%) established by French standard NF P 94-100. Large volume expansions (> 5%) in these treatments were explained by the precipitation of expansive

1 ettringite and because of delayed hydration due to the unavailability of water during the first 7 days of 2 curing. On the other hand, sulfate-spiked soil treated with binders having a high GGBS content resulted 3 in satisfactory immobilization of sulfates in the solid while avoiding the release of heavy metals into 4 solution. In addition, GGBS-treatments decreased the swelling potential of the sulfate-spiked soil, which 5 was demonstrated by measured volume expansions lower than 5%. Identification of sulfate-6 stabilization mechanisms in GGBS-treatment was a difficult task. However, mineralogical analyses 7 enabled the identification of ettringite, which did not produce volume expansion in the treated soils. The precipitation of ettringite in the GGBS treatments was also verified by modeling calculations. The 8 9 formation of ettringite was found to be one of the mechanisms controlling sulfate solubility. Further 10 experimental investigations are needed to identify other possible mechanisms of sulfate stabilization in 11 soils treated with GGBS.

12 The current work was restricted to a soil artificially contaminated with sulfate. Nevertheless, this 13 system may be expected to behave in a similar manner to a natural sulfate-rich soil where the main 14 source of sulfates is gypsum.

## 15 Acknowledgements

Funding: This work was supported by the French company "Razel-Bec", the French Ministry of Higher Education and Research and the National Association for Research and Technology (ANRT) in the framework of French Cifre fellowships.

### 19 References

- Alexander, M., Bertron, A., De Belie, N. (Eds.), 2013. Performance of Cement-Based Materials in Aggressive
   Aqueous Environments. https://doi.org/10.1007/978-94-007-5413-3
- Allan, M.L., Kukacka, L.E., 1995. Blast furnace slag-modified grouts for in situ stabilization of chromium contaminated soil. Waste Manag. 15, 193–202. https://doi.org/10.1016/0956-053X(95)00017-T
- Alloway, B.J. (Ed.), 2013. Heavy Metals in Soils, 3rd ed. Springer Netherlands. https://doi.org/10.1007/978-94 007-4470-7
- Blanc, P., Lassin, A., Piantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., Gaucher, E., 2012. Thermoddem: A
   geochemical database focused on low temperature water/rock interactions and waste materials, Applied
   Geochemistry. https://doi.org/10.1016/j.apgeochem.2012.06.002
- Bourg, A., Loch, G., 1995. Mobilization of Heavy Metals as Affected by pH and Redox Conditions, in:
   Biodynamics of Polluants in Soils and Sediments. Springer-Verlag. https://doi.org/10.1007/978-3-642 79418-6
- Brady, P. V, Walther, J. V, 1990. Kinetics of quartz dissolution at low temperatures. Chem. Geol. 82, 253–264.
   https://doi.org/https://doi.org/10.1016/0009-2541(90)90084-K

- Brown, P.W., Bothe, J. V., 1993. The stability of ettringite. Adv. Cem. Res. 5, 47–63.
   https://doi.org/10.1680/adcr.1993.5.18.47
- Burkart, B., Goss, G.C., Kern, J.P., 1999. The Role of Gypsum in Production of Sulfate-Induced Deformation of
   Lime-Stabilized Soils. Environ. Eng. Geosci. 5, 173–187. https://doi.org/10.2113/gseegeosci.V.2.173
- C. Helgeson, H., 1969. Thermodynamic of Hydrothermal Systems at Elevated Temperatures and Pressures,
   American Journal of Science. https://doi.org/10.2475/ajs.267.7.729
- Cabane, N., 2004. Sols traités à la chaux et aux liants hydrauliques : Contribution à l'identification et à l'analyse
   des élèments perturbateurs de la stabilisation. Université Jean Monnet Saint-Etienne.
- 9 Celik, E., Nalbantoglu, Z., 2013. Effects of ground granulated blastfurnace slag (GGBS) on the swelling
- 10 properties of lime-stabilized sulfate-bearing soils. Eng. Geol. 163, 20–25.
- 11 https://doi.org/10.1016/j.enggeo.2013.05.016
- Centre de recherches routières, 2004. Code de bonne pratique pour le traitement des sols à la chaux et/ou aux
   liants hydrauliques. Bruxelles.
- Chaouche, M., Gao, X.X., Cyr, M., Cotte, M., Frouin, L., 2017. On the origin of the blue/green color of blast furnace slag-based materials: Sulfur K-edge XANES investigation. J. Am. Ceram. Soc. 100, 1707–1716.
   https://doi.org/10.1111/jace.14670
- Chen, Q.Y., Tyrer, M., Hills, C.D., Yang, X.M., Carey, P., 2009. Immobilisation of heavy metal in cement-based
   solidification/stabilisation: A review. Waste Manag. 29, 390–403.
- 19 https://doi.org/10.1016/j.wasman.2008.01.019
- Chen, W., Brouwers, H.J.H., 2007. The hydration of slag, part 2: Reaction models for blended cement. J. Mater.
   Sci. 42, 444–464. https://doi.org/10.1007/s10853-006-0874-1
- Cody, A.M., Lee, H., Cody, R.D., Spry, P.G., 2004. The effects of chemical environment on the nucleation,
   growth, and stability of ettringite [Ca3Al(OH)6]2(SO 4)3·26H2O. Cem. Concr. Res. 34, 869–881.
   https://doi.org/10.1016/j.cemconres.2003.10.023
- Colas, J., 2012. Etude de la valorisation des déblais de chantiers de tunnels en granulats à béton. Université
   Paris-Est. https://doi.org/tel-00806513
- 27 Dermatas, D., 1995. Ettringite-Induced Swelling in Soils: State-of-the-Art. Appl. Mech. Rev. 48, 659–673.
- Dove, P.M., Crerar, D.A., 1990. Kinetics of quartz dissolution in electrolyte solutions using a hydrothermal
   mixed flow reactor. Geochim. Cosmochim. Acta 54, 955–969. https://doi.org/https://doi.org/10.1016/0016 7037(90)90431-J
- Escadeillas, G., Hornain, H., 2008. La durabilité des bétons vis-a-vis des environnements chimiquement
   agressifs, in: La Durabilité Des Bétons. pp. 613–705.

1 Eštoková, A., Palaščáková, L., Singovszká, E., Holub, M., 2012. Analysis of the chromium concentrations in 2 cement materials. Procedia Eng. 42, 123-130. https://doi.org/10.1016/i.proeng.2012.07.402 3 Eswaran, H., Gong, Z.-T., 1991. Properties, Genesis, Classification, and Distribution of Soils with Gypsum, in: 4 Occurrence, Characteristics, and Genesis of Carbonate, Gypsum, and Silica Accumulations in Soils, 5 SSSA Special Publication SV - 26. Soil Science Society of America, Madison, WI, pp. 89–119. 6 https://doi.org/10.2136/sssaspecpub26.c6 7 Feng, P., Miao, C., Bullard, J.W., 2016. Factors Influencing the Stability of AFm and AFt in the Ca-Al-S-O-H 8 System at 25°C. J. Am. Ceram. Soc. 99, 1031–1041. https://doi.org/10.1111/jace.13971 9 Glasser, F.P., Zhang, L., 2001. High-performance cement matrices based on calcium sulfoaluminate-belite 10 compositions. Cem. Concr. Res. https://doi.org/10.1016/S0008-8846(01)00649-4 11 Harris, P., von Holdt, J., Sebesta, S., Scullion, T., 2006. Recommendations for Stabilization of High-Sulfate 12 Soils in Texas. Transp. Res. Rec. J. Transp. Res. Board 1952, 71-79. https://doi.org/10.3141/1952-08 13 Hewlett, P., 2004. Lea's Chemistry of Cement and Concrete, Science. https://doi.org/10.1016/B978-0-7506-14 6256-7.50031-X 15 Hunter, D., 1988. Lime-induced heave in sulfate-bearing clay soils. J. Geotech. Eng. 114, 150-167. 16 Kindness, A., Macias, A., Glasser, F.P., 1994. Immobilization of chromium in cement matrices. Waste Manag. 17 14, 3-11. https://doi.org/https://doi.org/10.1016/0956-053X(94)90016-7 18 Klimchouk, A., 1996. The Dissolution and Conversion of Gypsum and Anhydrite. Int. J. Speleol. 25, 21 – 36. 19 https://doi.org/10.5038/1827-806X.25.3.2 20 Kogbara, R.B., AI-Tabbaa, A., 2011. Mechanical and leaching behaviour of slag-cement and lime-activated slag 21 stabilised/solidified contaminated soil. Sci. Total Environ. 409, 2325-2335. 22 https://doi.org/10.1016/j.scitotenv.2011.02.037 23 Kolani, B., Buffo-Lacarrière, L., Sellier, A., Escadeillas, G., Boutillon, L., Linger, L., 2012. Hydration of slag-24 blended cements. Cem. Concr. Compos. https://doi.org/10.1016/j.cemconcomp.2012.05.007 25 Kota, P.B.V.S., Hazlett, D., Perrin, L., 1996. Sulfate-bearing soils : Problems with calcium-based stabilizers. 26 Transp. Res. Rec. 62-69. https://doi.org/10.3141/1546-07 Lackovic, J.A., Nikolaidis, N.P., Chheda, P., Carley, R.J., Patton, E., 1997. Evaluation of Batch Leaching 27 28 Procedures for Estimating Metal Mobility in Glaciated Soils. Groundw. Monit. Remediat. 17, 231–240. 29 https://doi.org/10.1111/j.1745-6592.1997.tb00598.x 30 Legifrance, 2014. Arrêté du 12 décembre 2014 relatif aux conditions d'admission des déchets inertes dans les 31 installations relevant des rubriques 2515, 2516, 2517 et dans les installations de stockage de déchets 32 inertes relevant de la rubrique 2760 de la nomenclature des i. France.

- Leisinger, S.M., Bhatnagar, A., Lothenbach, B., Johnson, C.A., 2014. Solubility of chromate in a hydrated OPC.
   Appl. Geochemistry 48, 132–140. https://doi.org/10.1016/j.apgeochem.2014.07.008
- 3 Lothenbach, B., Kulik, D.A., Matschei, T., Balonis, M., Baquerizo, L., Dilnesa, B., Miron, G.D., Myers, R.J.,
- 4 2019. Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-
- 5 activated materials. Cem. Concr. Res. 115, 472–506. https://doi.org/10.1016/j.cemconres.2018.04.018
- Lothenbach, B., Le Saout, G., Ben Haha, M., Figi, R., Wieland, E., 2012. Hydration of a low-alkali CEM III/B–
   SiO2 cement (LAC). Cem. Concr. Res. 42, 410–423.
- 8 https://doi.org/https://doi.org/10.1016/j.cemconres.2011.11.008
- Mahedi, M., Cetin, B., White, D., 2018. Performance Evaluation of Cement and Slag Stabilized Expansive Soils,
   Transportation Research Record Journal of the Transportation Research Board.
   https://doi.org/10.1177/0361198118757439
- Mehta, P.K., 1983. Mechanism of sulfate attack on portland cement concrete Another look. Cem. Concr. Res.
   https://doi.org/10.1016/0008-8846(83)90040-6
- Mehta, P.K., 1973. Mechanism of expansion associated with ettringite formation. Cem. Concr. Res.
   https://doi.org/10.1016/0008-8846(73)90056-2
- Midgley, H.G., Bhaskara Rao, P., 1978. Formation of stratlingite, 2CaO.SiO2.Al2O3.8H2O, in relation to the
   hydration of high alumina cement. Cem. Concr. Res. https://doi.org/10.1016/0008-8846(78)90005-4
- 18 Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2) : a computer program for
- speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, Water Resources Investigations Report. https://doi.org/10.3133/wri994259
- Peysson, S., 2005. Contribution à l'étude de la Stabilisation de Déchets par du Ciment Sulfo-alumineux.
   L'Institut National des Sciences Appliquées de Lyon.
- Puppala, A.J., Griffin, J.A., Hoyos, L.R., Chomtid, S., 2004. Studies on Sulfate-Resistant Cement Stabilization
   Methods to Address Sulfate-Induced Soil Heave. J. Geotech. Geoenvironmental Eng. 130, 391.
   https://doi.org/10.1061/(ASCE)1090-0241(2004)130:4(391)
- Puppala, A.J., Wattanasanticharoen, E., Punthutaecha, K., 2003. Experimental evaluations of stabilisation
   methods for sulphate-rich expansive soils 25–35.
- Schwertmann, U., 1991. Solubility and dissolution of iron oxides. Plant Soil 130, 1–25.
   https://doi.org/10.1007/BF00011851
- 30 Sinyoung, S., Songsiriritthigul, P., Asavapisit, S., Kajitvichyanukul, P., 2011. Chromium behavior during cement-
- production processes: A clinkerization, hydration, and leaching study. J. Hazard. Mater. 191, 296–305.
   https://doi.org/10.1016/j.jhazmat.2011.04.077
- 33 Société Française de Chimie, 2016. Exploitation du gypse [WWW Document]. URL

- 1 http://www.societechimiquedefrance.fr/extras/Donnees/espace\_travail/mine/caso/texcaso.htm
- Sorrentino, F., 2011. Chemistry and engineering of the production process: State of the art. Cem. Concr. Res.
   41, 616–623. https://doi.org/10.1016/j.cemconres.2011.03.013
- Talluri, N., Puppala, A., Chittoori, B., Gaily, A., Harris, P., 2013. Stabilization of High-Sulfate Soils by Extended
   Mellowing. Transp. Res. Rec. J. Transp. Res. Board 2363, 96–104. https://doi.org/10.3141/2363-11
- Tasong, W.A., Wild, S., Tilley, R.J.D., 1999. Mechanisms by which ground granulated blastfurnace slag
  prevents sulphate attack of lime-stabilized kaolinite. Cem. Concr. Res. 29, 975–982.
  https://doi.org/10.1016/S0008-8846(99)00007-1
- 9 Taylor, R., Richardson, I.G., Brydson, R.M.D., 2010. Composition and microstructure of 20-year-old ordinary
   10 Portland cement–ground granulated blast-furnace slag blends containing 0 to 100% slag. Cem. Concr.

11 Res. 40, 971–983. https://doi.org/https://doi.org/10.1016/j.cemconres.2010.02.012

- Vitkova, M., Ettler, V., Mihaljevič, M., Šebek, O., 2011. Effect of sample preparation on contaminant leaching
   from copper smelting slag, Journal of hazardous materials. https://doi.org/10.1016/j.jhazmat.2011.09.102
- Wang, L., Roy, A., Seals, R., Metcalf, J., 2003. Stabilization of Sulfate-Containing Soil by Cementitious Mixtures
   Mechanical Properties. Transp. Res. Rec. 1837, 12–19. https://doi.org/10.3141/1837-02
- Warren, C.J., Reardon, E.J., 1994. The solubility of ettringite at 25°C. Cem. Concr. Res. 24, 1515–1524.
   https://doi.org/10.1016/0008-8846(94)90166-X
- Wild, S., Abdi, M.R., Leng-Ward, G., 1993. Sulphate Expansion of Lime-Stabilized Kaolinite: II. Reaction
   Products and Expansion. Clay Miner. 28, 569–583. https://doi.org/DOI: 10.1180/claymin.1993.028.4.07
- Wild, S., Kinuthia, J.M., Jones, G.I., Higgins, D.D., 1999. Suppression of swelling associated with ettringite
   formation in lime stabilized sulphate bearing clay soils by partial substitution of lime with ground
   granulated blastfurnace slag. Eng. Geol. 51, 257–277. https://doi.org/10.1016/S0013-7952(98)00069-6
- Wild, S., Kinuthia, J.M., Jones, G.I., Higgins, D.D., 1998. Effects of partial substitution of lime with ground
   granulated blast furnace slag (GGBS) on the strength properties of lime-stabilised sulphate-bearing clay
   soils. Eng. Geol. 51, 37–53.
- Wild, S., Tasong, W.A., 1999. Influence of ground granulated blastfurnace slag on the sulphate resistance of
   lime-stabilized kaolinite. Mag. Concr. Res. 51, 247–254. https://doi.org/10.1680/macr.1999.51.4.247
- Winnefeld, F., Lothenbach, B., 2010. Hydration of calcium sulfoaluminate cements Experimental findings and
   thermodynamic modelling. Cem. Concr. Res. https://doi.org/10.1016/j.cemconres.2009.08.014
- Zandi, M., Russell, N., Edyvean, R., Hand, R., Ward, P., 2008. Interpretation of standard leaching test BS EN
   12457-2: is your sample hazardous or inert?, Journal of environmental monitoring : JEM.
- 32 https://doi.org/10.1039/b712957b