

# MODELING AND EVALUATION OF THE PERFORMANCE OF THE STABILIZATION/SOLIDIFICATION PROCESS OF HAZARDOUS COMPOUND PbO BY TOXICITY CHARACTERISTIC LEACHING PROCEDURE TEST

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*This article focuses on the study of the release of  $Pb^{2+}$ , stabilized/solidified by hydraulic binder (cement CEM II-42.5) for 28 days in an acid medium. Three mortars were prepared with different percent of PbO namely 0.6, 0.96 and 1.2%. Vicat needle indicated that lead retards the hydration process of mortars compared to the control sample. In the study interval [0.6%-1.2%], the increase in the percentage of PbO in mortars decreased the mechanical strength. The release of lead during TCLP test (Toxicity Characteristic Leaching Procedure) and the effectiveness of the process of Solidification/Stabilization depended on the initial concentration of the pollutant ( $Pb^{2+}$ ), and of the time of leaching. The use of X-ray diffraction allowed the identification of the new complex crystalline phases within the structure of Stabilized/Solidified samples, namely:  $Pb_2Al_4(OH)_8(CO_3)_4 \cdot 3H_2O$  and  $Pb(OH)_2$ . This study was completed by modeling the experimental data which revealed that the release process is much more a surface phenomenon (dissolution or precipitation). The evaluation of degradation of samples gave no sign of any major deterioration of the stabilized/solidified materials.*

**Keywords:** Hazardous compound (PbO); TCLP test; Leaching; X-ray diffraction; Modeling; Degradation

## 1. Introduction

Many articles and conferences have treated the immobilization of heavy metals to restore a green environment [1-15]. An improper removal of heavy metals can cause serious environmental and ecological problems, because water is considered as the main vector that transports toxic pollutants into the environment [4, 7, 15]. These threats have started a special attention to appropriate treatment technologies of heavy metals [5, 11, 12, 16]. One of the powerful techniques is Solidification/Stabilization (S/S) by hydraulic binders, especially cement. The use of cement as hydraulic binder is one of the most used methods because of its low cost, good mechanical properties, chemical fixation, low porosity and the resulting alkaline pH making these metals insoluble with a reduced environmental impact [17]. Several recent research tasks, on the immobilization of heavy metals, have been carried out by many researchers throughout the world [1-15]; however, the relationship between the incorporation of waste in the cement matrices and leaching is not fully understood.

Solid wastes generated by industrial activity, are considered as the most hazardous waste due to their generation in large quantities and their dangerous polluting character due to the presence of heavy metals, namely: lead, nickel, chromium, arsenic, zinc [9-11, 18]. Lead (Pb) is considered as one of the top five most toxic heavy metals [9, 11], due to its harmful effects that can touch groundwater, soil, fauna and flora.

The present article focuses on the evaluation of the immobilization of PbO by stabilization/solidification process using cement CEM II-42.5. To do this, the release of lead ( $Pb^{2+}$ ) was followed during Toxicity Characteristic Leaching Procedure test TCLP. This paper studies also the interactions between the hydrated cement phases and lead ( $Pb^{2+}$ ). The empirical model of Cote was used jointly with statistical criteria to evaluate: the effectiveness of S/S process, to predict the release of lead ( $Pb^{2+}$ ) and the degradation of the mortars made up using XRD analysis. This scientific approach will help to understand the elimination process of lead-rich industrial wastes before its landfilling in hazardous waste storage centers.

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Table 1

Compositions of stabilized/solidified mortars

Indicative composition	Composition %				Water/Cement ratio
	Sand	Cement	Water	PbO	
C-0	62.53	24.98	12.49	-	0.5
C-0.6	61.93			0.6	
C-0.96	61.57			0.96	
C-1.2	61.33			1.2	

## 2. Materials and methods

### 2.1. Materials and preparation of stabilized/solidified samples

The materials used in the composition of mortars were: cement (CEM II-42.5) of the plant of Ain El-Kebira Algeria, hazardous compound PbO, normalized sand and finally deionized water to avoid contamination by trace elements [19]. The pollutant content of PbO is generally 0.6%, 0.96% and 1.2% (by weight) for pollution levels considered as plausible [19]. The mixes made up are recorded in Table 1.

An important problem that can occur during samples preparation is surface carbonation: atmospheric carbon dioxide can quickly give rise to a thin layer of calcite CaCO<sub>3</sub> on the surface which can obstruct the surface porosity and have significant consequences on the kinetic of leaching [20]. This leads us to adapt a method of samples preparation which protects them to the maximum of the air. We used a water/cement ratio of 0.5 to promote the pollutants diffusion [19].

Each sample was prepared in a mixer of 3 kg. First, normalized sand and pollutant (PbO) are mixed at medium speed in order to obtain a homogeneous mixture. Cement and deionized water are then added and the mixture is mixed for a few minutes. After mixing, the mortars were poured into moulds of 4x4x16 cm<sup>3</sup> and 8x8x21 cm<sup>3</sup> for preparation of monolithic blocks of 4x4x4 cm<sup>3</sup>, then they are stored away from the air at room temperature (20 ± 3°C) for 28 days for hardening.

### 2.2. Methods

#### 2.2.1. Setting times

Vicat needle was used to determine the initial and final setting times according to the NA 1942 standard [21], in order to study the influence of PbO on cement hydration.

#### 2.2.2. Mechanical strengths

After 28 days of hardening, prismatic samples of size 4x4x16 cm<sup>3</sup> have subjected to mechanical tests according to the NA 234 standard [22]. The test consists in determination of the tensile and compressive strengths of prismatic specimens of mixes made up. Each sample was analyzed in triplicate.

#### 2.2.3. X-ray diffraction analysis

XRD analysis was used for the characterization of stabilized/solidified samples at

different time (before and after leaching) by X'Pert PRO PANalytical Diffractometer. The samples were analyzed as powders (particle size < 80 µm).

#### 2.2.4. Thermogravimetric analysis TGA

In our case, TGA analysis technique was used to study the influence of the addition of PbO on the hydration degree of the cement. The instrument used in our study was SETARAM TG-DTA 92. During the test, the sample was placed in the furnace; the temperature was increased from ambient to a temperature of 1200 °C with a heating rate of 10 °C/min that remains constant along the test. At the end of the test, we obtained a curve giving the loss of mass as a function of the temperature rise. The hydration degree α (t) after 28 days of hardening was then calculated with the equation 1 [23]:

$$\alpha(t) = \frac{m_{el}(t)}{W_{el}(\infty) \times m_c} \times 100 \quad (1)$$

Where:

- m<sub>el</sub> (t) is the mass of water related to cement at the instant « t » in (kg);
- m<sub>c</sub> - the anhydrous mass of cement introduced into the sample in (kg);
- W<sub>el</sub>(∞) - amount of water required for complete hydration of the cement (%); it is very approximately estimated according to the cement composition by Bogue formula [23].

#### 2.2.5. Toxicity Characteristic Leaching Procedure test (TCLP)

TCLP test aims to assess the leachability potential of stabilized/solidified samples in time (modified test 50 hours instead of 18 hours) as defined by the EPA method 1311 [24]. The samples made up were crushed to reduce their sizes to a diameter less than 9.5 mm. The extraction fluid used in TCLP test was: extraction fluid 1 (the solution was prepared by mixing of 5.7ml glacial CH<sub>3</sub>CH<sub>2</sub>OOH and 64.3ml of 1N NaOH and dilution to a volume of 1 liter, the pH of this fluid has to be 4.93 ± 0.05). The amount of extraction fluid was equal to 20 times the volume of the solid phase. The bottles were placed on rotary agitation apparatus for 50 hours with a rotation speed of 30 ± 2 rpm under stirring. At the end of this period of time, the leachate obtained was filtered. Leachates obtained was then acidified to pH 2 with HNO<sub>3</sub> 65% in order to determine Pb<sup>2+</sup> concentration by flame atomic absorption

spectrophotometry (FAAS) Aurora Instruments AI 1200.

**2.2.6. Monolithic leaching test (MLT) [25]**

As regards this test, a monolithic block of 4x4x16 cm<sup>3</sup> is placed in contact with a fixed volume of leachant. Leachants used is that of TCLP test (extraction fluid 1). The leachant is renewed after 0.25; 0.75; 1; 2; 5; 7; 20 and 28 days, giving a total of 64 days of continuous leaching, this duration is the equivalent to 96 years of leaching. At each leachant renewal, Liquid/Surface ratio (L/Sf) is maintained constant and equal to 10 cm<sup>3</sup>/cm<sup>2</sup>. The test was performed at room temperature (23 ± 1 °C) and protected from light and air penetration (CO<sub>2</sub>). At the end of the test, we determine the intensity and dynamics of release of Pb<sup>2+</sup>, then, monolithic blocks were subjected to XRD analysis in order to evaluate the degraded thickness of monolithic blocks in terms of peak intensities of portlandite.

**2.2.7. Modeling and simulation of Pb<sup>2+</sup> release in the leachate**

By combining the cumulative fractions forms of three equations developed in the model of Cote [26-28], the semi-empirical expression of cumulative fractions leached (CFL) of waste can be derived from the following general form:

$$CFL(t) = \frac{M(t)}{M_0} = K_1(1 - e^{-K_2 t}) + K_3\sqrt{t} + K_4 t \tag{2}$$

The first term of equation (2) represents the contribution of the species whose release kinetics is controlled by species exchange between the sample surface and the leachant. The second term, is the solution of the equations of diffusion (Fick's law), representing the contribution of species whose release is controlled by pure diffusional transport. The third term expresses the release of species controlled by first order dissolution kinetics. Our predictive study will therefore be carried out using the empirical model of Cote coupling diffusion, chemical reaction and surface phenomenon. The parameters K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub> and K<sub>4</sub> were determined using the convergence of the model of Cote by simplex method on the experimental data of the released chemical species. For the validity of the Cote model, we used four different statistical criteria, namely: residual variance, correlation coefficient, Student test and Fisher Snedcor test. R<sup>2</sup> is the proportion of the variance of y explained by the explanatory variables. It is used to test the quality of fit of y by  $\hat{y}$  and is expressed by the following relation:

$$R^2 = \frac{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \tag{3}$$

The unexplained part by regression called residual variance is given by the following amount:

$$S_r^2 = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y})^2 \tag{4}$$

The estimation of the influence of the regression coefficients is performed by Student test which is based on statistics:

$$T = \frac{|C_j|}{\sigma(C_j)} \tag{5}$$

On the other hand, the overall validity of the model is carried out by Fisher test, which is based on the following statistic:

$$F = \frac{\sum_{i=1}^n (y_i - \bar{y})^2 / m - 1}{\sum_{i=1}^n (y_i - \hat{y})^2 / n - m} = \frac{\frac{R^2}{m-1}}{\frac{1-R^2}{n-m}} \tag{6}$$

**3. Results and discussions**

**3.1. Initial and final setting times**

Initial and final setting time results of samples are given in Figure 1.

It seems that the increase of PbO amount in the mixtures increases the initial and final setting times of cement. This can be explained by the fact that the addition of lead contributes to the formation of new phases which slow down the hydration of cement grains, the hydrates formation and consequently the decrease of mechanical strengths is determined.

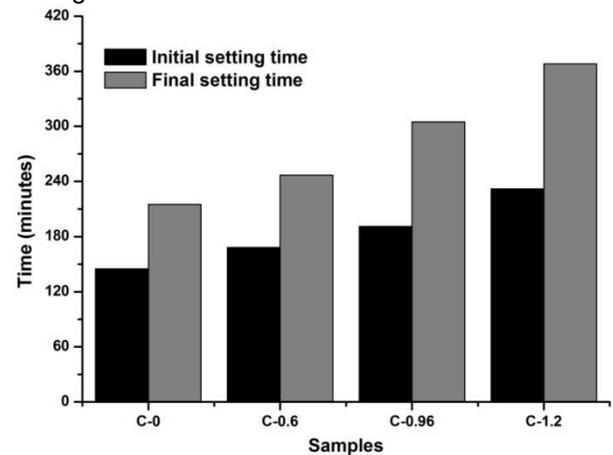


Fig. 1 - Initial and final setting times of samples.

**3.2. Mechanical strengths**

The results of compressive and tensile strengths of samples are illustrated in Figure 2.

Mechanical strengths of samples are in accordance with those required by X31-211 standard [29]. The results show that the mechanical strength values recorded for the mortars with PbO content are very low compared to those without PbO (C-0). This can be attributed to the influence of lead in the hydration of cement. Lead can precipitate as oxides, sulphates and

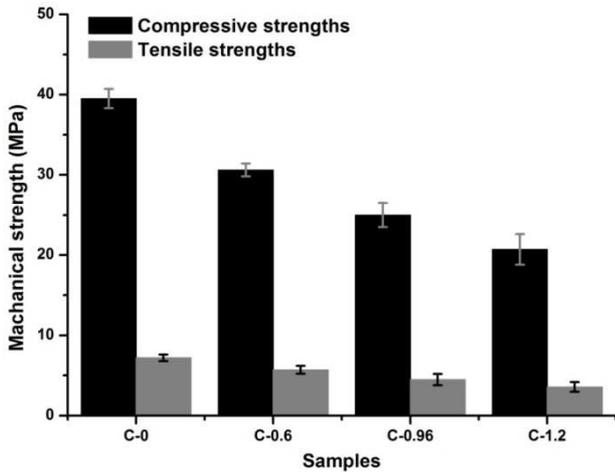


Fig. 2 - Tensile and compressive strengths of samples at 28 days of hardening.

carbonates, as it can replace calcium in the structure of portlandite and calcium silicate hydrate C-S-H. It can form new compounds and complex ions such as:  $Pb(OH)_2$ ,  $Pb(OH)^{-3}$  and other phases that retard hydration and setting time of mortars [30]. To better illustrate the effect of PbO addition on mechanical strengths of the samples, TGA analysis were performed in order to evaluate the hydration degree of stabilized/solidified mortars after 28 days of hardening. The results obtained are illustrated in Figure 3.

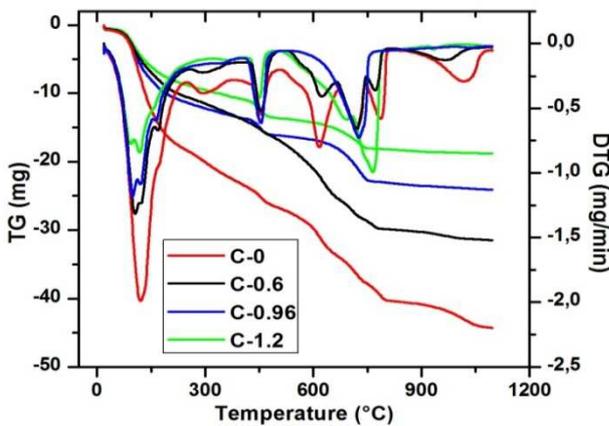


Fig. 3 - TGA analysis and hydration degree of samples after 28 days of hardening.

According to the TG curves of samples (Figure 3), it was possible to observe three major ranges of loss of mass, namely:

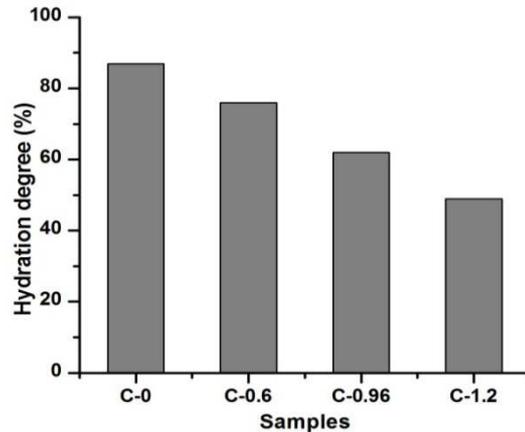
- Range 1 (100°C-400°C): the losses of mass are attributed to the dehydration of C-S-H, ettringite and calcium aluminate hydrate [31];
- Range 2 (400°C-600°C): the losses of mass are due to the decomposition of portlandite  $Ca(OH)_2$  formed during hydration [31];
- Range 3 (600°C-800°C): the losses of mass are due to the decarbonation of calcium carbonate ( $CaCO_3$ ) [31].

Also, we noticed that the total mass loss of C-0 sample (without PbO) is greater compared to samples containing PbO, this shows that the quantity of hydrates formed in C-0 sample is greater compared to samples with PbO. In addition, we note that the hydration degree of mortars containing PbO is lesser than that of control mortar. For mortars doped by PbO, it was proved that the hydration degree decreases with the increase of PbO amount. The addition of PbO in large amounts decelerates and blocks the formation of portlandite and calcium silicate hydrate "C-S-H" which determine the strength to of the mortars. The results of TGA analysis and hydration degree complete and are in a good correlation with the results concerning setting times, mechanical strength and TGA analysis.

### 3.3. Toxicity Characteristic Leaching Procedure test (TCLP)

The results of chemical parameters namely: the pH, cumulative concentrations and cumulative fractions leached of  $Pb^{+2}$  during TCLP test are presented in Table 2.

According to the results shown in Table 2, we recorded on the one hand, at pH and t (time) lower respectively than 6.36 and 18 hours (zone 1), an increase in the cumulative concentrations of lead. In zone 1, solubilization of  $Pb^{2+}$  is strongly dependent on pH; this can be attributed to the concentration gradients between pore water of



cementitious material and aggressive leachant; the difference between concentrations creates a transfer of ions by diffusion and a release of  $Pb^{2+}$  contained on the outer surface of mortar particles (water-washing phenomenon) [32].

On the other hand, at pH and t (times) higher than 5.36 and 18 hours (zone 2), the pH of the leachant continues its increase and the variation of the cumulative concentrations of  $Pb^{2+}$  becomes very low. This stabilization is due essentially to: (i) the dissolution of portlandite (when pH is lower than 12.5) [33], (ii) the decomposition of ettringite and C-S-H until a silica gel residue is obtained (when pH is lower than 10.6

Table 2

Chemical parameters of stabilized/solidified mortars after 50 hours of leaching

Indicative composition	pH	Cumulative time (h)	[Pb <sup>2+</sup> ] (μmol/L) in leachate	[Pb <sup>2+</sup> ] <sub>0</sub> (μmol/L) initial concentration	CFL
C-0.6	5.19	2	12.75	50500	2.525 e-04
	5.21	4	17.83		3.531 e-04
	6.36	18	28.50		5.644 e-04
	7.54	26	28.26		5.596 e-04
	9.61	42	28.60		5.667 e-04
	10.47	50	28.94		5.731 e-04
C-0.96	5.08	2	14.59	80780	1.806 e-04
	5.12	4	21.35		2.643 e-04
	6.29	18	32.37		4.007 e-04
	7.76	26	32.27		3.995 e-04
	9.58	42	32.37		4.007 e-04
	10.66	50	32.61		4.037 e-04
C-1.2	5.05	2	17.83	103400	1.724 e-04
	5.10	4	23.48		2.271 e-04
	6.30	18	38.65		3.738 e-04
	7.96	26	38.16		3.691 e-04
	9.48	42	38.89		3.761 e-04
	11.75	50	38.16		3.692 e-04

and 8.8, respectively) [33] and (iii) the dissolution of strongly soluble phases (KOH and NaOH) which neutralize the acidity of the leachant (i.e. the pH becomes close to that of the strongly basic interstitial solution of cement mortar) and consequently the Pb<sup>2+</sup> release becomes very weak [33].

Also, it was observed that leachant concentrations of stabilized/solidified Pb<sup>2+</sup> are very low compared to the amount of PbO initially added in the mixes; this explains that Pb<sup>2+</sup> was retained in the structure of cement matrices. To better illustrate the influence of PbO on the hydration product of cement CEM II, XRD analysis were performed on the samples with PbO after 28 days of hardening.

The XRD patterns in Figure 4 show that the addition of PbO has an important influence on the hydration of cement. According to Figure 4, we observe:

- The presence of anhydrous cement compounds "C<sub>2</sub>S and C<sub>3</sub>S", this confirms the results obtained during TGA analysis;
- The presence of portlandite Ca(OH)<sub>2</sub>, which is the product of hydration reactions;
- The detection of SiO<sub>2</sub>, which is due the presence of normalized sand. The small peaks for SiO<sub>2</sub> after leaching are due to the migration of a quantity of silica (SiO<sub>2</sub>) to the leachate during TCLP test;
- The formation of new crystalline phases, namely: Pb<sub>2</sub>Al<sub>2</sub>(OH)<sub>8</sub>(CO<sub>3</sub>)<sub>4</sub>3H<sub>2</sub>O and Pb(OH)<sub>2</sub>. The latter explains the success of Pb<sup>2+</sup> trapping within the cement matrices of samples in the form of the less soluble complex phases.

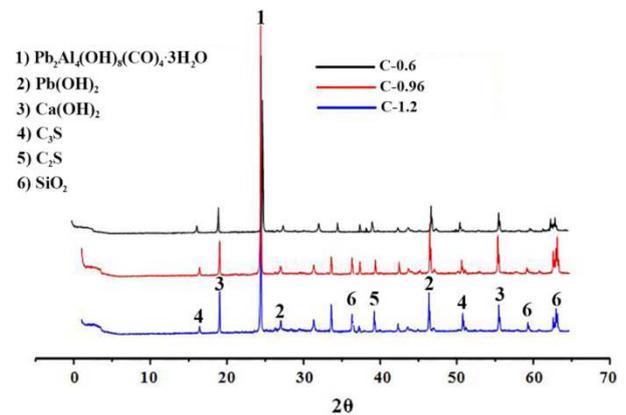


Fig. 4 - Influence of PbO on the hydration products of cement CEM II after leaching.

### 3.4. Modeling of leaching

Modeling the experimental data of cumulative fractions leached by the empirical model of Cote gave a great similarity between the experimental and simulated values as shown in Figure 5. Tests of validity of the models used and their parameters are recorded in Table 3.

The parameters recorded in Table 3 revealed:

- That the phenomenon of surface (dissolution or precipitation) outweighs the process;
- That the constants K<sub>4</sub> and K<sub>3</sub> which respectively evaluate reaction and diffusional components indicate that the phenomenon of chemical reaction and diffusion are completely absent in the medium considered.

Statistical tests of the models adopted have resulted in general:

Table 3

Simulated parameters and statistical tests of the proposed model for stabilized/solidified mortars

Mechanisms controlling the release of Pb <sup>2+</sup> for C-0.6					
	Surface phenomenon $K_1(1 - e^{-K_2 t})$		Diffusion $K_3\sqrt{t}$	Chemical reactions (dissolution or precipitation) $K_4 t$	Correlation coefficient
Coefficients	K <sub>1</sub>	K <sub>2</sub>	K <sub>3</sub>	K <sub>4</sub>	R <sup>2</sup>
	0.00057	0.26468	-	-	0.999
Student test T (n-m, α/2=3.365)	98.17	-	-	-	
Fisher test (F <sub>tabulated</sub> =13.70)	∞				
Residual variance	1.52 e-10				
Mechanisms controlling the release of Pb <sup>2+</sup> for C-0.96					
Coefficients	K <sub>1</sub>	K <sub>2</sub>	K <sub>3</sub>	K <sub>4</sub>	R <sup>2</sup>
	0.0004	0.28146	-	-	0.997
Student test T (n-m, α/2=3.365)	176.34	-	-	-	
Fisher test (F <sub>tabulated</sub> =13.70)	∞				
Residual variance	2.39 e-11				
Mechanisms controlling the release of Pb <sup>2+</sup> for C-1.2					
Coefficients	K <sub>1</sub>	K <sub>2</sub>	K <sub>3</sub>	K <sub>4</sub>	R <sup>2</sup>
	0.0003	0.26596	-	-	0.999
Student test T (n-m, α/2=3.365)	67.80	-	-	-	
Fisher test (F <sub>tabulated</sub> =13.70)	∞				
Residual variance	1.37 e-10				

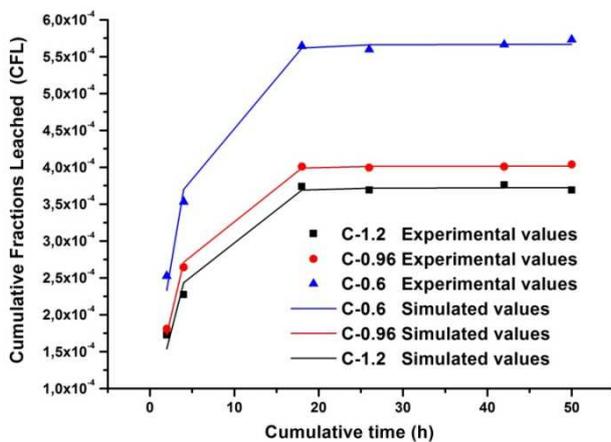


Fig. 5 - Cumulative fractions leached of solidified/stabilized samples versus time.

- A residual variances of the order of zero;
- A values of determination coefficients close to unity;
- Values calculated from Fisher tests are much greater than the values tabulated from Fisher tests, which validate the models on the whole;
- Values of Student tests indicate that all the coefficients of the models were retained except those that evaluate the coefficient K<sub>3</sub>;
- The release of lead (Pb<sup>2+</sup>) is governed by the surface phenomenon that has been revealed by the simplex method and confirmed by statistical tests.

### 3.5. Evaluation of the degradation of monolithic blocks during MLT test

To evaluate the degradation of synthesized materials we used two criteria

#### 3.5.1. Evaluation of the degradation in viewpoint cumulative concentration leached

To illustrate the degradation in viewpoint cumulative concentration leached by monolithic blocks in the medium of study, we used the criterion of rate leaching which is given in column 4 of Table 4.

Table 4

Leached rates of Pb<sup>2+</sup> during MLT test

Indicative composition	Initial concentration of Pb <sup>2+</sup> (C <sub>0</sub> ) in μmol/l	Cumulative concentration leached (C <sub>i</sub> ) in μmol/l	Leached rates (%) $= \frac{C_i}{C_0} \times 100$
C-0.6	50500	28.93	5.72 e-02
C-0.96	80780	32.60	4.03 e-02
C-1.2	103400	38.16	3.69 e-02

From the values of Table 4 (fourth column), there has been no significant deterioration in the mortars with PbO content. The low amounts of Pb<sup>2+</sup> leached for 64 days mentioned in Table 4 (third column) are very weak; this last observation shows that Pb<sup>2+</sup> is well fixed in the mortar structure.

### 3.5.2. Evaluation of the degradation in terms of portlandite peak intensities

This method consists in measuring the average intensity of the peaks of portlandite (before and after leaching) at different depths of the monolithic block recovered after MLT test. It is used as a criterion for material degradation [34].

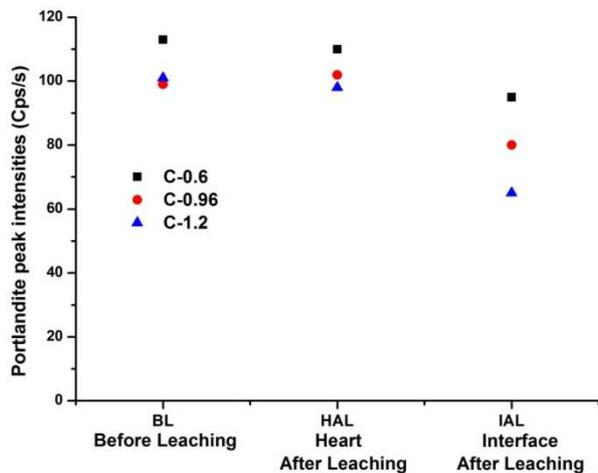


Fig. 6 - Evolution of the average peak intensities of portlandite before and after leaching of samples.

According to the evolution of the average peak intensities of portlandite (Figure 6), we can note the following ideas:

- The intensity of portlandite is of the same order of magnitude between scans BL (before leaching) and HAL (heart after leaching) is observed; this explains that the heart of blocks after leaching is non-degraded;

- A slight decrease of portlandite peak intensities between scans BL (before leaching), HAL (heart after leaching) and IAL (interface after leaching), this can be explained by the dissolution of portlandite of surfaces that are exposed to the medium of study;

- C-1.2 is little degraded with respect to C-0.6 and C-0.96; this is due to its low mechanical strength and hydration degree compared to C-0.6 and C-0.96.

### 4. Conclusion

At the end of this study, we conclude the following:

- The addition of PbO to cement increases the initial and final setting times;

- TGA analysis shows that the addition of PbO in large amounts decelerates and blocks the formation of portlandite and calcium silicate hydrate "C-S-H" which give improved strength to materials and consequently a decrease in the mechanical strength;

- TCLP test used to evaluate the leachability potential of stabilized/solidified  $Pb^{2+}$  reveals that the latter is retained into the phases formed during hydration of cement, such as:  $Pb(OH)_2$  and  $Pb_2Al_4(OH)_8(CO_3)_4 \cdot 3H_2O$  which are observed by XRD analysis;

- The phenomenon observed when stabilized/solidified  $Pb^{2+}$  mixes are brought into contact with leachants is much more a surface process;

- Studies carried out in terms of degradation of the samples gave no sign of any major deterioration of the stabilized/solidified materials;

- The results simulated by Cote model and statistical tests revealed that the surface phenomenon outweighs the diffusion phenomenon and that of the chemical reactions;

- The low amounts of leached Pb during MLT and TCLP tests justify the efficiency of the process of Stabilization/Solidification in the retention of hazardous wastes.

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