Kinetic study of the immobilization of galvanic sludge in clay-based matrix

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Abstract

The viability of inertization of galvanic wastes through their incorporation in clay-based materials, such as common formulations for tiles and bricks, is here studied by determining the leaching kinetics in different media. Metals immobilization is assured by firing at reasonably high temperatures, since intimately contact and/or reaction between residue and clay particles is promoted but also due to formation of insoluble metal oxides that rest unreactive towards clay grains. For most metals, leaching rate follows a zero-order kinetic law, with values between 0.001 to 0.1 mg/(g day cm^2). Leaching velocity tends to increase with rising atomic numbers: Zn < Cu < Ni < Cr. These values depend exponentially on the relative sludge content.
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1. Introduction

Inertization is the process used to decrease the releasing velocity of hazardous substances into the environment. In general, it is assured by fixing waste species in a suitable matrix. However, as time is passing some release occurs and instead of a complete inertization, considered as an definitely retention, it is more correct to assume that substances are immobilized and the control of releasing rate is the key control issue [1]. This can be reached by assuring that phases obtained upon treatment remain unaltered in current environmental conditions (pH, temperature, and pressure). Since the contact with external/aggressive agents is minimized by encapsulating the waste particles, this is a common way to improve immobilization degree. Several studies were conducted to find the most suitable encapsulation matrix for a certain waste, involving cement, polymers, and ceramic-based materials [2–7].

Ceramic products (namely bricks and tiles) are generally very heterogeneous, since they consist of clay raw materials with a very wide-ranging overall composition [8,9]. For this reason, such materials can tolerate the presence of different types of wastes, even in considerable amounts [10]. Their processing present interesting potential for wastes encapsulation purposes, since an effective physical and chemical barrier might be created that minimizes the contact between hazardous substances and the outside. The firing step is determinant in the final immobilization degree, since major combining reactions between clay and waste particles occur upon heating and sintering phenomena also promote the physical consolidation of the material by reaching a suitable microstructure. Moreover, highly (thermodynamic) stable phases tend to be formed at high temperatures amongst the single waste particles. For example, metallic components tend to form oxides in which the oxidation degree is maximum, being less soluble than precursor phases [11]. The chemical nature of phases and final microstructure of the material strongly determines its behaviour, namely stability and solubility degrees.

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The addition of industrial and urban wastes to brick raw materials often has positive effects on the properties and/or on the processing conditions (e.g., decreasing firing temperature), but requires a careful study of the overall effects. From an environmental viewpoint, the process control deserves a wide understanding of reactions involving the waste elements and their stability in current using conditions. Specific requirements involve [1]:

(i) waste characterization;
(ii) definition of clay-based material/product based on phase equilibrium diagrams and characterization (aesthetic and functional properties) and identification of the possible applications;
(iii) processing optimization, concerning the nature of phases and final microstructure;
(iv) durability prediction.

As previously mentioned, it is common to use phase equilibrium diagrams to predict the nature and extension of reactions between components, and final stable phases nature (vitreous or crystal) and composition. However, these theoretical predictions correspond to reasonably simple compositions and thermodynamically stable situations, which are very far from actual systems and practical conditions. As a consequence, lab tests are necessary to account for kinetic effects and estimate the durability in different environmental conditions. Ribeiro et al. [12] defined the durability as the product of a kinetic stability function (f_1) and a thermodynamic stability function (f_2) of resulting products:

$$\text{durability} = f_1(E_{\text{kinetic}}) f_2(E_{\text{thermodynamic}}) \qquad (1)$$

Thermodynamic stability corresponds to theoretical predictions of resistance to environmental conditions. In that sense, function f_2 traduces the coupled effect of phase formation at high temperatures and its behaviour at room conditions, obtained from plots representing the activity as a function of pH. The kinetic stability function mathematically describes solubilization, in aqueous medium and at room temperature, of materials formed at high temperatures, and is generally represented as a function of pH and time. Despite some existing theoretical predictions based on solubility determinations, real estimations require laboratory work [13].

In this work, attempts to determine potential and limitations of inertization of galvanic wastes by their incorporation in clay-based materials were studied. The fully characterization of wastes and determination of effect of several experimental variables are described elsewhere [14,15]. Current paper focuses on the evaluation of leaching kinetics of sludge-containing samples in different media.

2. Experimental

The selected galvanic sludge is generated by the physicochemical treatment of wastewaters from different electroplating plants and has the following average chemical composition (wt.%, XRF): Al (15.7%), Ca (4.00%), Cu (1.03%), Cr (2.20%), Fe (0.37%), Ni (7.12%), Zn (1.36%). Its complete characterization is given elsewhere [16]. As inertization matrix, a typical bricks-making formulation involving the mixture of two red clays was used, showing the following average chemical composition (wt.% in a dry basis,

Table 1
Description of samples and experimental conditions applied to evaluate the long time immobilization of galvanic sludge through the clay-based matrix

Test number	Mass (g)	Sample	Thermal treatment	Extracting medium
1	1.99	Waste	Control	Water
2	1.33	Waste	Fired	Water
3	2.01	Mixture 50%	Control	Water
4	1.61	Mixture 50%	Fired	Water
5	1.99	Mixture 1:10	Control	Water
6	1.81	Mixture 1:10	Fired	Water
7	2.00	Waste	Control	Ammonium chloride
8	1.26	Waste	Fired	Ammonium chloride
9	2.07	Mixture 50%	Control	Ammonium chloride
10	1.59	Mixture 50%	Fired	Ammonium chloride
11	1.98	Mixture 10%	Control	Ammonium chloride
12	1.87	Mixture 10%	Fired	Ammonium chloride
13	1.32	Waste	Fired	Acetic acid
14	2.00	Waste	Control	Acetic acid
15	2.02	Mixture 50%	Control	Acetic acid
16	1.63	Mixture 50%	Fired	Acetic acid
17	2.1	Mixture 10%	Control	Acetic acid
18	1.93	Mixture 10%	Fired	Acetic acid
19	1.30	Waste	Fired	Sulphuric acid
20	2.05	Waste	Control	Sulphuric acid
21	2.06	Mixture 50%	Control	Sulphuric acid
22	1.59	Mixture 50%	Fired	Sulphuric acid
23	1.86	Mixture 10%	Fired	Sulphuric acid
24	1.96	Mixture 10%	Control	Sulphuric acid

obtained by XRF): MgO (1.54%), Al_2O_3 (28.0%), SiO_2 (46.1%), K_2O (3.86%), TiO_2 (0.67%), and Fe_2O_3 (17.6%).

The argillaceous material was obtained by disaggregation of red clay collected in Vilar de Nantes (Portugal) that is commonly used to process bricks and tiles. In the actual work only the finer fraction (less than 250 μm) was used. The galvanic sludge was dried at 100 °C during 72 h, until no detectable mass changes are reached. The mixture between the clay and the dry sludge was done in a balls mill, during 2 h. Two batches were prepared, corresponding to sludge/clay ratios (w/w) of 10 and 50%. Samples of about 2 g were then collected from the mixed batch and uniaxially pressed in small disks (thickness = 3 mm, diameter = 2.5 cm; pressure of 20 metric ton).

A first set of non-fired pressed samples (dry clay + waste) was used and here named "control". A second set was fired at 1000 °C for 10 h. Leaching tests were done by immersion in different extraction solutions: distilled water, 0.5 M ammonium chloride (pH 4.8), 0.5 M acetic acid (pH 2.5), and 0.5 M sulphuric acid (pH 0), as summarized in Table 1. Leaching tests were performed by using a solids/liquid ratio of 1/10% (w/v). Samples (20 mL) were collected after 3, 30, 90 and 270 days of exposure, the initial volume being completed by adding fresh solution. Concentrations of chromium, calcium, aluminium, copper, iron, nickel, and zinc in extracted solutions were determined by AAS.

3. Results

Fig. 1 shows the evolution of weight loss of the waste upon firing up to 1100 °C. A total loss of about 15% was noticed at low temperature (up to 500 °C), being more than duplicated above 1000 °C. A reasonable constant loss rate is observed with rising temperature, except between 700 and 800 °C where a plateau is reached.
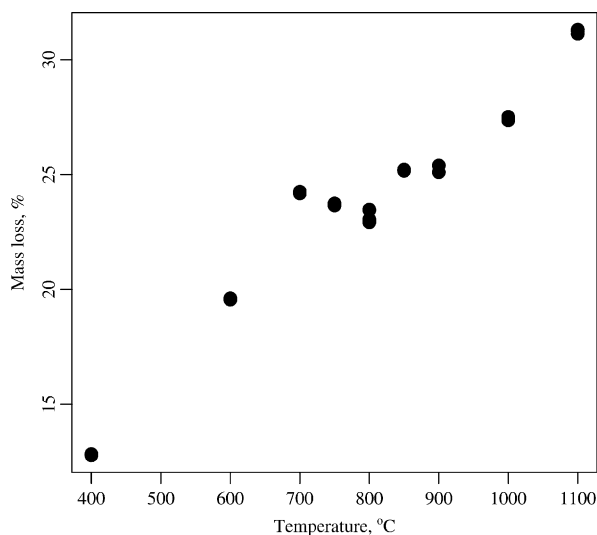

Fig. 1. Weight loss of the sludge registered upon firing.
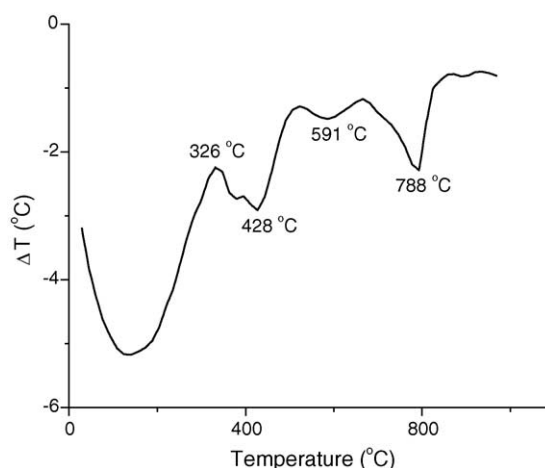

Fig. 2. DTA of the sludge, obtained at heating rate of 10 °C/min.

Differential thermal analysis was carried out to help at the identification of the nature of main transformations (Fig. 2). A strong endothermic reaction is shown up to 200 °C, due to dehydration phenomena (moisture removal). The thermal decomposition of nickel hydroxide and concomitant formation of nickel oxide is predicted at temperatures above 230 °C [17], but the non-detection of the exothermic peak due to NiO crystallization is probably consequence of the relatively low amount of nickel in the sludge. A new endothermic peak is observed in the temperature range 320–430 °C, which can be related with the decomposition of chromium hydroxide. A slight change on the heat loss rate is observed at about 400 °C, traducing the probable crystallization of chromium oxide, expected to occur at 420 °C [18]. At about 500 °C, a new low-intense endothermic reaction is registered, probably related to calcium hydroxide decomposition. The weak character of the reaction suggests the presence of minor amounts of calcium carbonate and the probable predominance of the sulphate, which decomposition occurs at much higher temperature (above 970 °C). Such presence of calcium sulphate and calcium oxide in the ultimate fired sludge and sludge/clay composites was confirmed by X-ray diffraction analysis. The endothermic concavity observed above 700 °C can be due to decomposition of aluminium sulphate (and carbonate), and/or decomposition of zinc hydroxide. Finally, at about 870 °C a slight peak is noticed that might correspond to the crystallization of zinc oxide, despite its presence had not been confirmed by XRD [16].

The incorporation of sludge in clay-based products might originate several macroscopic defects if the mixing and/or the milling (grain size control) steps are not carefully adjusted. Fig. 3 illustrates some of those defects. Sludge particles are directly exposed to leaching agents and removal of residue-containing species is favoured. In this situation, it is fundamental to assure that reactions occurring in the core of single waste particles lead to formation of stable and less soluble species. Implemented processing conditions should
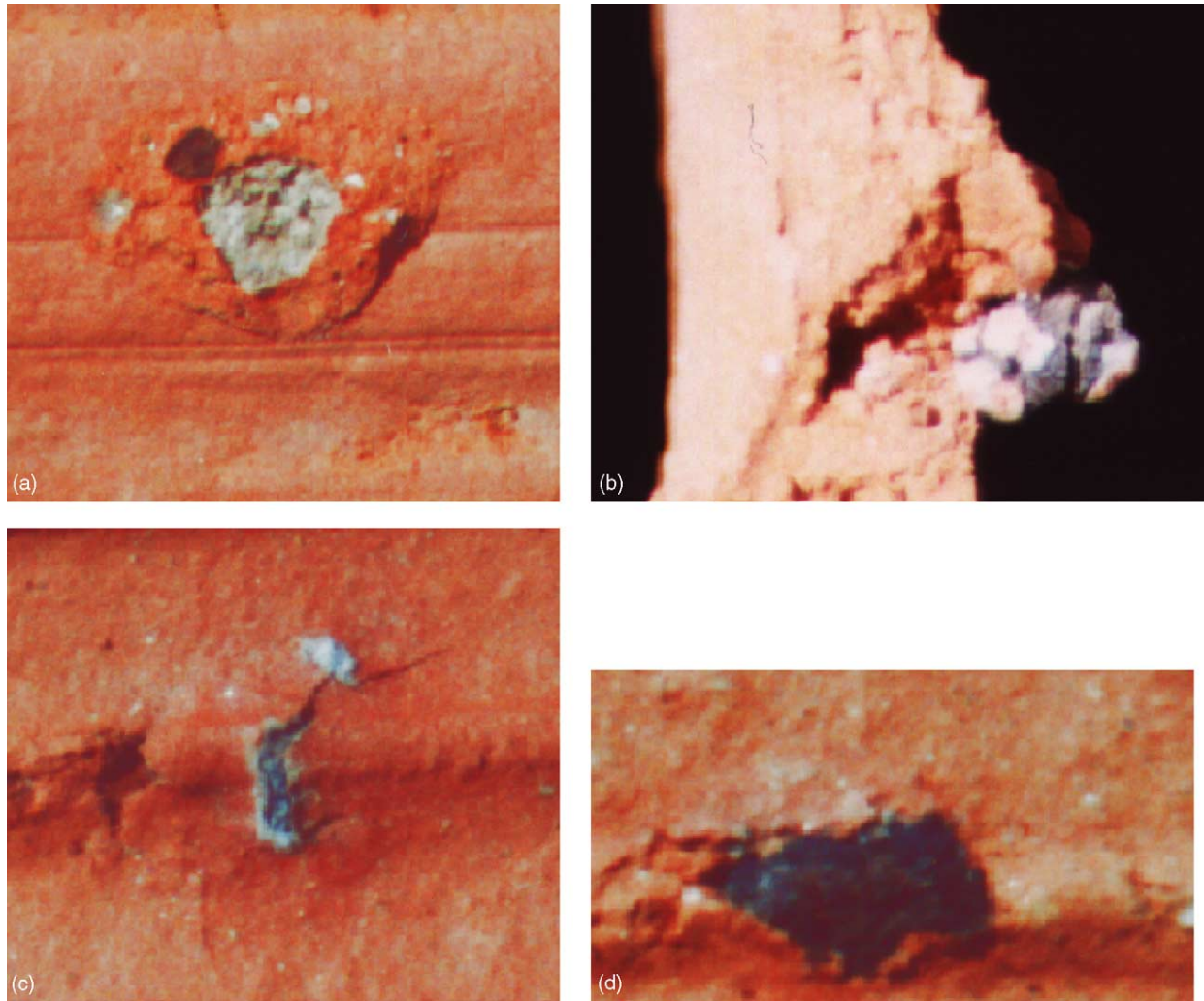
Fig. 3. Morphological aspects of the fired samples: (a) detail of an incrust of waste on the clay-based material surface, observed when the dispersion/milling is unsuitable; (b) gases released from wastes during the calcination tend to fissure the material; (c) waste crowded which affects the clay-based product surface; (d) deficient inertization, since the waste can be easily removed.

minimize those problems by favouring the intimate contact between both components.

The experimental data are shown in Fig. 4 by plotting the released concentration of each heavy metal as a function of leaching time for both the control (dry sludge + clay mixtures) and fired sludge + clay mixtures at different sludge/clay weight ratios. The MANOVA statistical test was used to study the effect of the three independent variables: thermal treatment (two levels – control and firing); kind of leaching solution (four levels: water, NH_4Cl, acetic acid, H_2SO_4), and

the % of sludge in the clay matrix (three levels: 10, 50 100%) in the release of metals from each disk samples (see Table 2).

In general, p-values under 0.05 correspond to a significant effect and values under 0.001 mean a very significant variable. By looking to results in Table 2 we conclude that all variables exert a significant effect on the immobilization of species. However, the more effective are the thermal treatment and the leachant solution. Some changes are noted by comparing the extraction of different metallic species but the nature of leachant was always found as the most influent parameter.

Table 2
MANOVA test results (p-values) given the statistical relevance of the experimental variables

| Main factor	Al	Ca	Cr	Fe	Ni	Cu	Zn	MANOVA
Thermal treatment: control and firing (TE)	0.11	<0.05	<0.05	<0.001	<0.01	<0.05	<0.01	<0.001
Percent of sludge in the clay matrix: 10, 50, 100% (ME)	0.31	<0.01	0.20	0.47	0.09	0.18	0.11	<0.01
Kind of leaching solution: water, NH_4Cl, acetic acid, H_2SO_4 (SE)	<0.01	<0.05	<0.01	<0.001	<0.05	<0.05	<0.05	<0.001
Interaction TE:SE	0.08	0.29	<0.01	<0.001	<0.05	0.08	<0.05	<0.001
Interaction TE:ME	0.51	0.56	0.84	0.31	0.11	0.24	0.12	<0.05
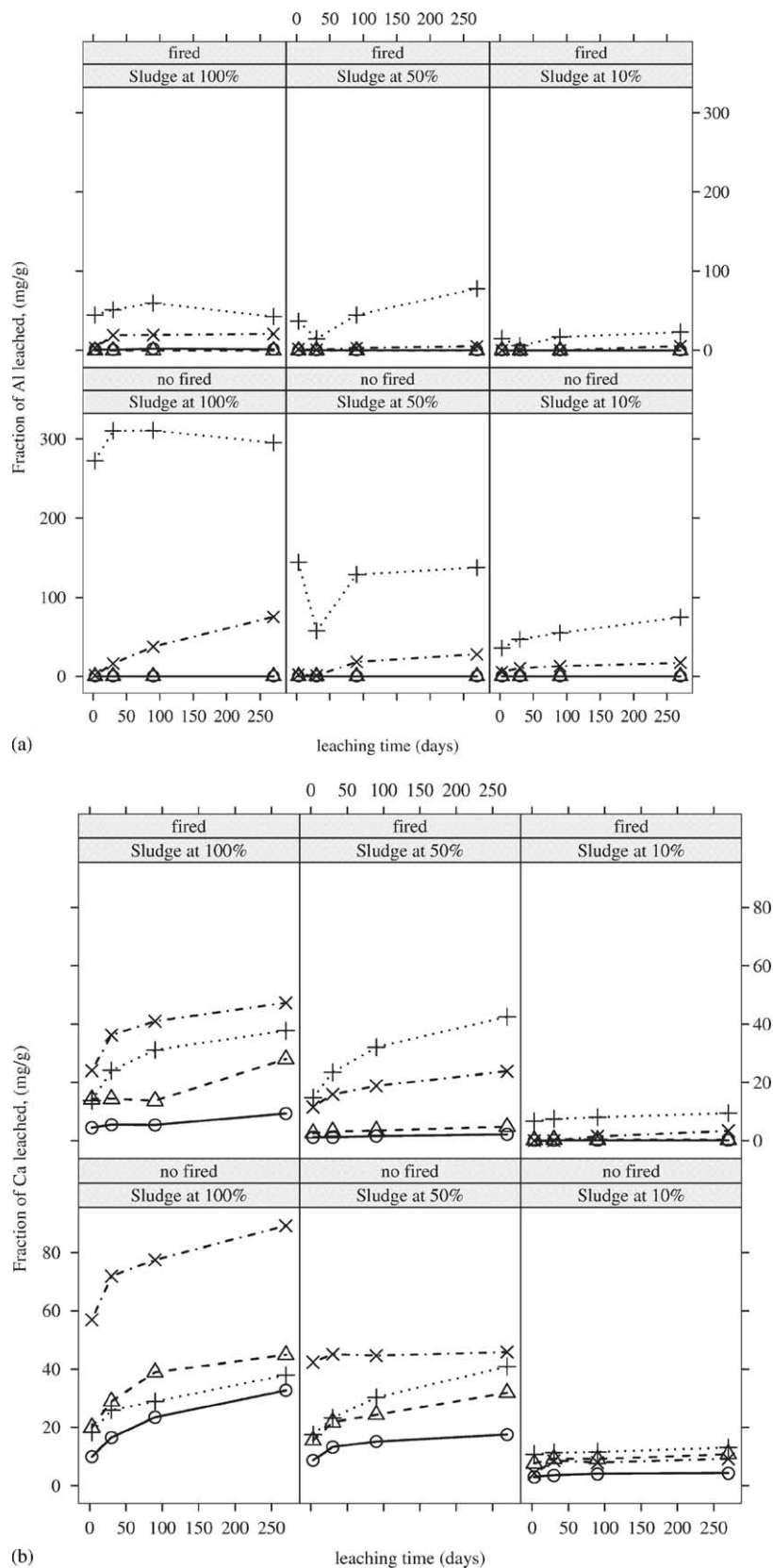
Fig. 4. Extracted concentrations of each metallic species as a function of the leaching time obtained for both control (dry sludge + clay mixtures) and fired sludge + clay mixtures. Samples contain different proportions of sludge (wt.%: 10, 50 and 100): (a) Al, (b) Ca, (c) Cr, (d) Fe, (e) Ni, (f) Cu and (g) Zn. Leaching solution: (◯) water; (△) ammonium chloride; (×) acetic acid; (+) sulphuric acid.
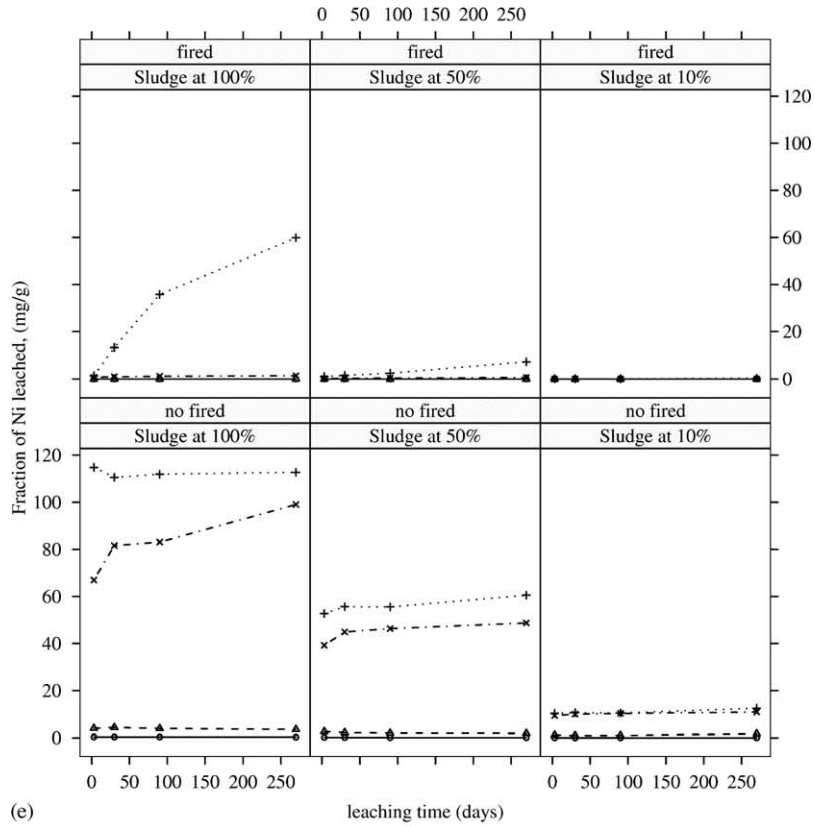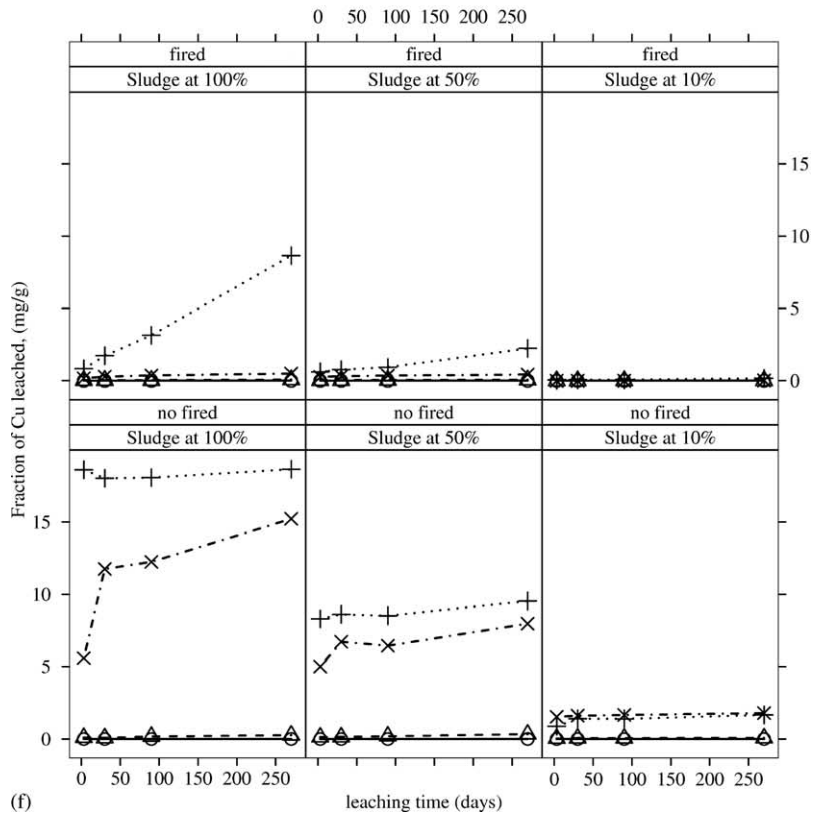
(c)

(d)
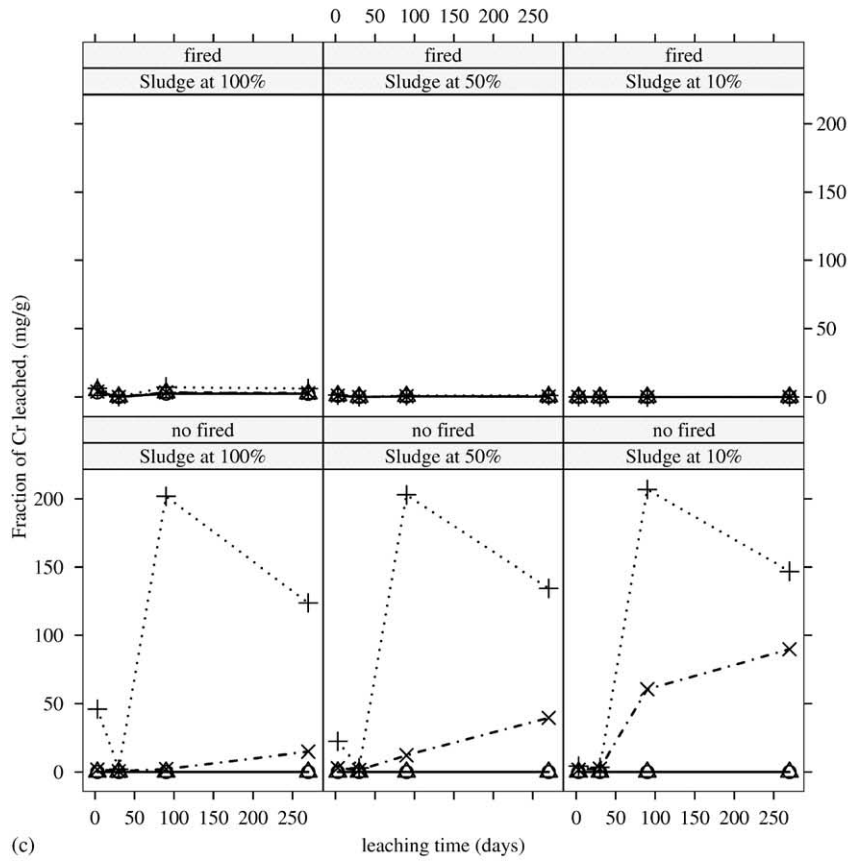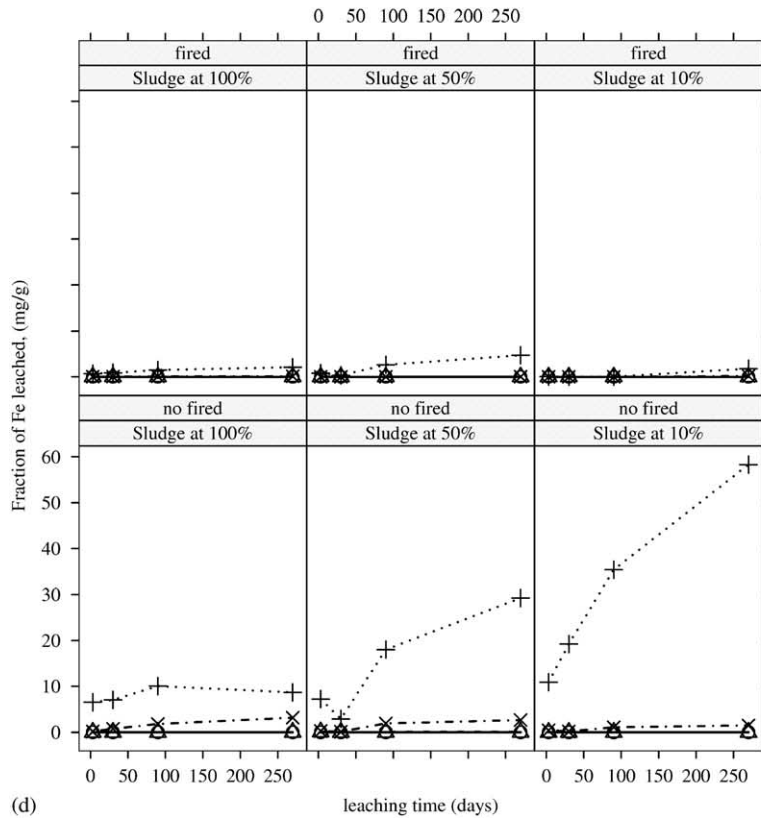
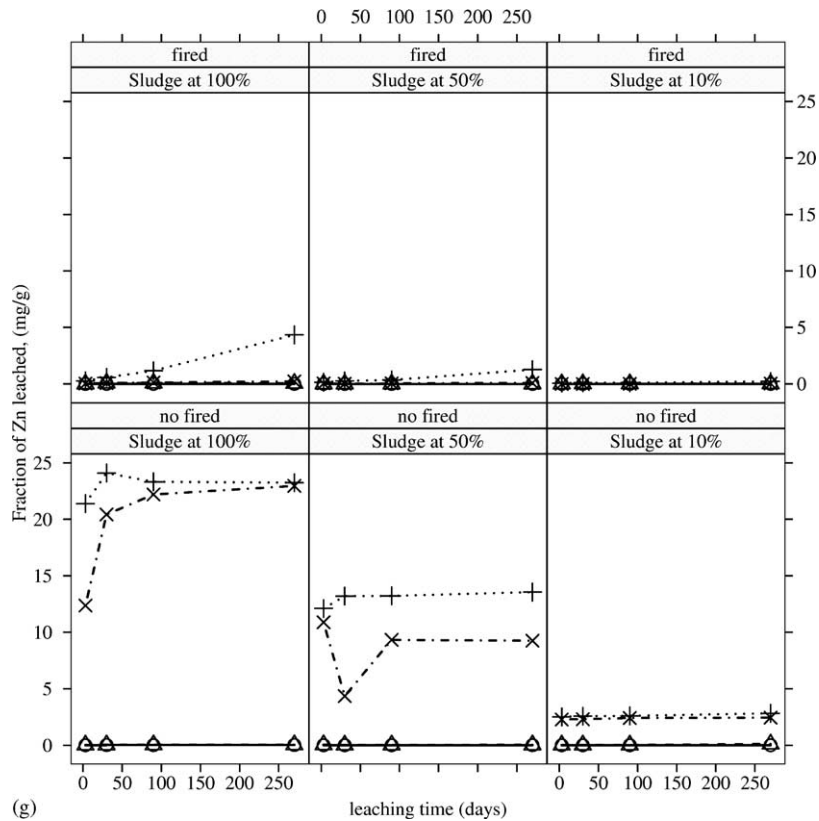Fig. 4. (*Continued*)

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A post hoc analysis was used to find the main differences between the effects of the thermal treatment and leaching solutions. Main results from this test are:

(i) The effect of firing on Cr leaching behaviour is significantly different from that observed with all the other metallic species; the sulphuric acid is by far the most effective leachant (e.g., extracted concentrations about $4\times$ higher than those observed by using acetic acid on the control pure waste samples).

(ii) The extraction of nickel seems to be significantly affected by all the experimental variables.

(iii) Cu leaching behaviour is similar to that of Ni: strong acidic media is much more effective than H_2O or ammonium chloride solutions.

(iv) For zinc the differences between control and fired samples are weak but still significant. Both acids show now more similar extraction capabilities and again much higher than the other two media.

(v) The main feature on the extraction of Al and Fe is the strong relevance of the sulphuric acid.

Sulphuric acid leaching of zinc, copper, nickel and aluminium from fired samples can be described by a zero-order kinetic function ($dC/dt = v = $ constant). For remaining experimental conditions or extraction of other elements, this law is not applicable. Even so, extrapolated values of zero-order kinetic parameters obtained by assuming

mean extraction rate values were obtained (Fig. 5). Mean extraction rate of element M is given by

$$v_m = \frac{[M]_{final} - [M]_{initial}}{t_{final} - t_{initial}} \tag{2}$$

Experimental results confirm that calcination or dilution (use of high relative amount of clay) diminishes leaching amounts of metals. This effect results more obvious for highly extracted species such as nickel. In non-fired samples nickel hydroxide decomposes at pH values under 5.5 but firing promotes its decomposition and formation of nickel oxide, which is only slight soluble (in alkaline solutions) or completely insoluble (in water). By contrast, firing does not significantly affect calcium immobilization (see Fig. 5), since soluble calcium sulphate persists on samples previously fired at $1000\,^{\circ}C$. In all cases, shrinkage of the ceramic and sludge particles promoted by sintering tends to enlarge the average particles size and diminishes specific surface area of samples. In that sense, exposure area for leaching is reduced and lower removal levels are expected [14].

Fig. 5 shows leaching rate of relevant metals, ordered from left to right according to their higher atomic mass. For fired samples, the leaching velocity tends to decrease with increasing atomic mass values, as illustrated for zinc. As previously mentioned, leaching rate also depend on the relative amount
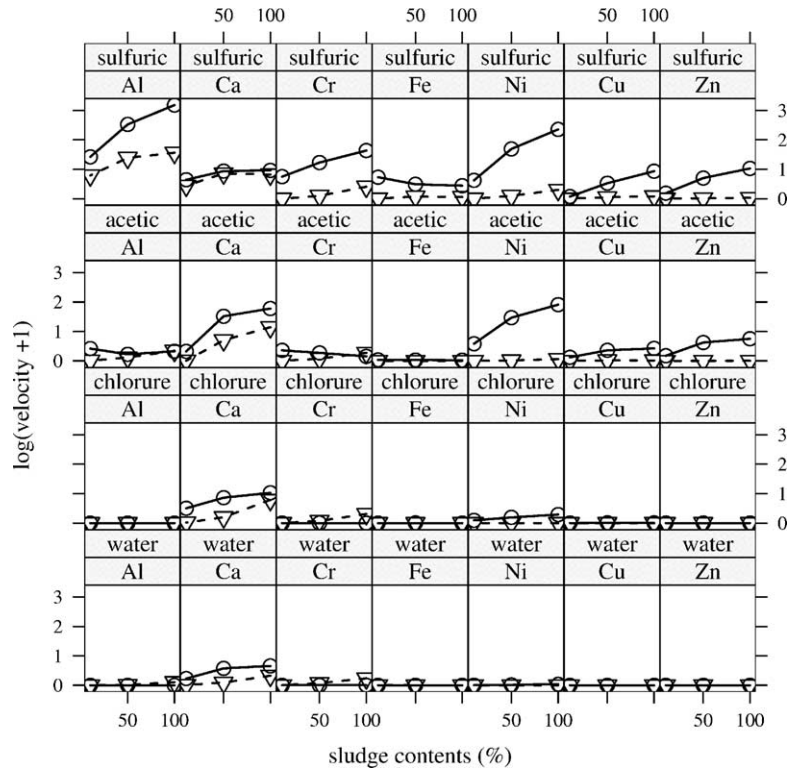
Fig. 5. Dispersion of values of kinetic constants of first-order extracting mechanisms of metals as a function of the sludge amount (wt.%) in the mixture and on the nature of leachant: (○) control samples; (▽) fired samples.

of clay in the mixture, according to the following equation:

$$\frac{dC}{dt} = m_1\, e^{-m_2(100-x)} \tag{3}$$

where m_1 and m_2 are typical constants for each element and x represents the waste percentage in the mixture. Fig. 6 gives
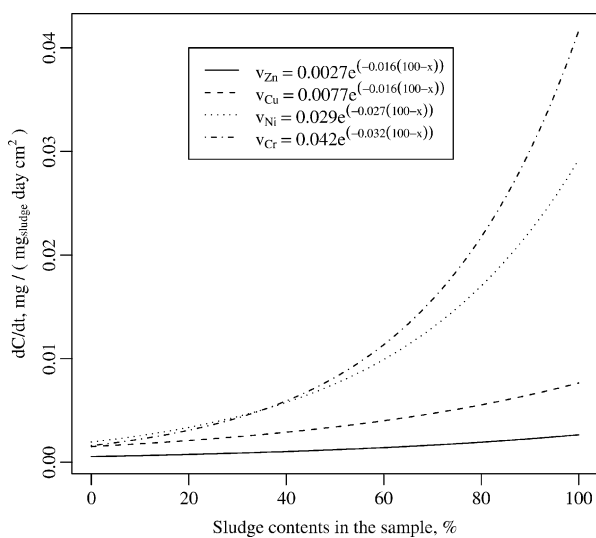

Fig. 6. Dependence on the leaching velocity of several metals on the waste content (wt.%) in the fired samples, estimated by using the sulphuric acid solution. The mathematical model that fits the curve is given by the equation $\frac{dC}{dt} = m_1\, e^{-m_2(100-x)}$.

extracting speed by sulphuric acid and corresponding dependences on the sludge content of fired samples. Relative removal rate can now be ordered according to the atomic mass of metals, suggesting that clay-based matrix acts as a filter.

Table 3 lists the immobilization efficiencies of each metal for all tested extracted solutions. Relative extraction capacity of both acetic and sulphuric acids is also related. In this table, the variable x represents the material fraction extracted by the acetic leachant compared to the fraction extracted by the sulphuric acid. Immobilization efficiency can be determined by the ratio of insoluble components and maximum extracted levels from control (non-fired) samples (Eq. (4)):

$$\text{Efficiency (\%)} = \frac{[M]_{\text{control}} - [M]_{\text{fired}}}{[M]_{\text{control}}} \tag{4}$$

where $[M]_{\text{fired}}$ is the M extracted amount by the solution A from fired samples and $[M]_{\text{control}}$ is the M extracted amount by the solution A from control sample. The effect of firing is

Table 3
Immobilization efficiency (%) estimated for each element

Metal	Immobilization efficiency (from Eq. (4)) (%)		x	
	Acetic acid	Sulphuric acid	Fired	Non-fired
Cu	96	77	0.14	0.73
Zn	99	92	0.08	0.79
Ni	99	98	0.38	0.84
Cr	99	95	0.10	0.99

now quite obvious in decreasing leaching amount of metals. In general, inertization efficiency is higher than 90% for fired samples, even when using aggressive extracting solutions (sulphuric acid). However, we should remind that leaching is a dynamic process and estimated inertization efficiencies only represent the applied time scale. Longer tests should be performed to account for later/continuous leaching occurrence.

4. Conclusions

Kinetic studies of leaching behaviour tested on different media proved that incorporation of galvanic sludges in clay-based ceramics is an effective technique for the immobilization of metals. Shrinkage of ceramic particles upon firing helps to create a physical barrier that confines sludge-containing species in the matrix. With increasing temperature chemical reactions between the two components are stronger and supplementary inertization is achieved. Moreover, temperature-induced transformations on single sludge particles promote the formation of less soluble metallic components, such as oxides. As a consequence, leaching rate tends to decrease by about two orders of magnitude when compared with non-fired samples.

Exponential-type dependence of leaching rate of most metals on the relative amount of clay in the mixture was observed, for acetic acid but mostly for sulphuric acid extraction. By using low relative amounts of clay in the mixture, leaching rate follows a zero-order kinetic law with values between 0.001 and 0.1 mg/(g day cm^2). Leaching velocity tends to increase with rising atomic numbers: $Zn < Cu < Ni < Cr$. By using high relative amounts of clay in the mixture, leaching rate of all metals is similar and essentially controlled by the permeability through the clay-based matrix.

Despite the apparent high inertization effectiveness of this method, careful controlled processing conditions should be followed to avoid or minimize the formation of macroscopic defects, such as incrusts or flaws. Mixing and milling steps are particularly sensitive.

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