

Leaching in Acidic and Neutral Media of Heavy Metals from Cementitious Matrices Containing Ashes Resulting of Moukondo Landfill Waste Burning in Brazzaville (Republic of Congo)

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Abstract Inadequate management of ashes generated by household waste burning in open air leads to sites pollution, particularly through contamination with heavy metals (Pb, Ni, Cr, Cu, Zn...). The objective of this study is to evaluate the chemical durability of cementitious matrices containing ashes from waste burning by using static leaching tests. To do this, several cementitious matrices were synthesized with different ash/cement/lime ratios (P0, P1, P2, P3, P4, P5 and P6). These cementitious matrices then underwent leaching static tests at 25°C in acid (pH=4) and neutral (pH=7) media. Static leaching tests carried out on monoliths made it possible to evaluate heavy metals immobilization effectiveness in cementitious matrices network. The results of this study highlighted the good chemical durability provided by the stabilization/solidification of ashes in cementitious matrices. All cementitious matrices leachates present very low heavy metals concentrations with are below the standard applicable to leachate discharge. Heavy metals concentrations in cementitious matrices leachates are also very largely below the heavy metals concentrations released by raw ashes leaching. Heavy metals retention rates inside cementitious matrices range between 80 and 99% for arsenic, lead, chromium, copper, nickel and zinc.

Keywords: heavy metals, cement, ashes, leaching, stabilization, solidification

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1. Introduction

Household waste management has become a major concern in the Republic of Congo. These last years, Congolese cities have been facing several problems linked to accelerated urbanization. Urbanization consequences in terms of household waste management and sanitation are very worrying. Alongside this situation, there is an exaggerated increase of urban population (67% of the Congolese population) because the congolese population increased from 3, 697,490 inhabitants in 2007 to 5, 203,073 inhabitants in 2018 [1]. This growth, which goes hand in hand with waste amount increase, leads to illegal landfills proliferation. Brazzaville, populated by nearly 2 million inhabitants, only has one large public landfillunlike what is found in most cities in the world. However, there are small illegal landfills scattered across vacant lots in the city. These multiple landfills scattered throughout the city cause enormous hygiene, health and sanitation problems, even if they are burned from time to

time [2]. These landfills lead to environmental risks, notably causing significant ecological imbalances in soil and in water, through leachates and atmospheric pollution linked to released fumes [3]. Landfills are real risks for air, soil and water pollution. They produce a flammable, corrosive and toxic gas called landfill gas. This landfill gas is composed of biogas, air and volatile compounds. Biogas is mainly composed of CH₄ and CO₂, two greenhouse gases that contribute to global warming [4]. Volatile compounds are responsible for bad odors (they contain sulfur landfill gas (sulphur derivatives, dioxins, etc.). Fermentation juice from these landfills seeps through the ground by infiltration and can contaminate drinking water resources [5,6]. In addition, in Congo, solid waste is usually burned on the ground in open air. The formation of smoke and ashes can be dangerous to environment, due to their pollutant load. Indeed, ashes obtained during waste burning can contain heavy metals such as mercury, lead and cadmium [7]. Recent studies have shown that ashes from combustion can accumulate in soil and contribute significantly to pollutants sorption in soil and organic contaminants leaching reducing [8,9], as

well as heavy metals [10]. These ashes, considered as hazardous final waste, require additional treatment in order to reduce their impact on environment. Several treatments can be considered for ash management, including solidification/stabilization. Indeed, solidification makes it possible to transform waste into a massive solid that is not very porous and not very permeable in order to limit as much as possible their dispersion in environment [11]. Stabilization consists of physical and/or chemical retention of polluting species in a solid matrix by absorption or ionic exchange mechanisms [12] in order to make them poorly soluble and poorly mobilized. This two processes product thus makes it possible to limit pollutants dispersion in the natural environment. The stabilization/solidification of waste containing more or less soluble heavy metals by addition of a hydraulic binder consists of producing a material in which wastes replace sand or aggregates so that metals remain “trapped” in cementitious matrix. Different physicochemical mechanisms at the interface can allow heavy metals trapping [13,14]. The aim of this study is to evaluate the retention power of heavy metals cementitious matrices containing waste ashes resulting from stabilization/solidification by hydraulic and pozzolanic binders in acidic and neutral media. This assessment is based on leaching tests inspired by standardized tests applied to porous materials obtained by ashes stabilization/solidification.

2. Material and Methods

2.1. Study Site

This study was carried out in Brazzaville in Republic of Congo. Located in Central Africa in equatorial forest heart, straddling the equator between latitudes 3°30' North and 5° South and longitudes 11° and 18° East, the Republic of Congo covers an area of 342,000 km². Located on the right bank of the majestic Congo River, the agglomeration of Brazzaville covers an area of nearly 265 km². Brazzaville is located in the southern part of Congo, between 4°6'15" and 4°22'30" southern latitude and between 15°6'0" and 15°19'15" east longitude, bounded to the north by the Djiri River, to the south and east by the Congo River, and to the west by the sub-prefecture of Goma-Tsé-Tsé [15]. The wild landfill chosen for this study was named «Landfill C». With a latitude of 4°13'13"S and a longitude of 15°15'46"E, it is located in «City of 17» quarter in district N°7 Mfilou. It has an inclined geomorphology and an approximately depth of 20m. It has been existing for over 20 years. Figure 1 shows a map of Brazzaville city and the localisation of landfill C chosen for this study. Figure 2 shows the wild landfill C.

2.2. Landfills Waste Sampling

Household waste collection in landfill C was carried out manually using gloves as well as a mask and garbage bags. Household waste batches were then weighed using a Pocket LBS scale. Ten (10) kilos were taken and transported to a drying place at the Faculty of Sciences

and Techniques of Marien Ngouabi University, within the plant chemistry and biohealth unit. Household waste was dried in the open air and at ambient temperature on plastic tablecloths of 2 m² each during two weeks. Household waste was burned in a garden incinerator for at least 1 hour. After burning, the residues obtained (ashes) were sieved using a 2 mm sieve, then ashes obtained were placed in plastic jars closed by a stopper to avoid any external contamination. It should be noted that these jars were carefully cleaned beforehand, then rinsed with distilled water to avoid any internal contamination. Figure 3 shows the jars containing ashes that were stored in laboratory at room temperature.



● : Wild landfill C

Figure 1. Map of Brazzaville city locating the wild



Figure 2. Wild landfill C



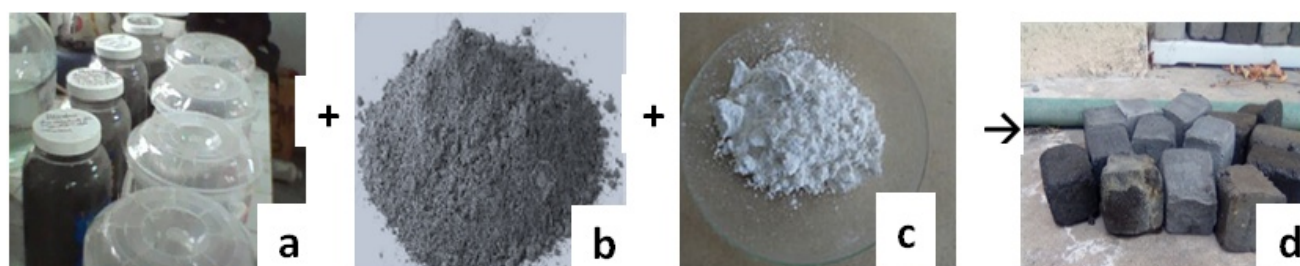
Figure 3. Ashes obtained after burning

Table 1. Composition of cement Portland of Dolisie (% weight)

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	NiO	PbO	Cr ₂ O ₃
64,8	17	6,5	4,6	3,3	2	1,8	/	/	/

Table 2. Formulations of cementitious matrices studied

Formulation (%weight)	P0	P1	P2	P3	P4	P5	P6
Ashes	0	50	70	50	50	70	70
Hydrated cement	100	50	30	40	30	20	10
Quicklime CaO	0	0	0	10	20	10	20
Water	150	250	250	270	270	270	270

**Figure 4.** Cementitious matrices synthesis a (ashes) + b (cement) + c (lime) → d (cementitious)

2.3. Materials Studied

In the context of our study, the hydraulic binder that we used is Portland limestone cement from the FORSPAK company in Dolisie in Congo. This Portland cement is of the CEM II/B-M 32.5R type. This cement is composed of (65-79)% clinker, (21-35)% pozzolan and fly ash then (0-5)% secondary constituents. Table 1 gives the composition by weight of the Dolisie cement used for our study. We used pascual hydrated lime as an admixture, manufactured in Spain and sold in Congo. Cementitious matrices synthesis was carried out according to the formulations contained in Table 2. The ash masses, hydrated cement and quicklime were weighed using a Pioneer-type precision balance. The different mixtures types (ashes + cement + lime + water) were mixed for 5 minutes in a container. The paste obtained is placed in molds measuring 2 cm x 2 cm x 2 cm to obtain a cementitious matrice (Figure 4). After synthesis, the cementitious matrices were dried at ambient temperature (25°C).

2.4. Static Leaching Tests of Cementitious Matrices

All leaching experiments in our study were carried out in static mode on monolith in a non-agitated closed environment. It consists of placing cementitious matrices monoliths in an altering solution in a rigid glass bottle so that all sample surfaces are in contact with solution. These experiments were carried out over short times, far from saturation, to avoid external contamination of solutions. The glass bottles were cleaned before each leaching experiment with 1N hydrochloric acid, then rinsed 5 times with deionized water. After leaching, cementitious matrices samples are then removed from the leaching solution and then dried and weighed. Then, a part of leachate is taken in order to measure pH. A single temperature was chosen for our experiments: 25°C. This temperature was chosen because it avoids evaporation. The ratio surface of matrice / volume of altering solution

(S/V) was fixed for the entire leaching duration at 0.1. A low S/V ratio choice makes it possible to move away from saturation conditions and thus to follow pH evolution, masses losses and dissolution rates during alteration. We have selected two (2) solutions with different pH: a solution of distilled water at pH=7 and a slightly chloride acidic solution HCl at pH=4. The solution at pH=7 was chosen to compare with attack in a slightly corrosive medium and the slightly acidic solution at pH=4 was chosen to simulate acid rain attack. Twenty three (23) leaching times, between 0 and 180 days, were chosen in order to follow the cementitious matrices alteration kinetics.

2.5. Leachate Analysis Methods

The ICP-OES technique was used to analyze the overall chemical composition of leachate by dosing the major and minor the elements. These analysis were carried out using an inductively coupled plasma optical emission spectrometer (ICP-OES) by the DIN EN ISO 11885 method at the Fresenius Institute laboratory in Germany in collaboration with the SGS-Congo laboratory in Pointe-Noire. The measuring equipment used located in laboratory is Agilent Technologies 5110 ICP-OES type.

2.6. Determination of Heavy Metals Contents in Raw Ashes and Cement

In order to determine heavy metal contents in ashes and cement, we carried out leaching tests according to the X31-210 Afnor standard : 5g of ash or cement was placed in contact with 50g of distilled solution (solid/liquid ratio=0.1) with continuous stirring at room temperature (25°C) for 16 hours. After 16 hours of contact, leachate is filtered through filter paper and the solid is recovered and dried in an oven at 100°C to allow residual water evaporation. The filtrate obtained was analyzed by the DIN EN ISO 11885 method at the Fresenius Institute laboratory in Germany in collaboration with the SGS-Congo laboratory using optical emission spectrometry with Inductively coupled plasma (ICP-OES).

3. Results and Discussion

Cementitious matrices underwent static leaching and neutral (pH=7) media. Table 3 and Table 4 give heavy metals concentrations released by the cementitious matrices, respectively at pH=4 and pH=7.

3.1. Heavy Metals Leaching

3.1.1. Arsenic Leaching

Table 3 and Table 4 show arsenic behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 and 7 at 30, 90 and 180 days. Arsenic is not detected in all cementitious matrices leachates. None of cementitious matrices releases arsenic in solution whatever the pH and leaching times. The low leaching of arsenic is certainly due to the fact that arsenic can form calcium-arsenite complexes (Ca-AsO_3^{3-}) which limit its mobility and increase cement setting [16, 17]. In the presence of As^{5+} ions, hydration is delayed due to $\text{Ca}_3(\text{AsO}_4)_2$ formation, which is very poorly soluble [18]. Arsenic is therefore effectively immobilized when it is oxidized in +5 form [19]. As^{3+} ions can be significantly adsorbed by C-S-H; this adsorption capacity decreases when the Ca/Si increases [20].

3.1.2. Lead Leaching

Table 3 shows lead behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4. Only leachates from cementitious matrices P3, P4 and P6 contain lead released in solution. P6 releases low concentrations of lead in solution around 0.005 mg/l at all leaching times. P3 releases lead in solution only after 30 days with a concentration around 0.007 mg/l. P4 releases lead only at 90 days but with a much higher content around 0.13 mg/l. Figure 5 shows lead behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=7. At 30 days, lead was detected only in P1, P2 and P4 cementitious matrices leachates respectively at 0.037 mg/l, 0.4 mg/l and 0.37 mg/l. At 90 days, lead was detected mainly in P2 leachate around 0.81 mg/l and very weakly in P1 and P5 leachates. At 180 days, lead was detected only in P2, P3 and P5 cementitious matrices leachates respectively at 0.047 mg/l, 0.057 mg/l and 0.007 mg/l. During leaching tests, the contribution of cement as well as lime make the medium becomes basic. In the presence of a basic medium, oxides are formed in PbO or Pb(OH)_2 form or complex ions which can contain up to six lead atoms such as $[\text{Pb}_6\text{O(OH)}_6]^{4+}$ [21]. Thus, the low concentrations of lead in cementitious matrices leachates can be explained by the fact that during hydration of cement in a basic medium, lead precipitates mainly in Pb(OH)_2 hydroxide form and Pb(OH)_3^- complex ion [22]. This low leaching of lead can also be explained by the fact that, under its oxidation states +2 and +4, lead can replace calcium in hydrates. Lead thus delays the cement hydration because it precipitates on surface in a very poorly soluble form of calcium sulfate or carbonate and aluminum silicates, due to the impermeable layer, which hinders water diffusion and therefore hydration [20,23,24,25,26,27].

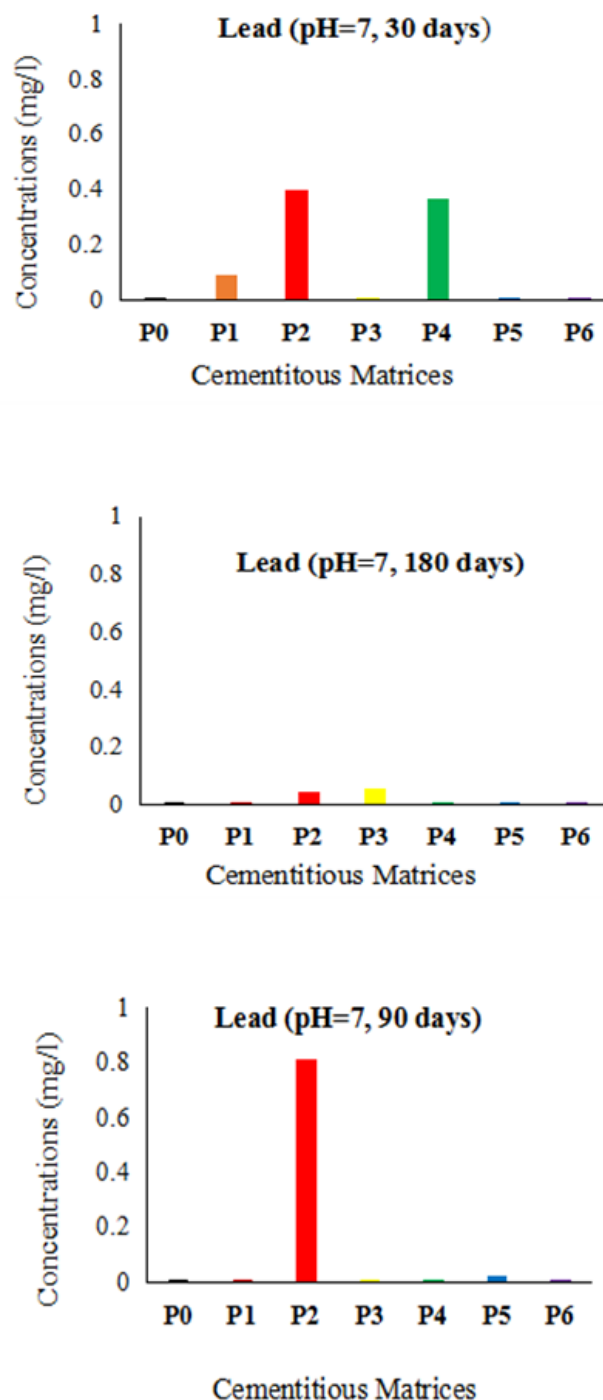


Figure 5. Lead leaching from cementitious matrices at pH=7 after 30, 90 et 180 days

3.1.3. Cadmium Leaching

Table 3 and Table 4 show cadmium behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 and 7 after 30, 90 and 180 days. Cadmium is not detected in any cementitious matrices leachates whatever pH or leaching time length. Cadmium, with its +2 oxidation state, can replace calcium in hydrates. During hydration, it can be found in hydroxide Cd(OH)_2 form, which has very low solubility in an alkaline medium or in CaCd(OH)_4 form [21] [26,28]. Cd(OH)_2 can serve as a nucleation center for C-S-H. Generally, cements are effective in stabilizing cadmium [29].

Table 3. Heavy metals concentrations in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 at 30, 90 and 180 days

pH=4 30 Days	Parameters	P0	P1	P2	P3	P4	P5	P6
	As (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Pb (mg/l)	<0,001	<0,001	<0,001	<u>0,007</u>	<0,001	<0,001	<u>0,005</u>
	Cd (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Cr (mg/l)	<u>0,2</u>	<u>0,071</u>	<u>0,008</u>	<u>0,060</u>	<u>0,15</u>	<u>0,011</u>	<u>0,11</u>
	Cu (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Ni (mg/l)	<0,001	<0,001	<0,001	<u>0,008</u>	<0,001	<0,001	<0,001
	Zn (mg/l)	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>
pH=4 90 Days	Parameters	P0	P1	P2	P3	P4	P5	P6
	As (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Pb (mg/l)	<0,001	<0,001	<0,001	<0,001	<u>0,13</u>	<0,001	<u>0,005</u>
	Cd (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Cr (mg/l)	<u>0,83</u>	<u>0,093</u>	<u>0,011</u>	<u>0,089</u>	<u>0,11</u>	<u>0,019</u>	<u>0,11</u>
	Cu (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Ni (mg/l)	<0,001	<0,001	<0,001	<u>0,008</u>	<0,001	<0,001	<0,001
	Zn (mg/l)	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>
pH=4 180 Days	Parameters	P0	P1	P2	P3	P4	P5	P6
	As (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Pb (mg/l)	<0,001	<0,001	<0,001	<0,001	<u>0,007</u>	<0,001	<u>0,005</u>
	Cd (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Cr (mg/l)	<u>0,22</u>	<u>0,12</u>	<u>0,006</u>	<u>0,016</u>	<u>0,032</u>	<u>0,032</u>	<u>0,14</u>
	Cu (mg/l)	<0,001	<0,001	<0,001	<u>0,009</u>	<0,001	<0,001	<0,001
	Ni (mg/l)	<0,001	<0,001	<0,001	<u>0,009</u>	<0,001	<0,001	<0,001
	Zn (mg/l)	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>

Table 4. Heavy metals concentrations in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=7 at 30, 90 and 180 days

pH=7 30 Days	Parameters	P0	P1	P2	P3	P4	P5	P6
	As (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Pb (mg/l)	<0,001	<u>0,087</u>	<u>0,4</u>	<0,001	<u>0,37</u>	<0,001	<0,001
	Cd (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Cr (mg/l)	<u>0,71</u>	<u>0,15</u>	<u>0,039</u>	<u>0,44</u>	<u>0,16</u>	<u>0,011</u>	<u>0,15</u>
	Cu (mg/l)	<0,001	<0,001	<0,001	<u>0,009</u>	<0,001	<0,001	<0,001
	Ni (mg/l)	<0,001	<u>0,057</u>	<u>0,3</u>	<0,001	<u>0,26</u>	<0,001	<0,001
	Zn (mg/l)	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>
pH=7 90 Days	Parameters	P0	P1	P2	P3	P4	P5	P6
	As (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Pb (mg/l)	<0,001	<u>0,01</u>	<u>0,81</u>	<0,001	<0,001	<u>0,02</u>	<0,001
	Cd (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Cr (mg/l)	<u>0,27</u>	<u>0,12</u>	<u>0,087</u>	<u>0,44</u>	<u>0,23</u>	<u>0,006</u>	<u>0,18</u>
	Cu (mg/l)	<0,001	<0,001	<0,001	<0,001	0,007	<0,001	<u>0,009</u>
	Ni (mg/l)	<0,001	<u>0,007</u>	0,62	<u>0,22</u>	<0,001	<u>0,022</u>	<0,001
	Zn (mg/l)	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>
pH=7 180 Days	Parameters	P0	P1	P2	P3	P4	P5	P6
	As (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Pb (mg/l)	<0,001	<0,001	<u>0,047</u>	<u>0,057</u>	<u>0,007</u>	<0,001	<0,001
	Cd (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
	Cr (mg/l)	<u>0,71</u>	<u>0,15</u>	<0,001	<u>0,063</u>	<u>0,024</u>	<0,001	<u>0,16</u>
	Cu (mg/l)	<0,001	<0,001	<0,001	<0,001	<0,001	<u>0,005</u>	<0,001
	Ni (mg/l)	<0,001	<0,001	<0,001	<u>0,055</u>	0,009	<0,001	<0,001
	Zn (mg/l)	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>	<u>0,009</u>

3.1.4. Chromium Leaching

Figure 6 shows chromium behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 after 30, 90 and 180 days. It can be observed that chromium has been leached by almost all cementitious matrices in acid medium. In acidic medium (pH=4), P0 cementitious matrices leachates have the highest

chromium concentrations at all leaching times, between 0.2 and 0.83 mg/l, while P2 cementitious matrices leachates have the lowest chromium concentrations, between 0.006 and 0.011 mg/l. It is the same in Figure 7 which presents chromium behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=7 after 30, 90 and 180 days. Indeed, in a neutral medium (pH=7) at 30, 90 and 180 days, P0 cementitious matrices leachates

have the highest chromium concentrations, between 0.27 and 0.71 mg/l, then P2 and P5 cementitious matrices leachates have the lowest chromium concentrations, between 0.001 and 0.039 mg/l. Chromium leaching, although higher than other metals, is still low. This low leaching can be explained by the fact that chromium can substitute for aluminum, calcium or silica in hydrates such as C-S-H in which CrO_4^{5-} can substitute for SiO_4^{4-} [30,31]. This leads to its majority retention within the cementitious matrix.

3.1.5. Copper Leaching

Table 3 shows copper behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 after 30, 90 and 180 days. At pH=4, copper in solution is detected only in P3 cementitious matrix leachate at 180 days with a concentration around of 0.009 mg/l. Table 4 shows the copper behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=7 after 30, 90 and 180 days. At pH=7, all leachates have copper concentrations under 0.001 mg/l except for P3 (0.009 mg/l) at 30 days, P6 (0.009 mg/l) at 90 days and P5 (0.005 mg/l) at 180 days. This low leaching of copper is due to the fact that copper has a retarding effect on hydration. The $\text{Cu}(\text{OH})_2$ and $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ forms which are produced during hydration [32] are retained within the cementitious matrix instead of being leached.

3.1.6. Nickel Leaching

Table 3 shows nickel behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 after 30, 90 and 180 days. At pH=4, nickel was only detected in P3 cementitious matrix leachates with concentrations around 0.008 mg/l at 30 and 90 days and 0.009 mg/l at 180 days. At pH=7, Figure 8 shows nickel behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates after 30, 90 and 180 days. At 30 days, P2 and P4 cementitious matrices leachates have nickel concentrations around 0.3 mg/l and P1 cementitious matrix leachates contain 0.057 mg/l of nickel. At 90 days, P2, P3 and P5 cementitious matrices release nickel into solution respectively with a concentration of 0.62 mg/l, 0.22 mg/l and 0.022 mg/l. We also note a very low nickel concentration in P1 cementitious matrix leachates (0.007 mg/l). At 180 days, nickel is detected only in the P3 and P4 cementitious matrices leachates respectively with concentrations of 0.055 mg/l and 0.009 mg/l. Nickel precipitates mainly in $\text{Ni}(\text{OH})_2$ hydroxide form which creates a passivation layer [33]. This could explain the low leaching of nickel retained inside cementitious matrices.

3.1.7. Zinc Leaching

Table 3 and Table 4 show zinc behavior in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH=4 and 7 after 30, 90 and 180 days. Zinc was detected in all leachates, both in acidic (pH=4) and neutral (pH=7) media, at all leaching times with low concentrations around 0.009 mg/l. The low leaching of zinc can be explained by the fact that it can replace calcium in hydrates by reducing cement permeability, probably by promoting the formation of ZnO hydroxide layer which greatly slows down the cement hydration. Cement and

Zn^{2+} delays Portlandite formation at the start of hydration [32, 34]. Other studies show that under basic conditions, in C-S-H, zinc does not seem to replace calcium but rather is incorporated into interfoliar spaces [35,36].

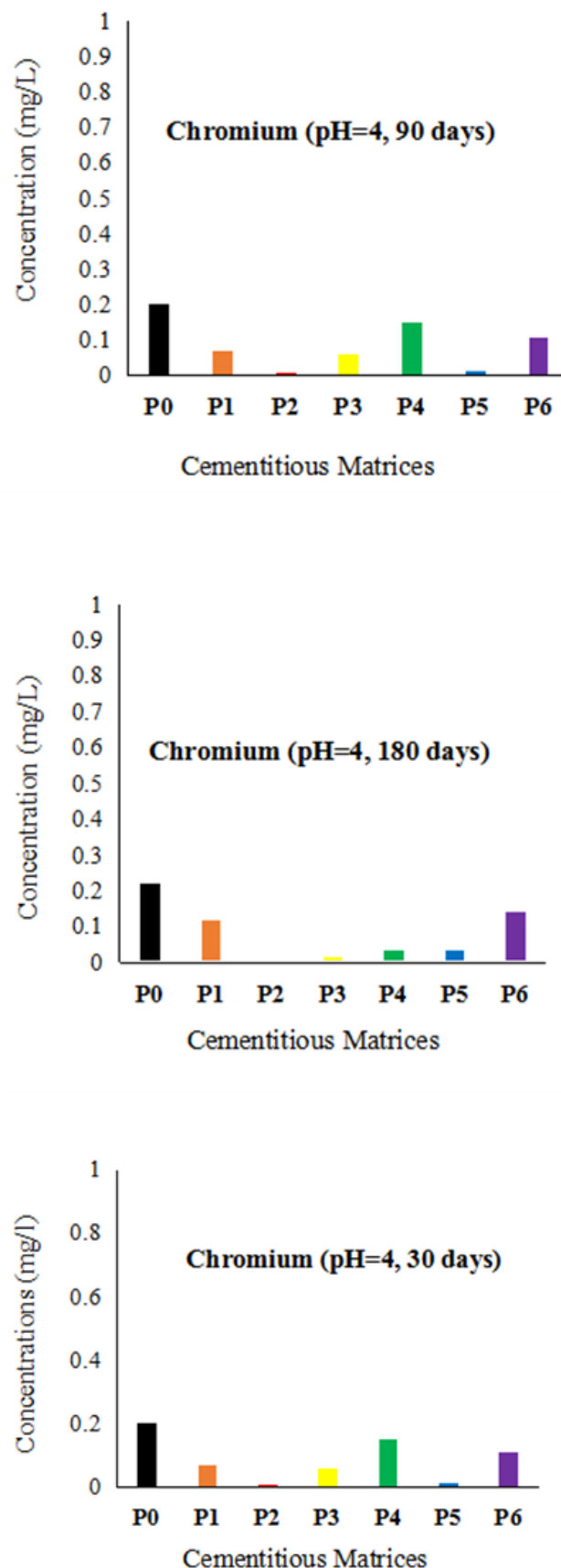


Figure 6. Chromium leaching from cementitious matrices at pH=4 after 30, 90 et 180 days

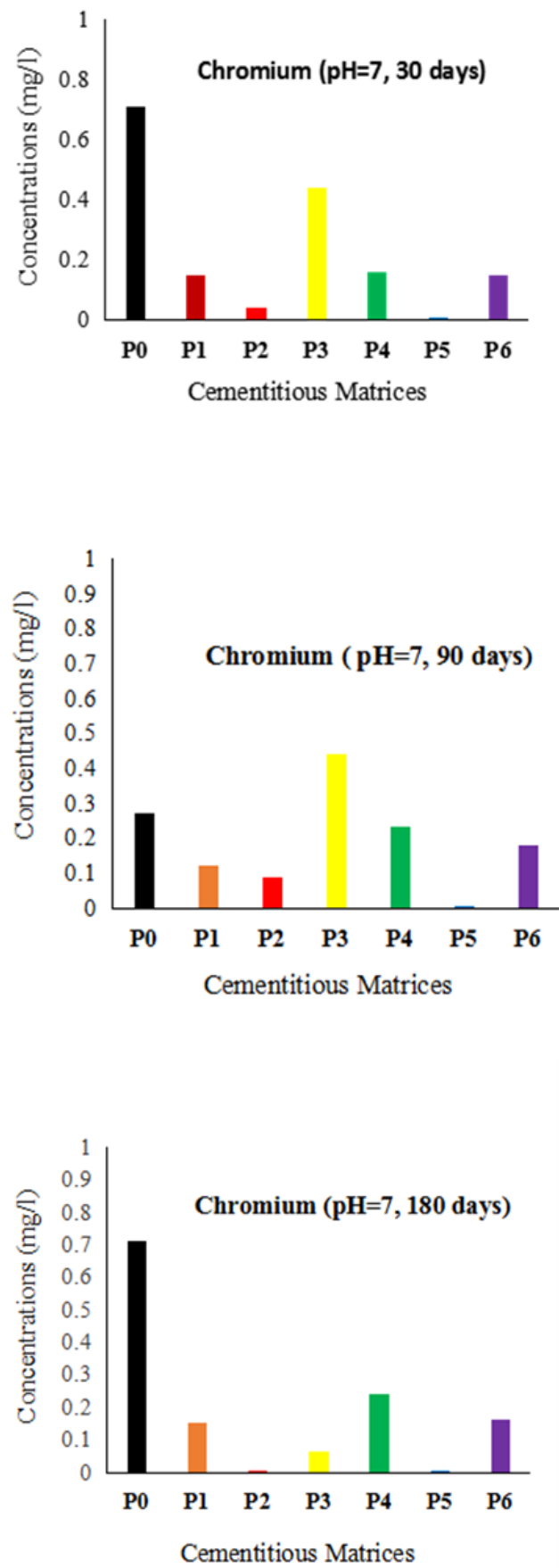


Figure 7. Chromium leaching from cementitious matrices at pH=7 after 30, 90 et 180 days

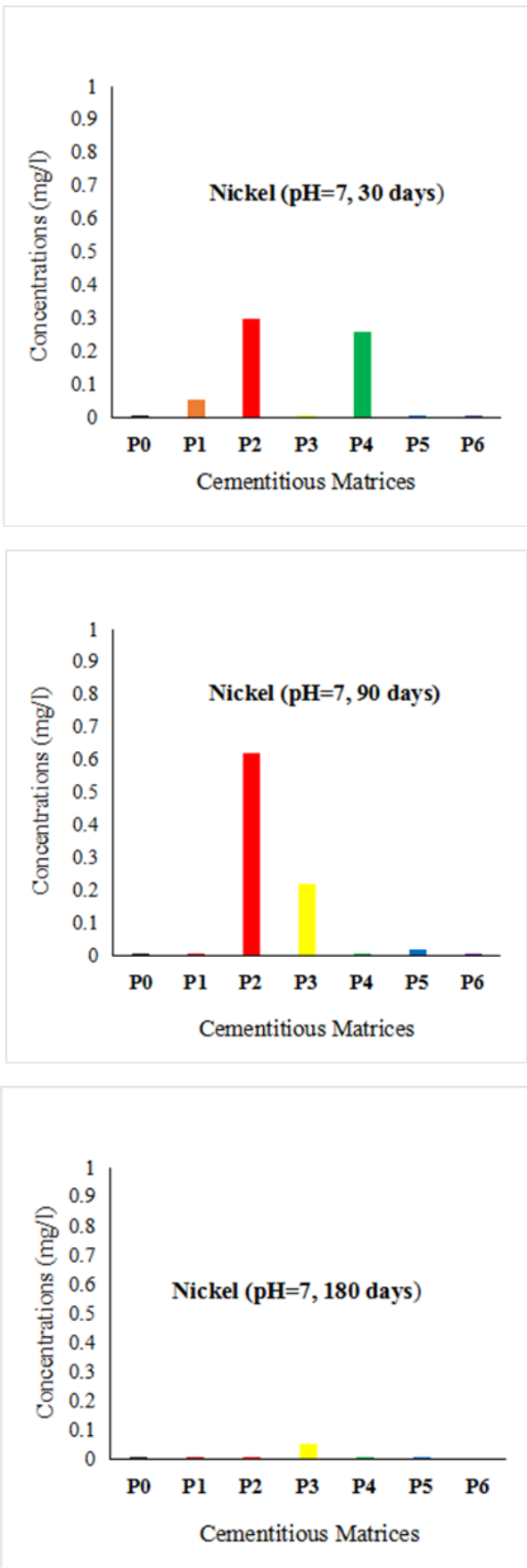


Figure 8. Nickel leaching from cementitious matrices at pH=7 after 30, 90 et 180 days

3.2. Retention of Heavy Metals in Cementitious Matrices

Table 5 and Table 6 present heavy metals contents in raw ashes, raw cement and P0, P1, P2, P3, P4, P5 and P6 cementitious matrices leachates at pH = 4 and 7 after 30, 90 and 180 days. When we compare heavy metals contents in cementitious matrices leachates to their concentrations in raw ashes leachates, we see that heavy metals concentrations in cementitious matrices leachates have concentrations very much lower than those in raw ashes leachates at all pH levels and at all leaching times. This clearly shows that heavy metals from the waste ashes have indeed been retained in cementitious matrices. Furthermore, all leachates from cementitious matrices formulations have leached heavy metals contents below the requirements of the standard applicable to landfill leachate discharge [37]. This demonstrates the effectiveness of the process adopted for the immobilization of heavy metals contained in ashes by Portland cement. This proves that, although solidification/stabilization does not necessarily imply stabilization in the strict sense of heavy metals, it still makes it possible to considerably reduce their leachability using physicochemical mechanisms responsible for their retention. Indeed, several physicochemical mechanisms at the solid/liquid interface can allow the heavy metals trapping [38, 39, 40]. A metallic element retained on material surface by adsorption, physisorption, complexation, precipitation, chemisorption will be put into solution more quickly and will therefore present more risks of toxicity than if it is inserted into material cement network [41].

3.3. Percentage of Heavy Metals Retention in Cementitious Matrices

3.3.1. Percentage of Heavy Metals Retention in Cementitious Matrices After 30 Days of Leaching

Table 7 presents heavy metals retention in cementitious matrices percentage results after 1 month of leaching in acidic (pH=4) and neutral (pH=7) media compared to raw

ashes. We observe that heavy metals concentrations released by cementitious matrices were reduced compared to the concentrations of the same elements released from raw ashes. Indeed, all formulations at 1 month have a heavy metals retentions greater than 80% for arsenic, 98% for lead, 50% for cadmium, 97% for chromium, 97% for nickel and 99% for copper and zinc. We thus note very good retention of all heavy metals in cementitious matrices at pH=4 and 7 after 30 days of leaching.

3.3.2. Percentage of Heavy Metals Retention in Cementitious Matrices After 90 Days of Leaching

Table 8 presents heavy metals retention percentage in cementitious matrices after 3 months in an acidic (pH=4) and neutral (pH=7) media compared to raw ashes. It is observed that heavy metals concentrations released by cementitious matrices were reduced compared to the concentrations of the same elements released from raw ashes. Indeed, all the formulations at 3 months present a retention of heavy metals greater than 80% for arsenic, 99% for lead, 50% for cadmium, 87% for chromium, 93% for nickel and 99% for copper and zinc. We also note a very good retention of all the heavy metals in cementitious matrices after 90 days and whatever the pH.

3.3.3. Percentage of Heavy Metals Retention in Cementitious Matrices After 180 Days of Leaching

Table 9 presents the results in percentage of heavy metals retention in cementitious matrices after 6 months in acidic (pH=4) and neutral (pH=7) media compared to raw ashes. We observe that heavy metals concentrations released by cementitious matrices were also reduced compared to the same elements concentrations released by raw ashes. Indeed, all formulations at 6 months have a retention of heavy metals greater than: 80% for arsenic, 96% for lead, 50% for cadmium, 87% for chromium, 93% for nickel and 99% for copper and zinc. We therefore note that also at 180 days and whatever the pH, we can observe very a good retention of all heavy metals in all cementitious matrices.

Table 7. Percentage of heavy metals retention in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices after 30 days at pH=4 and 7

P0 (100% Cement)			P1 (50% Cement, 50% Waste Ashes)			P2 (30% Cement, 70% Waste Ashes)			P3 (40% Cement, 50% Waste Ashes, 10% Lime)		
	pH=4	pH=7		pH=4	pH=7		pH=4	pH=7		pH=4	pH=7
%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80
%Pb	> 99	> 99	%Pb	> 99	> 99	%Pb	> 99	> 98	%Pb	> 99	> 99
%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50
%Cr	> 97	> 89	%Cr	> 98	> 97	%Cr	> 99	> 99	%Cr	> 99	> 93
%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99
%Ni	> 99	> 99	%Ni	> 99	> 99	%Ni	> 99	> 96	%Ni	> 99	> 99
%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99

P4 (30% Cement, 50% Waste Ashes, 20% Lime)			P5 (20% Cement, 70% Waste Ashes, 10% Lime)			P6 (10% Cement, 70% Waste Ashes, 20% Lime)		
	pH=4	pH=7		pH=4	pH=7		pH=4	pH=7
%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80
%Pb	> 99	> 98	%Pb	> 99	> 99	%Pb	> 99	> 99
%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50
%Cr	> 97	> 97	%Cr	> 99	> 99	%Cr	> 98	> 97
%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99
%Ni	> 99	> 97	%Ni	> 99	> 99	%Ni	> 99	> 99
%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99

Table 8. Percentage of heavy metals retention in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices after 90 days at pH=4 and 7

P0 (100% Cement)			P1 (50% Cement, 50% Waste Ashes)			P2 (30% Cement, 70% Waste Ashes)			P3 (40% Cement, 50% Waste Ashes, 10% Lime)		
	pH=4	pH=7		pH=4	pH=7		pH=4	pH=7		pH=4	pH=7
%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80
%Pb	> 99	> 99	%Pb	> 99	> 99	%Pb	> 99	> 96	%Pb	> 99	> 99
%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50
%Cr	> 87	> 95	%Cr	> 98	> 98	%Cr	> 99	> 98	%Cr	> 98	> 93
%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99
%Ni	> 99	> 99	%Ni	> 99	> 99	%Ni	> 99	> 93	%Ni	> 99	> 97
%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99

P4 (30% Cement, 50% Waste Ashes, 20% Lime)			P5 (20% Cement, 70% Waste Ashes, 10% Lime)			P6 (10% Cement, 70% Waste Ashes, 20% Lime)		
	pH=4	pH=7		pH=4	pH=7		pH=4	pH=7
%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80
%Pb	> 99	> 99	%Pb	> 99	> 99	%Pb	> 99	> 99
%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50
%Cr	> 98	> 96	%Cr	> 99	> 99	%Cr	> 98	> 97
%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99
%Ni	> 99	> 99	%Ni	> 99	> 99	%Ni	> 99	> 99
%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99

Table 9. Percentage of heavy metals retention in P0, P1, P2, P3, P4, P5 and P6 cementitious matrices after 180 days at pH=4 and 7

P0 (100% Cement)			P1 (50% Cement, 50% Waste Ashes)			P2 (30% Cement, 70% Waste Ashes)			P3 (40% Cement, 50% Waste Ashes, 10% Lime)		
	pH=4	pH=7		pH=4	pH=7		pH=4	pH=7		pH=4	pH=7
%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80
%Pb	> 99	> 99	%Pb	> 99	> 99	%Pb	> 99	> 98	%Pb	> 99	> 99
%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50
%Cr	> 96	> 89	%Cr	> 98	> 97	%Cr	> 99	> 99	%Cr	> 99	> 99
%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99
%Ni	> 99	> 99	%Ni	> 99	> 99	%Ni	> 99	> 93	%Ni	> 99	> 99
%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99

P4 (30% Cement, 50% Waste Ashes, 20% Lime)			P5 (20% Cement, 70% Waste Ashes, 10% Lime)			P6 (10% Cement, 70% Waste Ashes, 20% Lime)		
	pH=4	pH=7		pH=4	pH=7		pH=4	pH=7
%As	> 80	> 80	%As	> 80	> 80	%As	> 80	> 80
%Pb	> 99	> 98	%Pb	> 99	> 99	%Pb	> 99	> 99
%Cd	> 50	> 50	%Cd	> 50	> 50	%Cd	> 50	> 50
%Cr	> 99	> 99	%Cr	> 99	> 99	%Cr	> 97	> 97
%Cu	> 99	> 99	%Cu	> 99	> 99	%Cu	> 99	> 99
%Ni	> 99	> 97	%Ni	> 99	> 99	%Ni	> 99	> 99
%Zn	> 99	> 99	%Zn	> 99	> 99	%Zn	> 99	> 99

3.3.4. Influence of pH, Leaching Time and Formulations on Heavy Metals Quantities Released by Cementitious Matrices

The results obtained after 30, 90 and 180 days of leaching, both in acidic (pH=4) and in neutral media (pH=7), do not demonstrate pH or leaching time influence. Indeed, heavy metals retention rates in cementitious matrices are as high in acidic as in neutral media with the same order of magnitude whatever the pH or leaching time. Cementitious matrices formulations also do not seem to have had an obvious influence on heavy metal retention capacity because all the retention percentages are high for all cementitious matrices with the same order of magnitude.

4. Conclusion

The aim of this study was to experiment with

possibilities and conditions for valorizing “ultimate waste” ashes from household waste burning in cementitious matrices in order to reduce pollution of soil and surface water. For this, we implemented a process for developing cementitious matrices containing ashes from household waste burning. Then we carried out static leaching tests on these matrices at 25°C in acidic and neutral media at different leaching times. The results of this study made it possible to highlight the good chemical durability provided by the stabilization/solidification of ashes in cementitious matrices. Indeed, all leachates from P0, P1, P2, P3, P4, P5 and P6 cementitious matrices have heavy metal contents well below the standard applicable to leachate discharge. Furthermore, leachates from cementitious formulations presented low quantities of released heavy metals compared to raw ashes because heavy metals retention rates inside all cementitious matrices oscillate between 80 and 99% for arsenic, lead, chromium, copper, nickel and zinc.

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Competing Interests

Authors have declared that no competing interests.

References

- [1] INS, 2018. Annuaire Statistique du Congo. Edition 2020.
- [2] Kimbatsa F.G., Mouthou, J.L., Bakanahonda, S.F.L. 2018. The management of household waste by pre-collection operators in the districts 1 Makélékélé, 2 Baongo and 6 Talangai (Brazzaville, Congo). The Social Sciences journal "Kafoundal", 2, pp.12-27.
- [3] Ouiza Ould A. 2018. Impact of open landfills on the environmental quality of Oued Cheliff (Algeria). Thesis from Abdelhamid Ibn Badis Mostaganem University. Algeria. 193p.
- [4] Javad Asgari M., Safavi M., Mortazaeinezhad F. 2011. Landfill biogas production process. International Conference on Food Engineering and Biotechnology Ipcbee Iacsit Press, Singapore; 9.
- [5] Yukalang, N., Clarke, B. and Ross, K. 2017. Barriers to Effective Municipal Solid Waste Management in a Rapidly Urbanizing Area in Thailand. Int. J. Environ. Res. Public Health, 14, 1013.
- [6] Igboama, W.N., Hamed, O.S., Fatoba, J. O., Aroyehun, M. T., Ehiabihli, J.C. 2022. Review article on impact of groundwater contamination due to dumpsites using geophysical and physiochemical methods. Applied Water Science, 12: 130.
- [7] Vacenovska, B. and Drochytka, R. 2012. Development of a new reclamation material by hazardous waste solidification/stabilization. Advanced Materials Research, Vols. 446-449, pp 2793-2799.
- [8] Hiller E., Barta M., Milička, J. et al. 2009. Environmental fate of the herbicide MCPA in two soils as affected by the presence of wheat ash. Water Air Soil Pollut; 197(1-4):395-402.INS, 2018. Annuaire Statistique du Congo. Edition 2020.
- [9] Hiller E., Fargašová A., Zemanová L., et al. 2008. Influence of wheat ash on the MCPA immobilization in agricultural soils. Bull. Environ. Contam. Toxicol, 81(3): 285-8.
- [10] Qiu Y., Cheng H., Xu C., et al. 2008. Surface characteristics of crop-residue-derived black carbon and lead (II) adsorption. Water Res.; 42 (3):567-74.
- [11] Bouchelaghem, A., 1994. Stabilization and solidification of special industrial waste. Technique, Science and Methods, n°4, 9-13.
- [12] Conner J.R. 1990. Chemical fixation and solidification of hazardous wastes. New-York: Van Nostand Reinhold, 692.
- [13] Ecole d'Avignon. 2016. Techniques and practices of Avignon lime. Eyrolles bookstores. France.
- [14] Deschamps, T., Benzaazoua, M., Bussière, B., Belem, T. et Mbonimpa, M. 2006. Retention mechanisms of heavy metals in solid phase: case of stabilization of contaminated soils and industrial waste. Vertigo – The journal in environmental sciences, Vol7, no2.
- [15] Kimbatsa F.G., Mahoungou, E. et Berton Ofouémé Y. 2018. The importance of horticulture in the fight against food insecurity, poverty and environmental protection in Brazzaville (Republic of Congo). OpenEdition Journals Caribbean Studies. 38-40, pp.1-47.
- [16] Stronach, S.A., Marcheur, T.N.L., Macphée, D.E. et F.P. 1997. Reaction between cement and As (III) oxide: The system $\text{CaO-SiO}_2\text{-As}_2\text{O}_3\text{-H}_2\text{O}$ at 25° C. Waste Management, 12, 9-13p.
- [17] Ortego, D.J., Jackson, S., Yu, G.S., McWhinney, H., & Cocke D.L. 1989. Solidification of hazardous substances - a TGA and FTIR study of Portland cement containing metal nitrates. Journal of Environmental Science and Health, 24(6), pp.589-602.
- [18] Cartledge, F.K., Butler, L. G., Chalasani, D., Eaton, H. C., Frey, F.P., Herrera, E., TittlebaumetShou Lan Yang, M. E. 1990 : Immobilisation mechanisms in solidification/stabilization of Cd and Pb salts using Portland cement fixing agents, Environmental science and technology, 24, 867-873p.
- [19] Cocke, D. L. 1990. Binding chemistry and leaching mechanisms of hazardous substances in cementitious solidification/stabilization systems", J. Hazard. Mater, 24, pp. 231-253.
- [20] Cocke, D. L., Mollah, M. Y. A., Parga, J. R., Hess, T. R., et Ortego, T. R. 1992. An XPS and SEM/EDS characterization of leaching effects on lead- and zinc-doped Portland cement. J. Hazard. Mater. 30, 83-95.
- [21] Diet J.N. 1996. Stabilization/solidification of waste: disruption of the hydration of Portland cement by substances contained in metal hydroxide sludge. Doctoral thesis. National Institute of Applied Sciences of Lyon, 170p.
- [22] Topanou K.A.N. 2012. Management of household solid waste in the city of Abomey-Calavi (Benin): Characterization and recovery tests by composting. Joint thesis from the University of Abomey-Calavi (Benin) and Marseille (France), 194p.
- [23] Fowler, G. D., Asavapisit, S., Fromager, C. R. et Perry, R. 1995. A Study of the chemical effect of metal hydroxides upon cement hydration reaction. In: International congress on wastes solidification-stabilization processes, Nancy, France.
- [24] Macphee, D.E., Glasser, F.P. 1993. Immobilization science of cement systems. MRS, bulletin, March. 66-71p.
- [25] Kindness A., Macías, A. et F. Glasser. 1994. Immobilization of chromium in cement matrices. Waste management, 14, 3-11p.
- [26] Lin, C.K., Chen, J.N. et Li, C.C. 1997. NMR, XRD and EDS study of solidification/stabilisation of chromium with Portland cement and C3S. Journal of Hazardous Materials, 56, pp.21-34.
- [27] Tedoldia, D., Flanagan, K., Le Roux, J., Chebbo, G., Branchuc, P., Saada, M. and Gromaire, M.C. 2019. Evaluation of contaminant retention in the soil of sustainable drainage systems: methodological reflections on the determination of sorption isotherms. Blue-Green Systems Vol 1 No 1.
- [28] Al-Jabari, M. 2022. Integral waterproofing of concrete structures. Advanced concrete protection technologies by pore blocking and coating. Woodhead Publishing Series, p.1-36.
- [29] Poon, C. S., Peters, C. J., Perry, R., Barnes, P., Barker, A. P. 1985. Mechanisms of Metal Stabilization by Cement Based Fixation Processes." Sci. Total Environ, 41(1), 55-71.
- [30] Ben Maaouia, O. 2018. Suitability of aggregates from deconstruction concrete for reuse, with respect to Cr(VI): Impact of the properties of the cement matrix and identification of release mechanisms. Doctoral thesis from the University of PARIS-EST. 203p.
- [31] Ben Maaouia, O., Hamzaoui, R., Bennabi, A., Colin, J. and Colina, H. 2017. Study of the stabilization of hexavalent chromium in cementitious matrices of demolition concrete elders. 35th AUGC Meetings, ECN/UN, Nantes.
- [32] Ziegler, F., Giéreet, R., Johnson, C. A. 2001a. Sorption on Mechanisms of Zinc to Calcium Silicate Hydrate: Sorption and Microscopic Investigations. Environmental science and technology, 35, 4556-4561.
- [33] Ngamba, H. 2007. Decentralization and strengthening of urban management in Cameroon: Differentiated collection of household waste in Douala. City management report. 14-15p.
- [34] Ziegler, F., Scheidegger, A.M., Johnson, C. A., Dahn, R., Wieland, E. 2001b. Sorption Mechanisms of Zinc to Calcium Silicate Hydrate: X-ray Absorption Fine Structure (XAFS) Investigation. Environmental science and technology, 35, 1550, 1555p.
- [35] De Windt, L., Badreddine, R. 2007. Modelling of long-term dynamic leaching test applied to solidified/stabilized waste. Waste Management 27, 1638-1647p.
- [36] Trauchesse, R. 2013. Mixtures of sulfoaluminate and Portland cements. Thesis from the University of Lorraine, 265p.
- [37] Stengele R. H. and Ruedi M. 2012. Requirements for discharge of landfill leachate. Recommendations for its assessment, treatment and discharge. Federal Office for the Environment, Bern. The practical environment n 1223: 62 p.
- [38] Hodula, J., Dohnáková, B. and Drochytka, R. 2015. Solidification of hazardous waste with the aim of material utilization of solidification products. 7th Scientific-Technical Conference Material Problems in Civil Engineering. Procedia Engineering 108, 639 – 646
- [39] Peyronnard O. 2008. Methodological contributions for modeling the leaching behavior of mineral residues: Application to solidified metal hydroxide sludges. Thesis from INSA Lyon. France.

- [40] Manceau A., Marcus M. A. and Tamura N. 2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. In *Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science*. Reviews in mineralogy and Geochemistry, Mineralogical society of America, 49, 341-428p.
- [41] Rambure K. K. 2013. Towards new mineral matrices for the immobilization and recovery of final waste from the incineration of household waste. Thesis from Paris-Est University. France.



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