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Use of calcined clay as cementitious addition in mortars to immobilize heavy metals

(Uso de argila calcinada como adição cimentícia em argamassas para imobilizar metais pesados)

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Abstract

The aim of this study was to examine the use of calcined clay (CC), which is a pozzolanic material, as a substitute for 10% by weight of the amount of cement, for the stabilization/solidification (S/S) of hazardous waste using a hydraulic binder. For comparison, an ordinary Portland cement was used. The standard toxicity characteristic leaching procedure (TCLP) test showed that the average concentrations of heavy metals in the raw hazardous waste far exceeded those of the required standards. Leaching of heavy metals from the mortar was evaluated by the monolithic leaching test (MLT) under dynamic leaching conditions for 64 days in sulfated and neutral media. Tests of compressive strength, setting times, and X-ray diffraction were carried out. The addition of CC considerably improved the strength of the mortar specimens containing hazardous waste. Following the MLT test, CC cement-made mortar was more efficient in the S/S of heavy metals than mortar made without CC.

Keywords: calcined clay, hydraulic binder, heavy metals, compressive strength, leaching, stabilization/solidification.

Resumo

O objetivo deste estudo foi examinar a utilização de argila calcinada (CC), que é um material pozolânico, em substituição a 10% em massa da quantidade de cimento, para a estabilização/solidificação (S/S) de resíduos perigosos usando um ligante hidráulico. Para comparação, foi usado um cimento Portland comum. O teste padrão de procedimento de lixiviação de característica de toxicidade (TCLP) mostrou que as concentrações médias de metais pesados no resíduo perigoso excederam em muito as dos padrões exigidos. A lixiviação dos metais pesados da argamassa foi avaliada pelo teste de lixiviação de monolito (MLT) sob condições de lixiviação dinâmica por 64 dias em meio sulfatado e neutro. Testes de resistência à compressão, tempos de pega e difração de raios X foram realizados. A adição de CC melhorou consideravelmente a resistência das amostras de argamassa contendo resíduo perigoso. De acordo com o ensaio MLT, a argamassa com CC cimentícia foi mais eficiente no S/S de metais pesados do que a argamassa feita sem CC.

Palavras-chave*: argila calcinada, ligante hidráulico, metais pesados, resistência à compressão, lixiviação, estabilização/solidificação.*

INTRODUCTION

Hydraulic binders are increasingly used for waste treatment. They immobilize hazardous wastes within a cement matrix, as well as act as a binder to convert semi-solid waste into an adhesive solid. This reduces the mobility of the hazards within the monoliths. They also make a durable monolith that withstands environmental stresses [1]. Stabilization/solidification (S/S) technologies have been used for decades as a final treatment step prior to the disposal of both reactive and chemically hazardous wastes [2, 3]. The stabilization refers to an alteration of waste contaminants to a more chemically stable form, resulting in a more environmentally acceptable form of waste. Typically, the stabilization processes also involve some form of physical solidification [2, 3]. Although Portland cement has proven to be an effective stabilizing agent by itself, the use of additives often enhances and optimizes Portland cement S/S mixtures [4]. A series of binding materials (Portland cement, calcium aluminate cements, calcium sulfoaluminate cements, geopolymers, magnesia cements, metakaolin blended cement, and others [3, 5-13]) have been used for the S/S of different wastes. The cement-based S/S of hazardous wastes has the advantage of relatively low-cost, and ease of use and processing [14, 15]. The low water permeability, good long-term stability (both physical and chemical), high mechanical strength and durability, and the capacity of retention of heavy metals have made them a commonly used technique for the final processing of hazardous wastes. The S/S technique was identified by the Environmental Protection Agency (EPA) of the USA as the best technology available for 57 types of regulated hazardous wastes [14-

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16] and is one of the technologies most usually applied in Superfund programs in the United States.

In this paper, we studied the possibility of the S/S of hazardous waste generated by an Algerian unit of manufacturing of stainless steel objects using cement with calcined clay (CC). The CC was used as a substitute for a certain fraction of the cement. The use of CC as a substitute for cement has various advantages, the main ones being that cement is the most expensive component of concretes, which production requires a large consumption of energy and the production of 1 ton of cement releases approximately the same amount of carbon dioxide into the atmosphere [1, 17-26]. Their properties, which include high early strength, low shrinkage, freeze-thaw resistance, and sulfate resistance, make them ideal for long-term S/S in surface disposal facilities. The use of blended Portland-pozzolan cement results also in improved sustainability, sulfate resistance, and economic benefits [17-25, 27]. By grinding the clay to a fineness greater than or equal to that of the cement (63 μm), followed by calcination at 720 °C, the clay becomes very reactive and has a high pozzolanicity [17, 19, 22, 26]. The incorporation of a pozzolanic material in a cement mortar determines a chemical reaction in the presence of water between the amorphous SiO_2 of the pozzolanic material and the portlandite [$Ca(OH)_2$] released during hydration of the cement. In this reaction, calcium silicate hydrates are formed, which are responsible for increasing the compressive strength and also favor good durability. In order to characterize the massive, porous materials obtained by including hazardous waste, a methodology for evaluating their long-term leaching behavior is necessary. This is the context for the purpose of this study.

EXPERIMENTAL

Materials: the cement (CEM I 42.5) used came from the Ain El Kebira plant in Algeria. The oxide contents of the sample, as well as the loss on ignition (LOI), are presented in Table I. The specific surface area by Blaine air-permeability (SSB) of the cement was of the order of 3000 cm²/g. The clay used came from the city of Bejaia in Algeria. The chemical composition and LOI of the clay are given in Table I. It was possible to observe a high content of silica (SiO_2) and smaller proportions of Al_2O_3, CaO, SO_3, Na_2O, K_2O, MgO, Fe_2O_3, MnO, TiO_2, and P_2O_3. The calcined clay (CC) was produced in the laboratory by grinding raw clay to a fineness greater than or equal to that of cement (63 μm), followed by calcination at 720 °C for 1 h in a muffle furnace. The calcination temperature was chosen based on differential thermal analysis (DTA), while the calcining time was chosen after a large number of trials. The particle size distribution of the obtained CC is given in Fig. 1. The value of the specific surface area of CC calculated with the Blaine permeability apparatus was 9140 cm²/g. Hazardous waste was recovered from an Algerian unit of manufacturing of stainless steel objects. It was in the form of a friable mud.

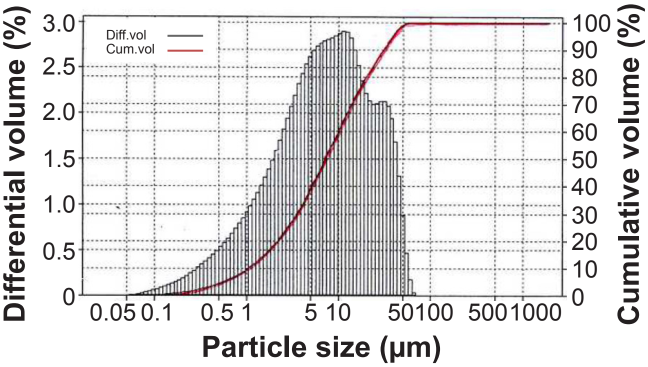

Figure 1: Particle size distribution curves of calcined clay (CC).
[Figura 1: Curvas de distribuição de tamanho de partículas da argila calcinada (CC).]

Preparation of samples: the preparation of the studied mortars was generally based on NF EN 196-1 standard [28] by replacing 10% (by weight) of the cement with CC and adding 25% of hazardous waste to cement. The proportion of replacement of cement with the CC was chosen, taking into account the scientific literature, while the proportion of hazardous waste addition was based on a large number of trials. In order to compare the results, mortars without CC and without hazardous waste were designed. The prepared mortars were labeled with an appropriate combination of symbols. The normal mortar without waste and CC was designated as MN, as well as the mortar that was prepared with CC and waste was designed as MCW. Meanwhile, the mortar prepared without CC but with waste was designated as MW. A water/cement ratio of 0.5 was used. Each formulation was prepared in a mixer of about 5 L capacity. First, demineralized water, CEN-standard sand according to EN 196-1 [28], and hazardous waste were mixed at medium speed for 10 min. The cement was then added to the mixture and then mixed again for a few minutes. We stopped mixing for a moment to scrape the bottom and walls of the container with a spatula to ensure the hydration of all the mixture. Samples for mechanical testing at 28 days (3 samples for each test) were prepared by molding the mixture in molds

Table I - Chemical compositions (wt%) of Portland cement CEM I 42.5 and clay.
[Tabela I - Composições químicas (% em massa) do cimento Portland CEM I 42.5 e argila.]

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	TiO_2	LOI
Cement	18.94	7.71	5.14	60.21	1.39	2.71	0.73	0.13	0.54	0.37	2.12
Clay	51.37	10.70	4.62	14.80	1.51	0.72	0.13	0.30	0.18	0.70	15.86

measuring 40x40x160 mm^3. Specimens of 80x80x210 mm^3 were also made for the monolith leaching test (MLT). The molds filled with mortars were then stored in an enclosure at 23±2 °C and relative humidity of 90%. The compositions of the mortars made up in this study are presented in Table II.

Table II - Mixture proportions of mortars.
[Tabela II - Proporções de mistura das argamassas.]

Component	MN	MCW	MW
Sand (g)	1350	1350	1350
Cement (g)	450	405	450
CC (g)	0	45	0
Water (g)	225	225	225
Waste (g)	0	112.5	112.5
Waste/cement (%)	0	25	25
CC/cement (%)	0	10	0

Methods of characterization: differential thermal analysis (DTA) was used for measuring the phase transformation of raw clay at a heating rate of 15 °C/min, with the temperature ranging from 30 to 1000 °C under air atmosphere. The test was carried out with a thermal analyzer (STA 409 PC Luxx, Netzsch). X-ray diffraction (XRD) analysis was carried out on the raw clay, hazardous waste, and cement mortar specimens (MCW) obtained before and after the MLT test. The identification of mineral phases contained in the samples was obtained by a software (X'Pert PRO, PANalytical). XRD measurements were performed on 1 g of the sample with a particle size <100 μm, using CuKα radiation at 40 kV/20 mA, CPS=1 k, width 2.5, speed 2 °/min, and scanned with an angle of 2° to 80°. Toxicity characteristic leaching procedure (TCLP): leaching test was performed according to the TCLP U.S. EPA-1311 method to determine metals mobility under natural worst-case conditions [29]. The liquid/solid ratio was 20 L/kg. The mixture was stirred for a period of 18 h at a rotation speed of 30±2 rpm and then filtered with a 0.45 μm filter. The pH of the mortars containing hazardous waste was measured and decreased by adding nitric acid to <2. The concentrations of Ni^{2+}, Zn^{2+}, and Ag^{2+} were determined using flame atomic absorption spectrometry (FAAS, AI 1200, Aurora Instr.). Initial and final setting times were measured in accordance with the NF EN 196-3 standard [30] using a Vicat apparatus in order to study the influence of the addition of CC as well as of the hazardous waste on the behavior of the samples. Mechanical testing: compressive strengths were measured in accordance with EN 196-1 standard [28] by means of a computer-controlled 200 kN type press (Ibertest). For each cement mixture, 3 specimens were tested.

Monolithic leaching test (MLT): the MLT aims to characterize mass transfer mechanisms by observing the fluxes of chemical elements released by porous monolithic blocks. The block measuring 40x40x40 mm was brought into contact with a fixed volume of leaching solution [31]. The lixiviant was demineralized water and a sulfated solution. The leaching test pieces were obtained by dry cutting the undried material, dedusting them with compressed air, and physically characterizing them (measuring weight) [31]. The solution was renewed periodically, and the dynamics of the release of certain elements were determined by the analysis of the eluates obtained [31] for two different environments, neutral and sulfated. The lixiviant (demineralized water and sulfated solution) was introduced in a liquid volume/surface of 10 cm^3/cm^2, so stationary conditions were not reached before the renewal of the solution. For each material, the monolithic block was placed in contact with a leachant. The blocks were introduced into flasks and placed on a grid 2 cm from the bottom to allow the lixiviant to circulate and, therefore, the transfer of material to be done by all the faces of the block [32]. The flasks were carefully closed to avoid as much air intake (and, therefore, carbonation) and evaporation of solutions [32]. For each material, we performed the test in parallel on two blocks. The experiment was performed at room temperature (23±1 °C). The period of change of the solution was 6 h, 18 h, 1 day, 2 days, 5 days, 7 days, 20 days, and 28 days [31, 32]. We thus obtained 8 solutions to analyze after filtration (0.45 μm) and acidification (pH≤2) with 65% nitric acid to determine the concentrations of the different chemical species (Ni, Zn, and Ag). Concentrations of these heavy metals in solutions after the MLT test were measured by FAAS. The results of the leaching test were presented graphically as a function of contact time or average time calculated by:

$$T_i = \left(\frac{\sqrt{t_i} + \sqrt{t_{i+1}}}{2} \right) \qquad \text{(A)}$$

where t_i is the duration of each leaching sequence measured in days.

RESULTS AND DISCUSSION

DTA of raw clay: the DTA curve for the clay used to prepare CC is shown in Fig. 2. Two endothermic peaks were seen. The 1st peak was attributed to the adsorbed water loss. The 2nd endothermic peak at 718.3 °C was related to the dehydroxylation. This is why we chose 720 °C as the calcination temperature. This heat-treatment, or calcination, broke down the structure of kaolin such that the alumina and silica layers became puckered and lost their long-range order. This dehydroxylation and disorder resulted in CC, a reactive transition phase. This can be summarized by the following reaction:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2\,Si_2O_5(OH)_xO_{2-x}+(2-x/2)H_2O \qquad \text{(B)}$$

with a low value of x (about 10% of residual hydroxyl groups in metakaolinite). The exothermic peak seen in the range of 800 to 900 °C (at 851.2 °C) was due to the recrystallization, which causes the reactivity decline, as

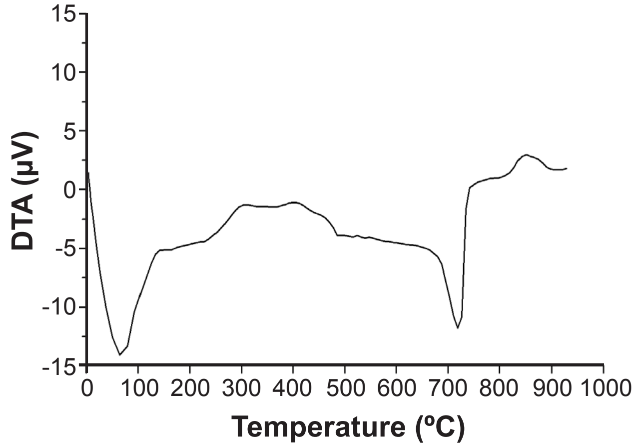

Figure 2: Differential thermal analysis (DTA) curve of the clay.
[Figura 2: Curva de análise térmica diferencial (DTA) da argila.]

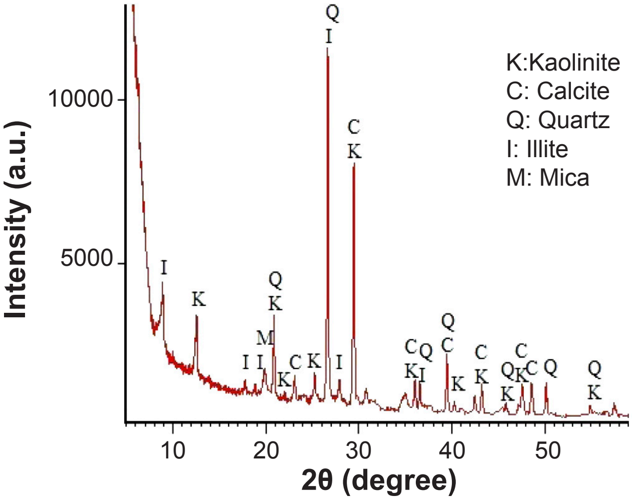

Figure 3: X-ray diffraction pattern of the clay.
[Figura 3: Padrão de difração de raios X da argila.]

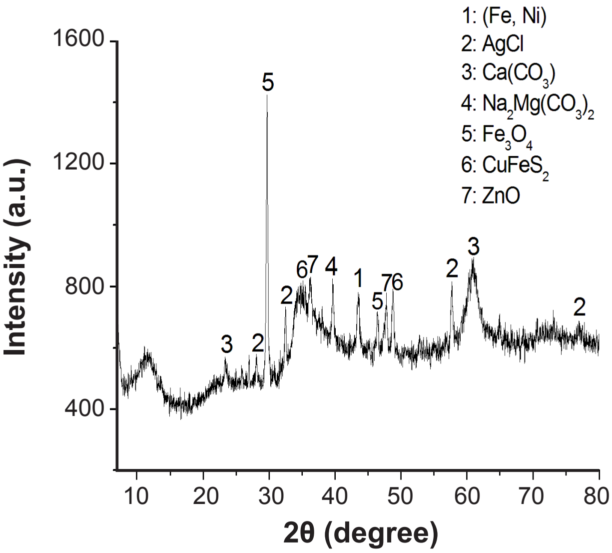

Figure 4: X-ray diffraction pattern of the hazardous waste.
[Figura 4: Padrão de difração de raios X do resíduo perigoso.]

Table III - Crystalline phases identified by XRD analysis of the hazardous waste.
[Tabela III - Fases cristalinas identificadas pela análise de DRX do resíduo perigoso.]

Mineral name	Chemical formula	PDF file
Taenite	(Fe,Ni)	00-047-1417
Chlorargyrite	AgCl	00-001-1013
Calcite	$CaCO_3$	01-088-1809
Eitelite	$Na_2Mg(CO_3)_2$	00-025-0847
Magnetite	Fe_3O_4	01-089-0951
Chalcopyrite	$CuFeS_2$	00-037-0471
Zincite	ZnO	01-075-1526

kaolin begins to convert to relatively inert ceramic materials such as spinel, silica, and mullite. *XRD analysis of clay*: XRD pattern of the clay used to prepare CC is shown in Fig. 3. This pattern shows that the main crystalline phases were kaolinite, quartz, and calcite.

Characterization of hazardous waste: Fig. 4 shows the XRD pattern of raw hazardous waste. The diffractogram highlights complex crystallized phases containing species such as nickel, zinc, and silver. Crystallized phases detected were (Fe,Ni), AgCl, $CaCO_3$, $Na_2Mg(CO_3)_2$, Fe_3O_4, $CuFeS_2$, and ZnO. Table III summarizes the mineral phases detected, their chemical formula, and their PDF files. These results clearly showed the hazardous nature of the waste used. *Toxicity characteristic leaching procedure (TCLP) of hazardous waste*: in order to determine its potential pollutant, the raw hazardous waste was characterized by the TCLP test. The results recorded in Table IV show that the concentrations of heavy metals, namely Ni, Zn, and Ag, were very large and far exceeded the standards required by the regulation [33].

Characterization of CC: the calcined clay was characterized by X-ray fluorescence analysis to determine its chemical composition. The results showed an amount of 54.37% of SiO_2, 14.70% of Al_2O_3, and 5.62% of Fe_2O_3. The loss on ignition was 4.86%. According to the ASTM C618 standard [34], CC can be classified as a pozzolan. This means that CC can react with the portlandite released during

Table IV - Results of the toxicity characteristic leaching procedure (TCLP) of hazardous waste (mg/kg).
[Tabela IV - Resultados do procedimento de lixiviação de característica de toxicidade (TCLP) do resíduo perigoso (mg/kg).]

Ni^{2+}	Pb^{2+}	Cr^{3+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	K^+	Ag^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-
200.9	0.011	2.32	0.045	166.8	0.619	0.022	155.5	0.7	0.009	879.7	105

hydration of the cement. This reaction makes it possible to produce supplementary calcium silicate hydrate.

Behavior of materials with hazardous waste. Initial and final setting times: the values of the initial and final setting times of the various compositions are shown in Fig. 5. In view of these results, it appeared that the presence of a large quantity of hazardous waste in the binding matrices accelerated the process of setting. This was mainly due to the quantitative and qualitative influences of the chemical elements present in the hazardous waste, namely heavy metals [35] because they can contribute to the formation of new compounds that accelerate the setting of the cement [35]. According to [2], cement and siliceous pozzolans react with metals and cause the formation of hydroxides, carbonates, and silicates of very low solubility. The addition of CC into cement paste with hazardous waste (PCW) accelerated the initial and final setting times compared to CC-free cement paste (PN). This was likely due to the finer particle size of the CC, which resulted in a much larger surface area available for reaction and, thus, a faster rate of hydration and setting. A similar result was found in [21]. The difference in setting time between PCW and PN pastes can also be attributed to the presence of heavy metals in hazardous waste. The cement paste with heavy metals (PW) also showed a low setting time compared to CC-free cement paste (PN). It has been stated that, according to the decomposition rate of minerals, heavy metals accelerate the hydration of tricalcium silicate (C_3S) and Portland cement [36].

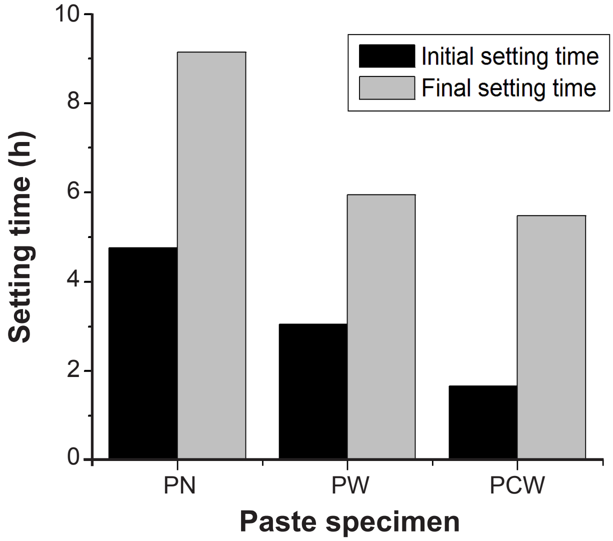

Figure 5: Initial and final setting time of the cement pastes.
[Figura 5: Tempo de pega inicial e final das pastas de cimento.]

Compressive strength: was determined for each mortar mixture after 28 days of hardening. Fig. 6 shows the evolution of compressive strength as a function of the type of mortar. Compressive strengths of materials containing hazardous waste were higher than the minimum value recommended by French standard X31-211 [33], which is 1 MPa. It was observed that the mortar without hazardous waste had greater strength (about 52.0 MPa) than materials containing hazardous waste. The decrease in compressive strength was likely due to the modification of the kinetics of cement hydration because of the presence of hazardous waste containing heavy metals. The decrease in compressive strength for the latter mortars may have been caused by the reduction of the cement/non-reactive material ratio in MW composition compared to MN composition. This can be explained by the 'dilution' effect [37, 38]. According to [39, 40], the decrease of the compressive strength in the material containing hazardous waste can also be due to the quality and quantity of hazardous waste. We also noted that between the two mortars containing hazardous waste, MCW had a better strength than MW. This can be explained by 3 elementary factors influencing the contribution that CC makes to strength when it partially replaces cement in mortars. These are the filler effect, the acceleration of cement hydration, and the pozzolanic reaction of CC with the portlandite [41].

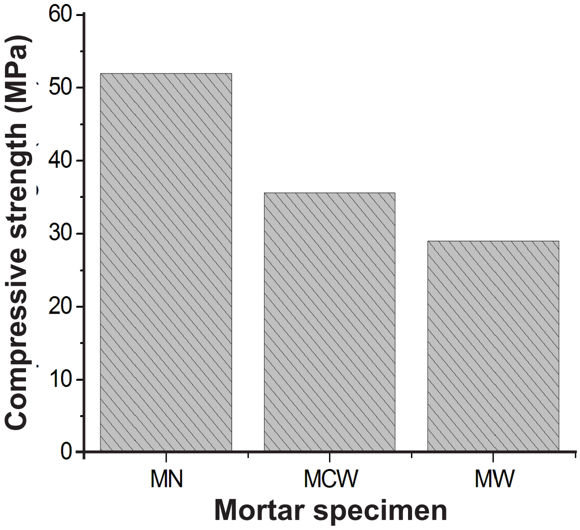

Figure 6: Compressive strength of the mortars.
[Figura 6: Resistência à compressão das argamassas.]

Behavior of materials containing hazardous waste in leaching test (MLT): leaching results of the monoliths obtained for the monitored chemical species are illustrated in Fig. 7. This figure shows the variation of leached flows during the average time of 64 days of leaching in two different media, neutral and sulfated, for mortars MW and MCW. For the two media studied, we generally observed the beginning of the diffusion type of release when the slope of the curve was -0.5 (the first 3 points on the graphs) [31]. This was due to concentration gradients between the pore water of highly charged binding material and lightly charged aggressive solution, creating transfer ion diffusion. This diffusional release resulted in the significant contribution of the monolithic outer surface of the block to leaching. The flows then decreased due to the exhaustion of the free waste on the outer surface of the monolithic block [31]. Low metal ion leachability was achieved because precipitates blocked pores and then reduced metal diffusion [4]. The release of the metals Ag, Ni, and Zn continued to decrease and became controlled by changes in concentration resulting from the diffusion and chemical reactions of dissolution-precipitation (chemical equilibrium conditions) [31]. Total leached flows of MW mortar were higher than for MCW mortar. This was probably due to the ability of the CC contained in MCW to refine the pore structure and improve the strength of the mortar. In fact, CC had a higher alumina content compared to the cement used. The reaction product that CC and portlandite ($CaOH_2$) formed were not only C-S-H, but also included C_4AH_{13}, C_3AH_6, and C_2ASH_8 [17, 34]. A clear correlation was drawn between the tricalcium aluminate (C_3A) content of a Portland cement and its susceptibility to sulfate attack [42].

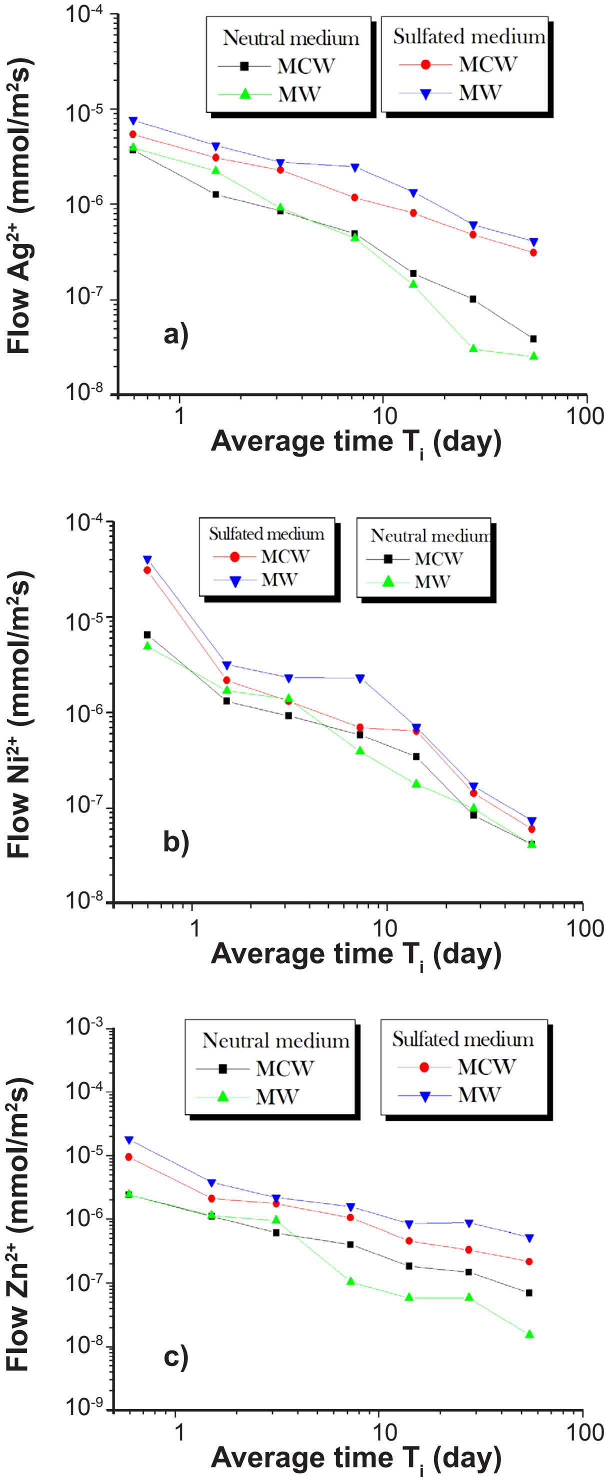

Figure 7: Ag^{2+} (a), Ni^{2+} (b), and Zn^{2+} (c) release as a function of average time (T_i) in the monolithic leaching test (MLT) for the MCW and MW mortars.

[Figura 7: Liberação de Ag^{2+} (a), Ni^{2+} (b) e Zn^{2+} (c) em função do tempo médio (T_i) no ensaio de lixiviação monolítica (MLT) para as argamassas MCW e MW.]

Fig. 7 shows that the total leached species in the sulfated medium was greater than that released into the neutral media. This was due to the ionic strength of the sulfated solution. When the blocks were exposed to the sulfated solution, ettringite was formed from the reaction of ingressing sulfates, C_3A/calcium aluminate hydrates, and monosulfoaluminate. The formation of ettringite during sulfate attack can produce significant volume expansion and can be detrimental to mortar life [43]. In addition, sulfate ions can react with portlandite to form gypsum, which can then lead to a decrease in the pore solution pH, destabilization of hydration products, and decalcification of the C-S-H. The net effect of this form of chemical attack is the loss of adhesion and strength. The increase in porosity increases the reactive surface (solid solution), so the release of pollutants is greater. These results confirmed the effectiveness of the stabilization/solidification (S/S) of hazardous waste and, thus, heavy metals using the blended cement with calcined clay (CC). To confirm the deterioration of the materials submitted to the sulfated medium and evaluate their degradation in terms of compressive strength, tests were performed on monolithic blocks recovered after 64 days of leaching. The results of compressive strength are illustrated in Fig. 8. XRD analyzes were performed at the end of the MLT test. The blocks were recovered and ground to a powder state. The patterns obtained are shown in Fig. 9. All the patterns showed a series

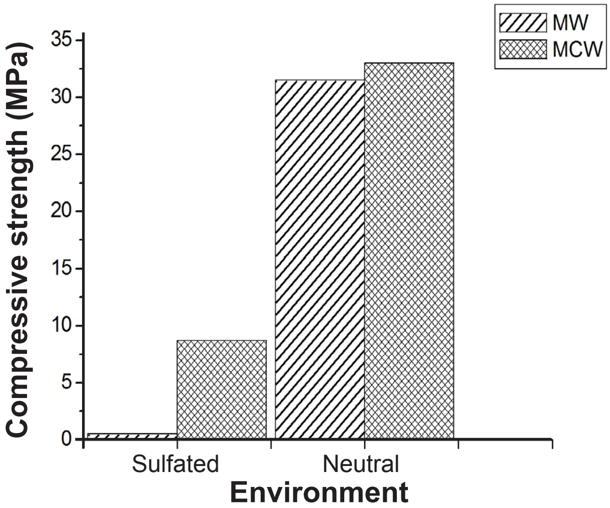

Figure 8: Compressive strength of monolithic blocks leached for 64 days.

[Figura 8: Resistência à compressão de blocos monolíticos lixiviados por 64 dias.]

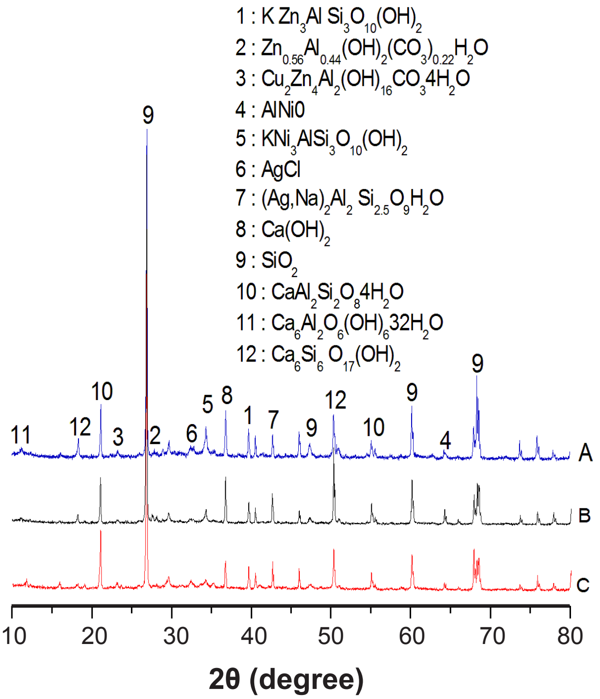

Figure 9: X-ray diffraction patterns of MCW mortar before (A) and after lixiviation in neutral medium (B) and sulfated medium (C).
[Figura 9: Padrões de difração de raios X da argamassa MCW antes (A) e após lixiviação em meio neutro (B) e meio sulfatado (C).]

of well-defined diffraction peaks. The XRD patterns showed the presence of mineral phases containing heavy metals (Zn, Ni, and Ag) before and after leaching. This demonstrated the effectiveness of the retention of heavy metals and containment of hazardous waste by the blended cement with CC and reinforced the results established by Giergiczny and Król [13], who concluded that mineral additions enter the hydration reactions in the mixtures and favor the formation of specific microstructure promoting the immobilization of hazardous elements.

CONCLUSIONS

The aim of this study was to investigate the effectiveness of the stabilization/solidification (S/S) of hazardous waste containing heavy metals in ecological cement matrices containing calcined clay as mineral addition. The following conclusions were obtained. Initial and final setting times were influenced by the presence of hazardous waste in the mortars studied. In fact, the addition of calcined clay (CC) into MCW cement paste accelerated the initial and final setting times compared to CC-free cement pastes. Regarding the compressive strength of the mortars studied, we concluded that the mortar without hazardous waste (MC) had higher strength compared to materials containing hazardous waste. We also noted that between the two mortars containing hazardous waste (MCW and MW), MCW had higher strength than MW. This can be explained by the contribution that CC made to strength when it partially replaced cement in mortars. According to the monolithic leaching test (MLT), the results showed that CC-cement-made mortar was more efficient in the S/S of heavy metals than mortar made without the introduction of CC. This result was valid for the two media studied: neutral and sulfated. In fact, total leached flows of MW mortar were higher than that of the MCW mortar. XRD analyzes of MCW, before and after the MLT test, showed the presence of heavy metals in the form of complex phases in the structure of the mortars studied, which showed the success of the containment of hazardous waste in blended cement with CC. So, mortars made with calcined clay as a mineral additive are suitable for use as matrices for the immobilization and stabilization of heavy metals.

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