

## Influence of leaching conditions on the release kinetics of lead, chromium and nickel from solidified/stabilized cementitious materials

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In this work, we investigate, on a laboratory scale, the influence of the leaching conditions on the release of various chemical elements from a cementitious material obtained by solidification of PbO, Ni<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> with blended cement (CEMII-B32.5, according to European Standards). The pH effects on the pollutants release and the composition of the initial pore solution (target elements: chloride, sulfate, sodium, potassium, calcium, lead, chromium and nickel) were assessed through an experimental procedure consisting of two equilibrium leaching tests [the acid neutralization capacity (ANC) and the pore water (PW) tests] and the maximum mobile fraction (MMF) test. Samples of the same material were submitted in parallel to dynamic leaching tests in order to assess the influence of the boundary conditions (instantaneous liquid/solid (*L/S*) ratio, solution renewal) on the leaching kinetics of the target elements. The comparison criteria were the leachate saturation state, the released cumulative quantities and the leaching flux. Generally, leachate quantities obtained by the ANC, PW and MMF tests were important. However, the lowest released amount was observed for the monolith leaching test, and leachate saturation slowed down the dynamic release. Finally, experimental results highlighted another important parameter: the influence of the liquid/solid contact type on leaching kinetics.

**Keywords:** solidified/stabilized waste; heavy metals; cement-based materials; leaching phenomena; pollutant release

### 1. Introduction

In accordance with the impact of human development on the planet all around the world, an environmental assessment should be undertaken to predict the consequences of wastes on human environmental quality and on the living beings' health. For example, the incineration of solid wastes (municipal and/or industrial) gives rise to solid residues. The solidification/stabilization of these residues by means of hydraulic binders is very common [1–4]. Since water is the main environmental pollution vector responsible for the transport, the transfer and the dispersion of soluble or insoluble pollutants from solid waste materials, the characterization of the leaching mechanisms is an important step in predicting the long-term behaviour of these stabilized materials. As a matter of fact, the tests for the estimation of leaching conducted in laboratory are the standardized tests (NNI, 1994; NEN 7345 – the Netherlands). In Europe, the European Committee for Standardization (ECS) has proposed a methodology for the environmental assessment by an intrinsic and dynamic characterization of granular materials (ECS-CEN/TC 292/WG6, 1997 – European standard ENV 12920) [5,6].

Over recent decades, several studies have focused on the characterization of waste materials and their leaching behaviour [7–13]. In this field, a number of studies were undertaken with regards to the assessment and modelling of

inorganic elements leaching from cement-based materials containing solidified wastes. A set of leaching procedures and testing conditions [7,8] have been applied to a large variety of materials: material compositions (different types of cement, waste and pollutants) [7,8,14], material particles sizes and porosity (monolithic or granular samples) [15] and solvent properties (demineralized water, alkaline, acidic or salt solution) [7,8,15]. These investigations have shown that the release behaviour of inorganic elements observed in different testing conditions allowed one to distinguish between two typical transfer mechanisms: (i) the pure diffusive transport for very soluble elements (alkaline metals) and (ii) the diffusion/dissolution-coupled process for the less soluble elements (for example, the amphoteric metals: nickel, lead and chromium). The chemical nature and transport properties of materials (porosity, diffusion coefficient) are considered as intrinsic parameters that partly determine the kinetics of pollutant release. Another set of parameters that characterize initial and boundary conditions, that is, the liquid hydrodynamics (continuous flow or sequential renewal with different contact times, *L/S* (ml g<sup>-1</sup>) ratio [15–17] and the solid/liquid reactor type (column, open continuous stirred reactor, closed reactor) [18]) may also contribute to the understanding of using the release kinetics of pollutants in granular materials. Among the various scenarios describing the phenomena of leaching

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conditions, the main ones are immersion in underground or surface water in foundations, water infiltration (rain) in consolidated materials and surface run-off water on landfill monolithic stabilized waste [19].

Accordingly, the aim of our study is not to propose a new leaching test, but to determine the influence of leaching conditions on the release of chemical elements contained in the porous matrix and to estimate the performance of the used scenario. In accordance with this purpose, we have a set up a series of experiments. Blended cement and heavy metals compounds were used in cement matrices. The monitoring of long-term release of pollutants and chemical elements is carried out using the monolith leaching test (MLT). The intrinsic properties of materials were characterized using two equilibrium liquid/solid tests. Each material was submitted to four dynamic tests in parallel under various leaching conditions. The main set of experimental tests is composed of the solid/liquid contact conditions, the materials' particle size and the liquid circulation.

## 2. Materials and experimental protocols

### 2.1. Materials manufacturing

Previous investigations [20–27] highlighted that heavy metals are the most widespread industrial wastes pollutants. In this study, chromium, lead and nickel were spiked as pollutants in synthetic samples. The used wastes were made up of sand and inorganic pollutants (PbO, Ni<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>). They were incorporated into cement-based materials manufactured using blended cement CEMII-B32.5 (from Ain El Kebira plant, Algeria), according to European standards [28–30], using demineralized water. The chosen pollutant content is usually 1% by mass, intended to ensure realistic pollution levels [7,8,14]. The other monitored elements during this study were chloride and sulfate as anions and sodium and potassium, calcium, lead, chromium and nickel as cations.

To ease the diffusion in the laboratory tests, a 0.5 water/cement ratio for cement pastes was used. Samples of 8 × 8 × 21 cm<sup>3</sup> size were cast. The formulations of solidified/stabilized materials (weight percent) are shown in Table 1. Each mixture is about 3 kg. Firstly, the sand and the pollutants were mixed at medium speed in order to obtain a homogeneous mixture. Secondly, cement was added and the mixture was mixed for several minutes. Then, water was added followed by a rapid mixing for a

few minutes. Demineralized water was used to avoid any additional trace of chemical elements in the sample. Afterwards, the mixing was stopped in order to scrape the bottom of the container in order to ensure the homogenization of the mix. The mortar was then poured into the mould. The problem that may occur during the sample conservation is the carbonation of the samples' surface. This phenomenon gives rise to a thin layer of calcite (CaCO<sub>3</sub>) that may block the pore surface and strongly modify leaching kinetics [31]. Therefore, after 24 hours, the samples are immersed under 1 cm of demineralized water to ensure a rate of 100% humidity. After that, the moulds are stored in a room under a controlled temperature of (20 ± 2 °C) for 27 days [7,8,14].

### 2.2. Experimental protocols

#### 2.2.1. Material compositions and mechanical properties

X-ray fluorescence analyses were used to determine the chemical elements (SiO<sub>2</sub>, CaO, SO<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, MgO, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) in dried materials, whereas the identification of mineral phases contained in dried materials stabilized/solidified was obtained by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses.

After 28 days of conservation, compressive and bending strengths were conducted using a press of type 65-L11M2 according to the EN196-1 standard to characterize the studied materials.

#### 2.2.2. Determination of transfer and leaching properties by analytical methods

Equilibrium and leaching tests of stabilized/solidified (s/s) materials were carried out according to the widely used common protocols [32–41]. For all experimental tests (equilibrium and dynamic leaching tests), leachates were analysed for pH and element concentrations. Leachates samples were filtered and acidified at pH = 2 with HNO<sub>3</sub> solution (65%) and then analysed for cations by atomic absorption spectrophotometry (AAS; unit AA-6501F according to the French standard NF-X 31151). Chloride and sulfate anions were analysed by Mohr and ultraviolet spectrophotometry, respectively (NF X 31151).

**2.2.2.1. Water absorption capacity.** The water absorption capacity (WAC) [42] of the material was determined from the mass balance of the samples (total soluble release and difference in sample weight before and after immersion in water). Its objective is to assess the open porosity in the material [43]. Its determination requires the measurement of the volume, water content, size and initial dry mass of the sample for each monolith before the MLT. It is possible also to calculate the water porosity through a calculated value of WAC as follows:

$$WAC = \left[ \frac{(m_f + \sum f_i + \sum p_i - m_{0S})}{m_{0S}} \right] \times 100, \quad (1)$$

Table 1. Mass fractions of stabilized/solidified materials based on blended cement CEMII-B32.5.

Material	Mass (%)						w/c
	Sand	Cement	PbO	Cr <sub>2</sub> O <sub>3</sub>	Ni <sub>2</sub> O <sub>3</sub>	Water	
S(PbO)	66	22	0.98	0	0	11.00	0.5
S(Cr <sub>2</sub> O <sub>3</sub> )	61	25	0	1.2	0	12.50	0.5
S(Ni <sub>2</sub> O <sub>3</sub> )	62	25	0	0	1	12.50	0.5

where  $m_f$  (kg) is the final mass of the sample,  $f_i$  (kg) is the mass of dried residue,  $p_i$  (kg) is the dry mass of particles retained by the filter paper and  $m_{0s}$  (kg) is the initial mass of the sample (before leaching). At the end of the MLT, the open pores were assumed to be saturated with water. Then, the porosity of the saturated material can be determined by relationship (2) by using the relative material density (monolithic blocks), determined by relationship (2) [7,8,14]:

$$P = WAC(\%) d \quad (2)$$

and

$$d = \frac{\rho \cdot \text{material}}{\rho \cdot \text{water}} \quad (3)$$

**2.2.2.2. Acid neutralization capacity test.** The objective of the acid neutralization capacity (ANC) test is to assess the ANC of the material and the pH influence on the elements' release. The pH-dependent release of the various monitored elements has an important effect on the leaching behaviour of the material. The experimental pollutant solubility as a function of pH was carried out on finely crushed materials in order to rapidly reach solid/liquid steady-state conditions. A finely crushed sample of each material (grain size <1 mm) was immersed in a given volume of solution at a determined pH. The same liquid/solid ratio ( $L/S$ ) was maintained constant for all the samples at 10 ml g<sup>-1</sup> of dried material. In order to cover a wide pH range [2–13], we used nitric acid (non-complexing and only slightly oxidizing) and sodium hydroxide. A preliminary study showed that 7 days were necessary for reaching a steady state at room temperature (23 ± 1 °C) under agitation by an end-over-end tumbler. After filtration (porosity of filter: 45 µm), the solution was analysed by using AAS for the elements (lead, nickel, chromium, sodium, potassium and calcium), the Mohr method for chloride and ultraviolet spectrophotometry for sulfate. The ions formation during Na and K analyses in AAS was suppressed by adding suppressors of ionization, such as Cs, under the form of ClCs with a lower ionization potential, or by decreasing the flame temperature through decreasing the rate of acetylene or the pressure in the gas mixture carburant-comburant.

**2.2.2.3. Pore water and maximum mobile fraction tests.** The objectives of the pore water and maximum mobile fraction (PW-MMF) tests were the assessment of the initial PW composition and the mass of easily soluble phases. The test allows the assessment of the constituents' solubilization under steady-state conditions between fine crushed material and demineralized water in closed vessels and for different liquid/solid ratios at room temperature (23 ± 1 °C) during 7 days of continuous stirring. The synthesized materials samples S(PbO), S(Cr<sub>2</sub>O<sub>3</sub>) and S(Ni<sub>2</sub>O<sub>3</sub>) were crushed to obtain grains of sizes <1 mm, then immersed in demineralized water with different  $L/S$  ratios: 200; 100; 50; 10; 5;

2; and 1.2 ml g<sup>-1</sup> (of dried material). The closed vessels were agitated for 7 days by an end-over-end tumbler. After that, the leachates were filtrated (filter porosity 0.45 µm) and characterized [7,8,14].

**2.2.2.4. Monolithic leaching test.** The protocol of leaching tests performed on monolithic blocks is consistent with the one proposed by the French association ADEME (Procedure thorough evaluation methods of stabilization/solidification by hydraulic binders) [7,8,14]. After a 28-day humid cure in a moist room, samples of dimension 8 × 8 × 21 cm<sup>3</sup> were dry-sawn to extract from their cores cubic samples of dimension 4 × 4 × 4 cm<sup>3</sup>. These samples were dusted; their masses and dimensions were measured to obtain some of their physical parameters (volume, area, equivalent area and equivalent height). For each material, the sample was immersed in demineralized water in a polyethylene container (glass is sensitive to prolonged alkaline exposure), which was hermetically closed to prevent air penetration (CO<sub>2</sub>) and water evaporation during the test. The sample was put on a grid allowing leachate to flow freely. A 10 cm<sup>3</sup>/cm<sup>2</sup> liquid/surface ratio was maintained constant at each solution renewal. The test was performed under a constant temperature (20 ± 2 °C) and protected from light [7,8,14]. The solutions were renewed after 0.25; 0.75; 1; 2; 6; 6; 20; and 28 days, giving a total of 64 days of continuous leaching. We obtained eight solutions to be analysed after filtration (0.45 µm): the pH, leaching solution conductivity, soluble fraction and concentrations of different elements and the possible masses ( $P_i$ ) of particles retained on the filter were needed for the calculation of the WAC. The evolutions in time of the experimental solution parameters are presented: the evolution of pH of successive solutions (Table 2) and released molar fluxes of the different elements (mmol/m<sup>2</sup>s) (Figure 1 and Table 2).

The total leachable amount is the amount of leached elements that can be solubilized and released into the environment after contact with the surrounding solution until its exhaustion. For less soluble elements, two experimental approaches were developed for the determination of

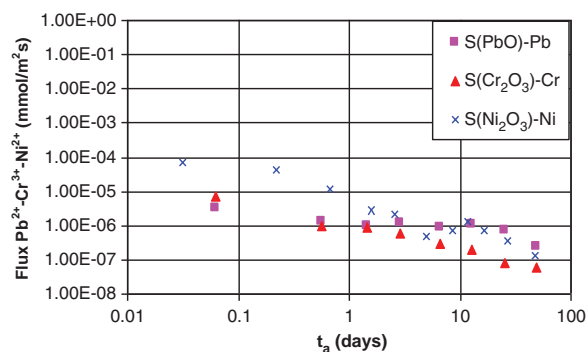


Figure 1. Pb<sup>2+</sup>, Cr<sup>3+</sup> and Ni<sup>2+</sup> fluxes versus time for the monolith leaching test (MLT) in S(PbO), S(Cr<sub>2</sub>O<sub>3</sub>) and S(Ni<sub>2</sub>O<sub>3</sub>) materials.

Table 2. Evolution of pH and leaching molar fluxes of the different chemical species of successive solutions, in monolith leaching test.

	Time (days)	pH	Flux of elements (mmol/m <sup>2</sup> s)				
			Ca <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	K <sup>+</sup>
S(PbO)	00.25	09.44	$2.87 \times 10^{-3}$	$3.59 \times 10^{-2}$	$6.86 \times 10^{-3}$	$2.42 \times 10^{-4}$	$2.87 \times 10^{-2}$
	00.75	11.90	$7.91 \times 10^{-4}$	$8.71 \times 10^{-3}$	$9.27 \times 10^{-4}$	$9.90 \times 10^{-5}$	$5.82 \times 10^{-3}$
	01.00	11.33	$4.56 \times 10^{-4}$	$5.13 \times 10^{-3}$	$5.67 \times 10^{-4}$	$3.58 \times 10^{-5}$	$1.71 \times 10^{-3}$
	02.00	11.75	$2.67 \times 10^{-4}$	$3.87 \times 10^{-3}$	$3.90 \times 10^{-4}$	$6.46 \times 10^{-5}$	$3.25 \times 10^{-3}$
	06.00	12.07	$1.49 \times 10^{-4}$	$1.24 \times 10^{-3}$	$1.57 \times 10^{-4}$	$1.35 \times 10^{-5}$	$7.95 \times 10^{-4}$
	06.00	11.90	$1.47 \times 10^{-4}$	$2.30 \times 10^{-3}$	$1.36 \times 10^{-4}$	$1.75 \times 10^{-5}$	$6.53 \times 10^{-4}$
	20.00	12.14	$5.31 \times 10^{-5}$	$6.10 \times 10^{-4}$	$5.10 \times 10^{-5}$	$7.63 \times 10^{-6}$	$1.05 \times 10^{-4}$
	28.00	12.29	$4.46 \times 10^{-5}$	$4.72 \times 10^{-4}$	$2.32 \times 10^{-5}$	$4.02 \times 10^{-6}$	$2.84 \times 10^{-5}$
S (Cr <sub>2</sub> O <sub>3</sub> )	00.25	11.74	$1.08 \times 10^{-2}$	$4.45 \times 10^{-2}$	$1.62 \times 10^{-2}$	$3.42 \times 10^{-3}$	$4.99 \times 10^{-3}$
	00.75	11.80	$7.86 \times 10^{-3}$	$1.38 \times 10^{-2}$	$5.86 \times 10^{-3}$	$1.99 \times 10^{-3}$	$1.24 \times 10^{-3}$
	01.00	11.76	$4.58 \times 10^{-3}$	$1.12 \times 10^{-2}$	$4.25 \times 10^{-3}$	$3.58 \times 10^{-4}$	$9.33 \times 10^{-4}$
	02.00	11.83	$1.05 \times 10^{-3}$	$5.61 \times 10^{-3}$	$1.61 \times 10^{-3}$	$6.46 \times 10^{-4}$	$1.37 \times 10^{-4}$
	06.00	11.90	$3.28 \times 10^{-4}$	$2.78 \times 10^{-3}$	$2.30 \times 10^{-4}$	$5.35 \times 10^{-5}$	$7.16 \times 10^{-5}$
	06.00	11.85	$6.52 \times 10^{-5}$	$1.82 \times 10^{-3}$	$1.54 \times 10^{-4}$	$3.75 \times 10^{-5}$	$6.34 \times 10^{-5}$
	20.00	11.92	$2.92 \times 10^{-5}$	$7.04 \times 10^{-4}$	$4.60 \times 10^{-5}$	$2.55 \times 10^{-5}$	$8.62 \times 10^{-5}$
	28.00	11.93	$2.04 \times 10^{-5}$	$5.04 \times 10^{-4}$	$2.26 \times 10^{-5}$	$3.02 \times 10^{-5}$	$4.32 \times 10^{-5}$
S (Ni <sub>2</sub> O <sub>3</sub> )	00.25	10.80	$9.98 \times 10^{-4}$	$2.91 \times 10^{-2}$	$3.09 \times 10^{-1}$	$3.42 \times 10^{-3}$	$4.38 \times 10^{-2}$
	00.75	11.21	$2.13 \times 10^{-4}$	$5.32 \times 10^{-3}$	$5.86 \times 10^{-2}$	$5.36 \times 10^{-4}$	$8.33 \times 10^{-3}$
	01.00	11.67	$1.29 \times 10^{-4}$	$4.65 \times 10^{-3}$	$4.36 \times 10^{-2}$	$8.65 \times 10^{-4}$	$7.02 \times 10^{-3}$
	02.00	11.52	$1.18 \times 10^{-4}$	$3.69 \times 10^{-3}$	$4.09 \times 10^{-2}$	$9.87 \times 10^{-5}$	$8.62 \times 10^{-3}$
	06.00	11.55	$2.23 \times 10^{-5}$	$1.68 \times 10^{-3}$	$1.34 \times 10^{-2}$	$5.26 \times 10^{-5}$	$3.39 \times 10^{-3}$
	06.00	11.47	$1.95 \times 10^{-5}$	$3.67 \times 10^{-4}$	$5.88 \times 10^{-3}$	$4.13 \times 10^{-5}$	$1.92 \times 10^{-3}$
	20.00	11.50	$8.91 \times 10^{-6}$	$1.23 \times 10^{-4}$	$2.95 \times 10^{-3}$	$4.50 \times 10^{-5}$	$3.48 \times 10^{-4}$
	28.00	11.34	$3.87 \times 10^{-6}$	$6.74 \times 10^{-5}$	$1.37 \times 10^{-3}$	$4.70 \times 10^{-5}$	$1.98 \times 10^{-4}$

this quantity: (i) the extracted maximum under extreme pH conditions during the test and (ii) the maximum mobilized fraction during the ANC test obtained by extrapolating curves to infinite  $L/S$ . These quantities, expressed in mg/kg of dry material, are then converted to a concentration in mmol/l of PW, called  $S_0$ , according to the relationship (4) [7,8,14]

$$S_0 = \frac{Q_{(\max \cdot \text{ext})} \times \rho}{Ma \times P \times 1000}, \quad (4)$$

where  $Q_{(\max \cdot \text{ext})}$  is the maximum extracted quantity of chemical elements (g/kg);  $\rho$  is the density of the chemical element (kg/m<sup>3</sup>);  $Ma$  is the molar mass (kg) and  $P$  is the porosity of the monolithic block (%).

### 3. Results and discussion

#### 3.1. Material compositions, physical and mechanical properties

The chemical composition of materials was determined by X-ray fluorescence. The results are summarized in Table 3. This table shows that the samples of the solidified/stabilized materials are rich in silica and calcium, reflecting mainly the chemical compositions of the used cement and sand. These elements are quite classical in cement-based materials, which are necessary for the formation of the two main hydrates, portlandite and

calcium-silicate-hydrates (C-S-H), in the porous matrix during the hydration step.

The mineralogical analysis of the synthesized materials shows the formation of more or less crystalline phases. These phases are mainly S<sub>1</sub>O<sub>2</sub>, CaCO<sub>3</sub>, Ca(OH)<sub>2</sub>, C-S-H, C<sub>6</sub>AS<sub>3</sub>H<sub>32</sub>, C<sub>4</sub>ASH<sub>12</sub>, Pb<sub>2</sub>Al<sub>4</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>, C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF, 2Ca(OH)<sub>2</sub>SiO<sub>2</sub>Ni<sub>4</sub>Ti<sub>3</sub>, ettringite: 3CaO Al<sub>2</sub>O<sub>3</sub> 3CaSO<sub>4</sub>32H<sub>2</sub>O, CaCrO<sub>4</sub>·2H<sub>2</sub>O and Ca<sub>2</sub>Cr(OH)<sub>7</sub>·3 H<sub>2</sub>O.

The major phases of S(Ni<sub>2</sub>O<sub>3</sub>), S(Cr<sub>2</sub>O<sub>3</sub>) and S(PbO) are portlandite, C-S-H and ettringite deriving from the hydration of cement. Phases Pb<sub>2</sub>Al<sub>4</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>, CaCrO<sub>4</sub>·2H<sub>2</sub>O and 2Ca(OH)<sub>2</sub>SiO<sub>2</sub>Ni<sub>4</sub>Ti<sub>3</sub> show that heavy metals incorporated as wastes in cementitious materials are solidified and trapped.

Table 4 shows the average compressive strength ( $R_c$ ) and bending strength ( $R_f$ ) and their standard deviations measured at 28 days. Each test was performed over three samples. One can remark on the differences between some results, while others are quite similar. However, one can note that the materials' mechanical properties are not strongly affected given the insufficient pollutant contents.

Water content ( $W$ ), ignition loss (IL), WAC, density ( $\rho_s$ ) and porosity ( $P$ ) of solidified/stabilized materials are also presented in Table 4. The results show that the porous matrix S(Ni<sub>2</sub>O<sub>3</sub>) has a slightly higher density and porosity compared to the other two materials.

Table 3. Chemical composition (% mass) of stabilized/solidified materials and their compounds.

Type	SiO <sub>2</sub>	CaO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
CEMII-B 32.5	23.76	62.15	1.20	0.36	0.13	2.18	5.17	5.05
Sand	58.21	23.26	0.06	0.37	0.08	1.14	0.54	nd
S(PbO)	61.80	22.82	1.21	1.01	0.14	0.67	3.16	2.18
S(Cr <sub>2</sub> O <sub>3</sub> )	61.02	24.35	1.32	1.08	0.19	1.02	3.09	2.23
S(Ni <sub>2</sub> O <sub>3</sub> )	61.50	23.85	1.10	1.05	0.15	0.85	3.05	2.15

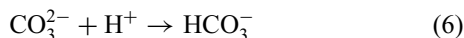
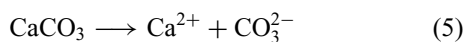
Table 4. Compressive ( $R_c$ ), bending ( $R_f$ ) strengths, water content ( $W$ ), ignition loss (IL), water absorption capacity, dry density and porosity of mortars studied.

	Material		
	S(PbO)	S(Cr <sub>2</sub> O <sub>3</sub> )	S(Ni <sub>2</sub> O <sub>3</sub> )
$R_c$ (MPa)	24.96	42.32	31.52
Standard deviation (MPa)	00.05	00.06	00.07
$R_f$ (MPa)	05.10	07.20	05.13
Standard deviation (MPa)	0.003	0.042	0.003
$W$ (%)	05.56	05.54	05.35
IL (%)	00.77	00.78	00.75
Absorption (%)	08.69	08.70	08.96
$\rho_s$ (kg.m <sup>-3</sup> )	1490	1400	1560
$P$ (%)	12.91	12.19	13.95

### 3.2. Transfer and leaching properties

#### 3.2.1. Acid neutralization capacity

The ANC test showed that the material has a high ANC. Figures 2 and 3 and Table 5 present the concentration evolution of different elements versus the pH. The equivalence pH value, equal to 9.2, corresponds to the limit of the hydrates' stability area of the main cement hydrates. Approximately 1.5–3 mol H<sup>+</sup>/kg of materials are necessary to neutralize the alkaline content. At values 11 and 12, the materials' pH increases slightly and linearly. This phenomenon may be attributed to (i) the consumption of elements containing alkaline, (ii) to the influence of portlandite (Ca(OH)<sub>2</sub>), which is consumed at pH = 12.4, and (iii) to the presence of C-S-H, whose limit stability is at pH = 11. A decrease of pH is observed between pH = 8 and 10, with the dissolution of carbonates (from sand), according to reaction (4). This dissolution is favoured by the addition of acid, which causes the formation of hydrogencarbonates according to reaction (5), which can make the environment highly acid:



Representing the concentrations released (mg/l) as a function of final eluate pH (Figure 4 and Table 5), as well as representing the final pH as a function of the initial acid or base amount (Figure 4 and Table 5), supply useful information concerning the global response of the studied material with regards to an acidic aggression (alkaline capacity), as

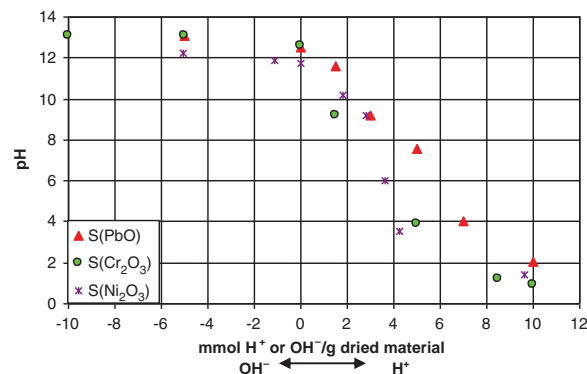
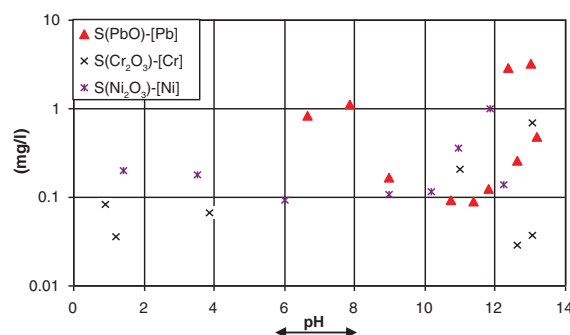


Figure 2. Acid neutralization capacity test versus materials.

Figure 3. Variation in concentration of Pb<sup>2+</sup>, Cr<sup>3+</sup> and Ni<sup>2+</sup> as function of pH in S(PbO), S(Cr<sub>2</sub>O<sub>3</sub>) and S(Ni<sub>2</sub>O<sub>3</sub>), respectively.

well as for each analysed pollutant. Indeed, small differences in solubility (ANC) were recorded in the different solidified materials. These differences are due to the nature of the chemical elements stabilized (Cr, Ni and Pb). As expected, the dissolution of alkaline metals and chlorides does not depend on the pH, whereas the solubility of calcium decreases when the pH increases and becomes very low for pH values above 12 (dissolution of portlandite). The behaviour of lead, chromium and nickel (amphoteric metals) depends strongly on the leachate pH. Their presence as oxides and hydroxides was expected (especially amorphous lead hydroxides).

#### 3.2.2. Pore water and maximum mobile fraction tests

Representing pH versus  $L/S$  ratio (Table 5), as well as representing pollutant concentrations versus  $L/S$  ratio (Figure 5

Table 5. Final released concentrations of the different chemical species as function of pH and  $L/S$  in ANC, PW and MMF tests.

	pH	K <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	L/S	K <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	pH	
		(mg/l)					(mg/l)					
S(PbO)	06.65	098	1908	454	278	PW test	01.24	390	045	456	0406	12.77
ANC test	08.97	100	0804	300	248		02.00	211	470	199	0313	12.69
	10.75	114	0684	248	216		05.00	078	499	143	0209	12.65
	11.36	118	0602	394	285		10.00	054	630	107	0128	12.61
	12.35	103	1088	350	184	MMF test	50.00	018	526	046	0027	12.38
	12.62	105	0446	285	153		100.0	011	255	039	0014	12.25
	13.00	093	0321	341	204		200.0	008	244	026	0009	12.17
S(Cr <sub>2</sub> O <sub>3</sub> )	00.89	091	9511	100	107	PW test	01.24	511	325	328	0390	12.73
ANC test	01.20	100	8178	100	104		02.00	390	636	263	0280	12.68
	03.87	101	6549	090	170		05.00	201	799	161	0121	12.61
	11.00	104	3238	144	195		10.00	120	763	163	0057	12.61
	12.61	120	0754	163	185	MMF test	50.00	060	100	048	0018	12.40
	13.05	163	0190	220	210		100.0	029	086	022	0009	12.23
	13.07	165	0110	215	212		200.0	014	067	003	0004	12.04
S(Ni <sub>2</sub> O <sub>3</sub> )	01.42	055	1219	034	301	PW test	01.24	345	073	245	2366	12.60
ANC test	03.52	066	1148	027	337		02.00	225	071	154	1952	12.58
	06.02	054	1038	027	363		05.00	149	069	123	1704	12.54
	08.96	064	0811	032	408		10.00	077	066	062	1390	12.52
	10.95	064	0412	033	505	MMF test	50.00	026	045	027	0722	12.32
	11.85	062	0205	028	700		100.0	025	030	026	0491	12.20
	12.25	046	0098	020	900		200.0	009	021	012	0308	11.93

and Table 5), contains information on the available quantities and solubility of different elements. A decrease in  $L/S$  ratio induces a pH increase (Table 5). Three pH levels were observed close to the three solidified/stabilized materials (S(PbO)-pH = 12.77, S(Cr<sub>2</sub>O<sub>3</sub>)-pH = 12.73 and S(Ni<sub>2</sub>O<sub>3</sub>)-pH = 12.60). These values are in accordance with the high concentrations of sodium and potassium observed in the pore solution, which govern the pH values. The evolution of sodium, potassium and chloride elements plotted on a logarithmic scale presents a linear profile (Table 5). The rapid decrease in their concentrations allows one to assume that these elements came from the progressive dilution of an initial available quantity; hence, the decrease of the ratio  $L/S$  induces only an increase in leach solutions' concentration. The calcium case is more complex because this element depends strongly on chemical context and pH (Table 5). Calcium is a divalent cation and the change in its concentration has a noted linear trend with pH values. The material's dissolution does not follow linear trends. The Ca<sup>2+</sup> concentrations decrease with the decrease in the  $L/S$  ratio (PW test) and increase with the increase of the  $L/S$  ratio (MMF test). The solubility of lead, chromium and nickel increases with the decrease of  $L/S$  (in the PW test), and it decreases with the increase of  $L/S$  (in the MFF test). In fact, the behaviour of calcium is governed by the dissolution of portlandite (Ca(OH)<sub>2</sub>) at pH > 12 and C-S-H below this pH value. The lead concentration does not match the amount of the initially added lead to the material. However, the concentrations of chromium and nickel match the solubility of solids incorporated into the solidified/stabilized materials. The initial composition

of the pore solution in each solidified/stabilized material (Table 6) is estimated from the  $L/S$  equivalent to the WAC. The  $L/S$  ratio is estimated from the WAC in the MLT.

### 3.2.3. Monolith leaching test: evolution of pH and elements studied

The dynamic MLT gives the physico-chemical parameters of eluates at the end of each leaching sequence: the concentration and flux released from each involved element (pH, conductivity, etc.) of the eluate of each sequence. The evolution of pH versus time is given in Table 5, while flux transfer versus the average time ( $t_a$ ) for the controlled chemical elements is presented in logarithmic scale in Figure 1 and Table 2. In a first leaching step, surface phenomena may make an important contribution. After this, the dissolution phenomena and the diffusion in the porous material govern the chemical elements' kinetics release. The results show low amounts and concentrations of the analysed leached elements. The pH of the eluate remains almost constant during the test for the three solidified/stabilized materials: 11.60 for S(PbO), 11.84 for S(Cr<sub>2</sub>O<sub>3</sub>) and 11.36 for S(Ni<sub>2</sub>O<sub>3</sub>) averages were recorded. Differences in the eluates' pH values in the three solidified/stabilized materials concord with different alkalinities. In the case of Na and Cl, the beginning of the release (the first points on the graphs) is of a diffusional type, since the curve of slopes is close to (-0.5) [44]. After that, the fluxes decrease rapidly due to source exhaustion. The release of calcium, lead, chromium, nickel and sulfate ions is governed both by diffusion through pore solution and by the conditions of chemical equilibrium.

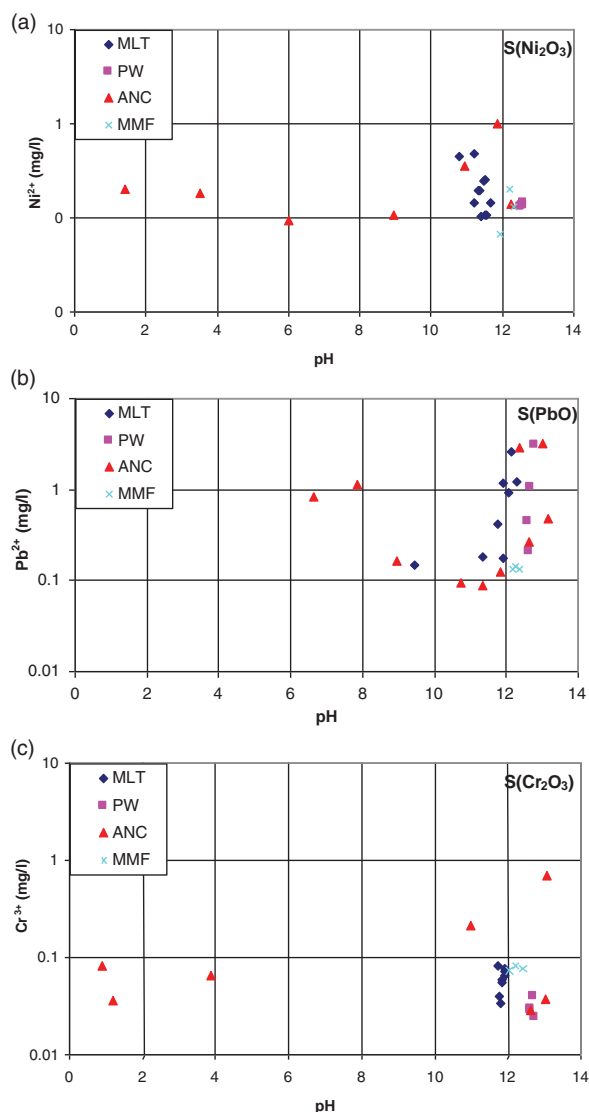


Figure 4. Elements released in the monolith leaching dynamic test (MLT) compared with the equilibrium tests (acid neutralization capacity (ANC) and pore water (PW) – maximum mobile fraction (MMF)) as a function of pH for nickel, lead and chromium elements in  $\text{S}(\text{Ni}_2\text{O}_3)$ ,  $\text{S}(\text{PbO})$  and  $\text{S}(\text{Cr}_2\text{O}_3)$ , respectively.

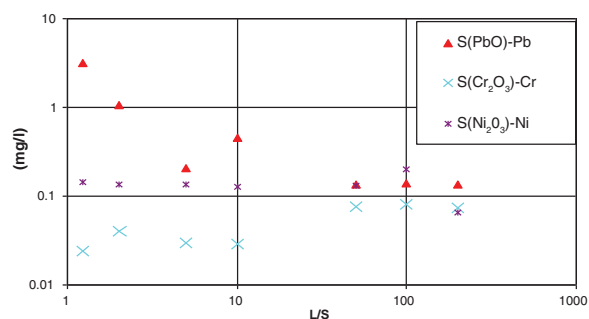


Figure 5. Evolution of concentration of  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  as function of liquid/solid ratio ( $L/S$ ) in  $\text{S}(\text{PbO})$ ,  $\text{S}(\text{Cr}_2\text{O}_3)$  and  $\text{S}(\text{Ni}_2\text{O}_3)$ .

The release of calcium remains dynamic, because the solubility limit is not reached in the materials at the end of the test. The solubility of sulfates depends on the solubilization of calcium. When the calcium flux release is important, the sulfates flux is also important. The dissolution mechanism of ettringite highlights this dependence. Monitoring simultaneously the behaviour of a chemical element in the three solidified/stabilized materials (Figure 1 and Table 2) shows differences in leaching fluxes. These differences are mainly due to the kinds and the levels of the heavy metals incorporated in each material, which modify the mechanism of leaching processes by physical and chemical retention.

#### 4. Comparison between acid neutralization capacity, pore water-maximum mobile fraction and monolith leaching tests

The aim of these comparisons is to monitor, simultaneously, the evolution of chemical elements' solubilization as a function of pH and  $L/S$  ratio. The differences between these tests are the nature of the used leachate (acid, base or demineralized water) and  $L/S$  ratio with which the liquid–solid contact is achieved. The concentrations obtained by the MLT for calcium and chlorides are lower than those obtained by testing the ANC test. This means that the release of these elements is not limited by calcium and chloride saturation in the leachate of the monoliths and that a dynamic state prevails. Concentrations obtained by the MLT of sodium, potassium, chromium, nickel and lead are close to those obtained by the ANC test. Therefore, leachates seem to be saturated by these elements. Comparisons between results of leached concentrations obtained from different tests for the solidified/stabilized materials are given in Figure 4 and Tables 2 and 5. These illustrations highlight the maximum leached amounts and the corresponding involved tests, which are shown in Table 6. As shown in Table 6, the leaching yields of calcium, lead [ $\text{S}(\text{PbO})$ ], chromium [ $\text{S}(\text{Cr}_2\text{O}_3)$ ] and nickel [ $\text{S}(\text{Ni}_2\text{O}_3)$ ] appear to be controlled by the ANC test. This is mainly due to the influence of the ionic strength on the solubility and mobilization of Pb, Cr and Ni ions. On the other hand, the leaching yields of sodium, potassium and chloride appear to be controlled by the PW test.

#### 5. Scanning electron microscopy analyses and location of the damage

Figure 6 shows a strongly corroded surface compared to a given surface from the heart of the leached material. Soluble phases, mainly portlandite, were dissolved from the surface, leading to the leaching of heavy metals trapped in these phases. It would be desirable to assess the mechanisms of the leaching kinetics in order to improve the efficiency of these kinds of solidified/stabilized materials.

Table 6. Leachable quantities available and maximum extracted quantities.

Dried materials	Element	Applied test	Leachable quantities available (g/kg)	Maximum extracted quantities (g/kg)
S(PbO)	K <sup>+</sup>	PW	21.71	03.90
	Na <sup>+</sup>	PW	12.11	04.56
	Cl <sup>-</sup>	PW	39.73	04.06
	Ca <sup>2+</sup>	ANC	19.09	19.09
	Pb <sup>2+</sup>	ANC	00.03	00.03
S(Cr <sub>2</sub> O <sub>3</sub> )	K <sup>+</sup>	PW	21.68	05.11
	Na <sup>+</sup>	PW	12.09	03.28
	Cl <sup>-</sup>	PW	39.67	03.91
	Ca <sup>2+</sup>	ANC	65.49	65.49
	Cr <sup>3+</sup>	ANC	00.01	00.01
S(Ni <sub>2</sub> O <sub>3</sub> )	K <sup>+</sup>	PW	21.22	03.45
	Na <sup>+</sup>	PW	11.92	02.45
	Cl <sup>-</sup>	PW	38.79	23.66
	Ca <sup>2+</sup>	ANC	12.19	12.19
	Ni <sup>2+</sup>	ANC	00.01	00.01

PW: pore water test ANC: acid neutralization capacity

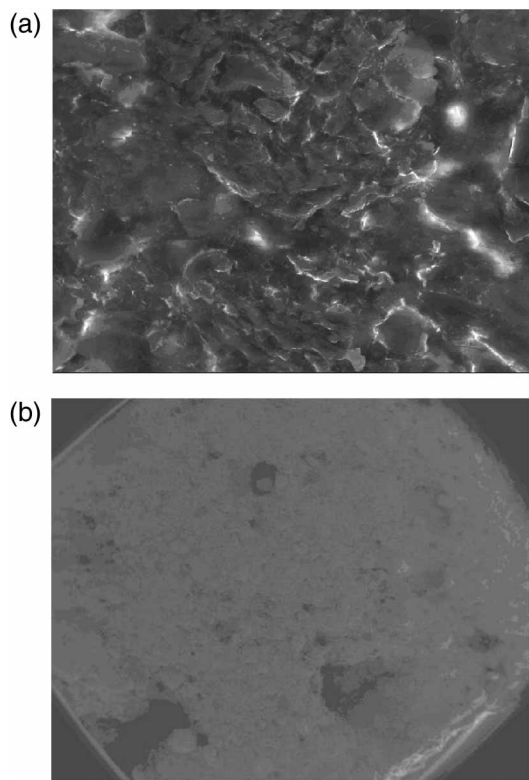


Figure 6. SEM images of (a) the leached surface and (b) the core of the material. (a) Magnification: 1200 $\times$ . (b) Magnification: 24 $\times$ .

## 6. Conclusion

This experimental study was carried out in order to determine the influence of laboratory leaching conditions on the release of different chemical elements contained in a cementitious material obtained by solidification of

PbO, Ni<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> with blended Portland cement (CEMII-B32.5 according to European Standards). The materials obtained by solidification/stabilization were first characterized to determine the intrinsic physico-chemical properties by applying two equilibrium tests. This approach allowed the assessment of the pH influence and the *L/S* ratio on the pollutants' dissolution kinetics. The composition of the initial pore solution and the soluble phases containing different elements were quantified. Then, the dynamic leaching test (sequential monolith and renewal) was applied. Differences were observed in the leaching behaviour of the monitored elements in the four tests. Comparisons between leaching behaviours were performed with regards to two quantitative criteria: eluate concentrations and elements' flux.

Generally, potassium and sodium concentrations (which are soluble elements) in the dynamic test eluates were significantly lower than in the equilibrium tests. pH values of eluate in dynamic and all equilibrium tests were mainly determined by alkalines and calcium concentrations. However, pH values observed in the dynamic test were lower than in the PW test. Calcium shows a visible artefact in its behaviour: the concentrations in the eluate are higher than those in the pore solution. The mechanism of calcium diffusion from the pore solution cannot explain its high concentration in eluates. As a matter of fact, the hypothesis of a material surface-layer dissolution phenomenon is more plausible. Eluates' concentrations in other elements were lower than those in pore solution. Their release seems to be controlled by the eluate saturation. The eluate saturation depends on the test protocol, in particular the liquid/solid contact conditions: the *L/S* ratio, immersion time and sample shape (leachate/solid exchange surface). The high specific exchange surface of the granular materials allows high leaching kinetics.



Globally, the assessment of the environmental impact of materials on leaching scenarios requires data such as pollutants fluxes and evolutions of eluates' concentrations. In this paper, the significant influence of the different leaching conditions on the observed leaching behaviour was highlighted. Therefore, the environmental prediction based on laboratory tests requires studies focusing on correlations between laboratory and in situ conditions with respect to the variety of mass transfer parameters (leaching renewal versus diffusion, etc.) and their influence on the leaching kinetics.

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