Effect of experimental variables on the inertization of galvanic sludges in clay-based ceramics

J.M. Magalhães [a], J.E. Silva [a], F.P. Castro [a], J.A. Labrincha [b],*

[a] *Department of Mechanical Engineering, University of Minho, Guimarães 4800, Portugal*
[b] *Ceramics and Glass Engineering Department, CICECO, University of Aveiro, Aveiro 3810-193, Portugal*

Abstract

The incorporation of several industrial wastes in ceramic matrixes had been attempted as an effective low expense technique for the fixation of metallic species in usable products or simply to reduce the residue volume for further disposal. However, the dominant mechanism of the inertization process and the relevant influent parameters are still unknown, mostly due to the complexity of the systems. This work reports the effect of several processing parameters such as the mixing time, the calcination temperature and duration, the relative amount of sludge, and the physical aspect of the sample (powdered or pressed pellets) on the fixing level of relevant species (SiO_2, SO_4^{2-}, Zn, Ni, Ca, Cu, Cr) by leaching in different media (aqueous, acetate, and citrate). Statistical tools were used to define the relevance of each experimental variable on the inertization process of the used galvanic sludge. The relative amount of sludge in the mixture, the calcination temperature and the agglomeration state of the sample were found to be the most influent parameters of the inertization process. The incipient reaction between sludge and ceramic matrix components points out for the dominance of a macro-encapsulation mechanism.
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1. Introduction

Industrial activities produce certain amounts of substances that are not consistent with the purposes of production processes. These by-products, which in most cases cannot be directly reused, represent production wastes aiming their transformation into innocuous products or their incorporation in inert media. Sludges produced by the physico-chemical treatment of wastewaters generated by electroplating operations are potentially eco-toxic residues [1]. This is because of the high mobility of metals, such as chromium, nickel, copper, and zinc, present in these wastes. Traditionally, their way of disposal is landfilling or as a soil conditioner. However, this way is unsuitable, not only because land is limited, but also because there are strict regulations in terms of location, categorized site, gas emissions, leachate compositions, etc. Alternative ways should be attempted, and research into the economical reuse of the

several wastes appeared in the recent years, including the incorporation in a clay-based ceramic matrix [2–8].

Chemical fixation is the process or technology used to reduce the toxicity or to immobilize or make insoluble one or more dangerous wastes [9]. It requires the occurrence of chemical reactions between one or more constituents of the waste or the involvement of species of a solid matrix added to the residue. The inertization/stabilization process might involve the following chemical and physical mechanisms [10]: (i) macro-encapsulation; (ii) micro-encapsulation; (iii) adsorption; (iv) absorption; (v) precipitation. The first two are the most common by incorporation in a clay-based ceramic matrix. The simple formation of a physical barrier that reduces the leachability is a typical macro-encapsulation process. The use of relatively high temperatures promotes the decomposition of easily leachable species such as hydroxides and the formation of more stable oxides [11]. Depending on the firing temperature and the nature of components, further reactions between those compounds and Si/Al-based ceramic oxides might occur, leading the formation of flogopites, vilemites, forsterites and glassy phases [12–14]. Experimental limitations of this method

* Corresponding author. Tel.: +351-2343-70250;
fax: +351-2344-25300.
E-mail address: jal@cv.ua.pt (J.A. Labrincha).

are generally imposed by the chemical complexity of the galvanic sludge, involving the presence of volatile species such as chlorides [15,16], or remaining soluble species like sulphates. High levels of calcium, arising from the use of lime in the acid neutralization, might also promote the chromium oxidation, increasing the hazardous character. The formation of $CaO \cdot CrO_3$ is then predicted [17].

Since the incorporation in a ceramic matrix is a very complex process, optimization of each processing step should be achieved [11]: (i) wet or dry mixing/milling, by adjusting its nature, duration, and speed in order to increase the specific surface area of the components and their fineness, improving the reactivity in the subsequent steps [18–20]; (ii) shaping technique that effects the intimate contact between the particles, the starting porosity and other kinetic-type controlling parameters; (iii) firing schedule, by adjusting the maximum level and duration and then playing both with thermodynamic and kinetic factors.

This work reports the effect of several processing parameters such as the mixing time, the calcination temperature and the duration, the relative amount of sludge, and the physical aspect of the sample (powdered or pressed pellets) on the fixing level of relevant species in the ceramic matrix.

2. Experimental

The selected galvanic sludge has the following average chemical composition (wt.%, XRF) respecting metallic species: Al (15.7%), Ca (4.00%), Cu (1.03%), Cr (2.20%), Fe (0.37%), Ni (7.12%), Zn (1.36%). Difference to 100% corresponds mostly to water (or hydroxides), and some sulphates and chlorides. Particles or agglomerates have sizes under 0.2 mm and the value of the specific surface area (41.29 m^2/g, as determined by BET) confirms its fineness. As inertization matrix, a typical brick-making formulation involving the mixture of two red clays was used, showing the following average chemical composition (wt.% in a dry basis, 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 experimental work was designed by following a two-level factorial plan and considering the following parameters:

(i) mixing/homogeneition time: duration of the wet mixture between the sludge and ceramic materials, changing from 24 to 96 h. A moisture level between 20 and 25 wt.% was used, which is a typical value in the current ceramic processing of this kind of products. This variable gives information about the role of adsorption reactions of metallic species towards the clay particles and also about the effect of desagglomeration degree of waste particles;

(ii) maximum firing temperature, changing from 850 to 1050 °C. Arrhenius-type behaviour is expected to the reaction extent and the region selected is related with

the type of ceramic products generally made with this material;

(iii) firing time at maximum temperature, changing from 3 to 70 h. As the previous parameter, it controls the extent of the reaction;

(iv) relative amount of sludge in the mixture, changing from 1 to 10 wt.%. If the reactions among the waste particle are dominant over those involving clay particles, the amount of sludge expectably should not effect the inertization extent;

(v) physical aspect or agglomeration degree, by testing powdered and pressed pellet samples (thickness = 0.5 cm; diameter = 4 cm). Kinetic factors are obviously influenced by this parameter.

Table 1 summarizes all the performed experiments (total of $2^5 = 32$) with respective notations reflecting the combination of variables. As an example, b represents the test for the combination of variable (iv) in the maximum

Table 1
Experimental design of tests involving five variables and two-level changes

Test	Parameters				
	TH[a]	TC[b]	tc[c]	PM[d]	EA[e]
(1)	−	−	−	−	−
a	−	−	−	−	+
b	−	−	−	+	−
ab	−	−	−	+	+
c	−	−	+	−	−
ac	−	−	+	−	+
bc	−	−	+	+	−
abc	−	−	+	+	+
d	−	+	−	−	−
ad	−	+	−	−	+
bd	−	+	−	+	−
abd	−	+	−	+	+
cd	−	+	+	−	−
acd	−	+	+	−	+
bcd	−	+	+	+	−
abcd	−	+	+	+	+
e	+	−	−	−	−
ae	+	−	−	−	+
be	+	−	−	+	−
abe	+	−	−	+	+
ce	+	−	+	−	−
ace	+	−	+	−	+
bce	+	−	+	+	−
abce	+	−	+	+	+
de	+	+	−	−	−
ade	+	+	−	−	+
bde	+	+	−	+	−
abde	+	+	−	+	+
cde	+	+	+	−	−
acde	+	+	+	−	+
bcde	+	+	+	+	−
acbde	+	+	+	+	+

[a] Mixing time: 24 h (−), 72 h (+).
[b] Firing temperature: 850 °C (−), 1050 °C (+).
[c] Firing (dwell) time: 3 h (−), 70 h (+).
[d] Relative amount of sludge: 1% (−), 10% (+).
[e] Agglomeration state: powder (−), pellet (+).

level (10%) with all other variables in their minimum level.

Leaching tests were performed to evaluate the fixing degree of the relevant species and several media were used, namely aqueous, acetate and citrate (these two in a concentration of 0.5 M of the respective acids). pH values of starting acetate and citrate solutions were 4.7 and 3.1, respectively. They remain almost unchanged after leaching in all conditions. Leaching was performed by using 5 g of solids and 50 ml solution, during 24 h under permanent stirring. The complete evaluation of the fixation ability of the ceramic matrix is only established by performing monthly leaching tests, not accomplished in the current work. However, fast and valid indications are still obtained in the actual conditions, which correspond to normalised requirements (DIN 38414-S4). Final concentration of relevant species was determined by atomic absorption spectrometry (AAS) for metals and by mass absorption spectrometry (MAS) for other species. Statistical tools (ANOVA and MANOVA) were used to define the relevance of each experimental variable on the inertization process. ANOVA method uses the variance of each individual variable, the concentration of each element being the independent element. MANOVA analyses at once the simultaneous effects of all the variables by using the concentrations of all species. In this work, we assume that a certain variable causes significant effects when the probability (p) to have similar inputs created by low and high level determinants (H_0 hypothesis) is lower than 5%. The significance degree (F) corresponds to the probability to reject H_0 hypothesis ($1-P$).

The complete characterization of the functional properties of some sludge-containing samples is given elsewhere [3].

In general, typical standard requirements for this type of products are fulfilled, as denoted by flexural strength values above 10 MPa.

3. Results

3.1. Leaching tests

The main components of the sludge are hydroxides. The simple transformation into the corresponding oxides, occurring upon heating, is an effective way to immobilize some metallic species since the oxides are normally much less soluble than hydroxides. As a consequence, eluates from the leaching with water only show the presence of chromium III, sulphate, calcium and silica (traces). For example, chromite (Cr_2O_3) results from the decomposition of chromium hydroxide at about 420 °C. Remaining chromium soluble species are scarce and leachable amount is low (Fig. 1).

Sulphate and calcium are strongly removed in all conditions (Figs. 2 and 3) independently to the leaching media in some cases. However, in most cases acidic media extract higher amounts of sulphates due to their low solubility in water (e.g. calcium and chromium). Calcium amount in the sludge reaches 4 wt.%, and about 62.5% is extracted by the citrate solution. On contrary, removal in aqueous solutions is low (see Fig. 3).

The presence of silica in the eluates results from the ceramic matrix. As happens with other ceramic and glass materials, the acetic solution is more effective in the removal of silica (Fig. 4). In the current situation, the removal is more
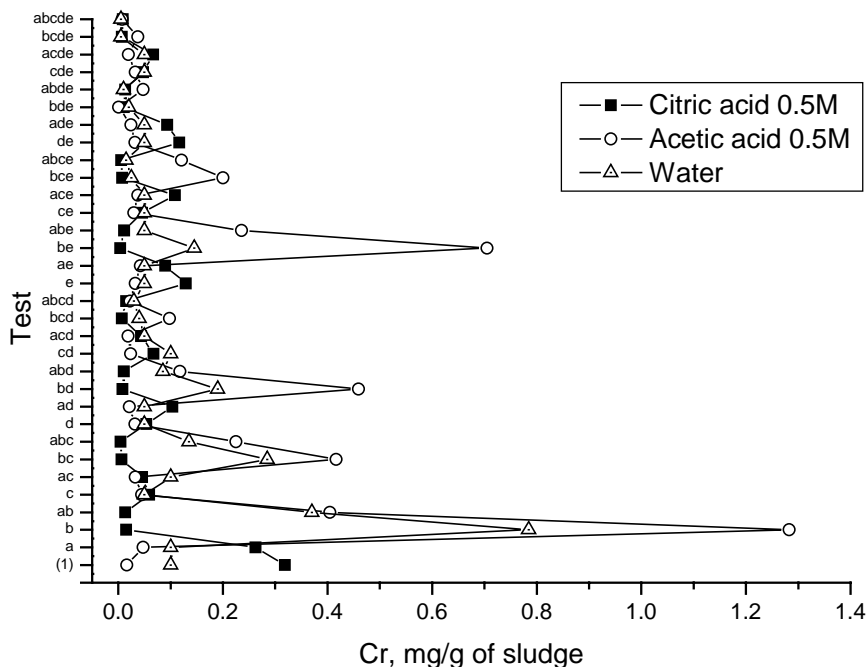

Fig. 1. Leaching of chromium in several media and by testing several experimental preparation conditions.
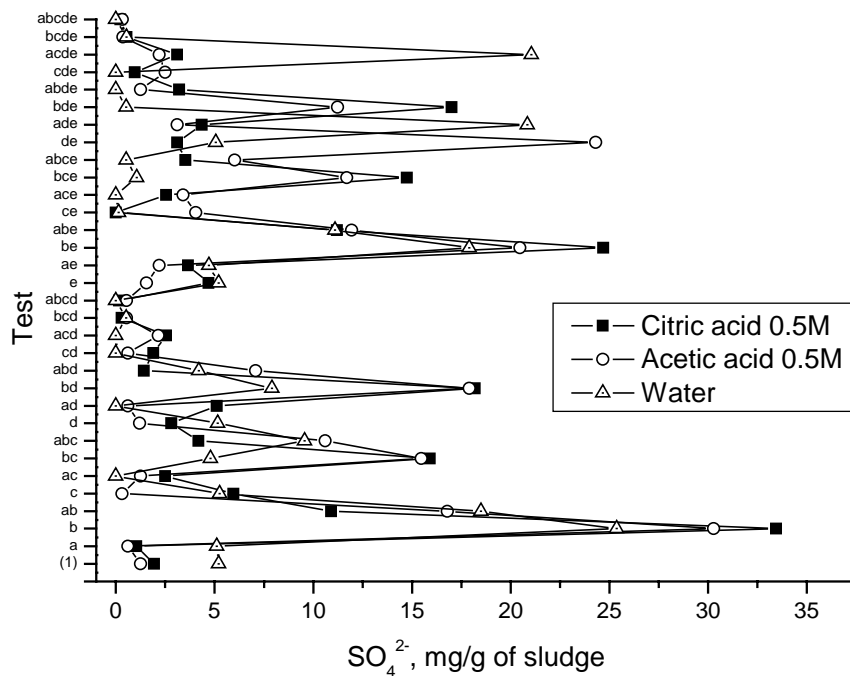
Fig. 2. Leaching of sulphates in several media and by testing several experimental preparation conditions.

effective from samples highly doped with sludge, probably due to its refractoriness nature or to microstructural opening imposed by sludge addition.

The acetate solution is also highly effective in the removal of zinc, especially from samples slightly doped with sludge (Fig. 5). This unexpected behaviour is difficult to explain, since Zn comes from the residue. Upon firing, Zn is partially lost by volatilization, this reaction being more evident with highly doped samples. Chemical affinity between Zn and Si species is also well known and an increasing tendency to form zinc silicates is expectable for Zn-rich mixtures, in other words for heavily containing sludge samples.
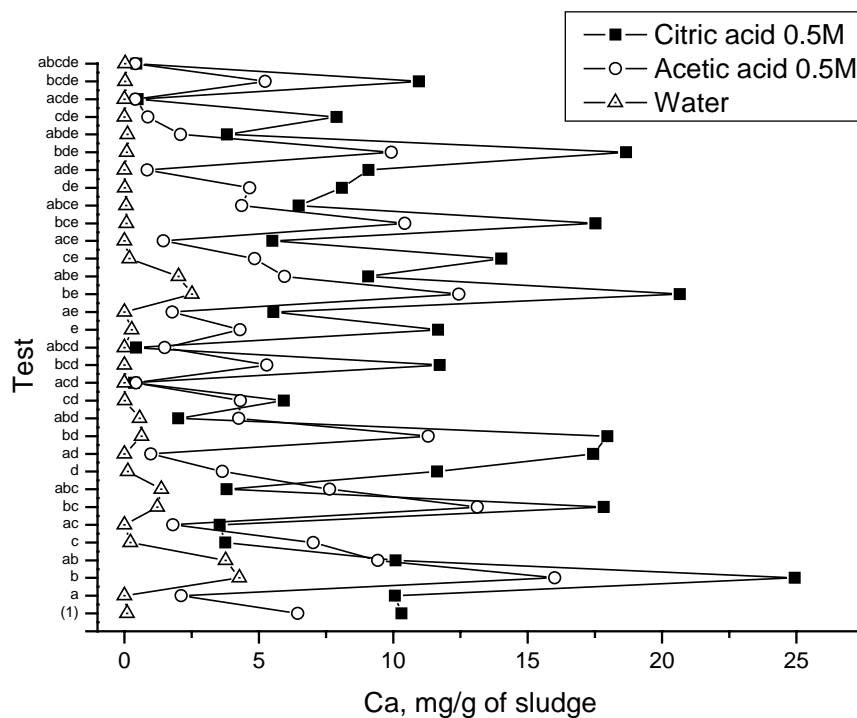

Fig. 3. Leaching of chromium in several media and by testing several experimental preparation conditions.
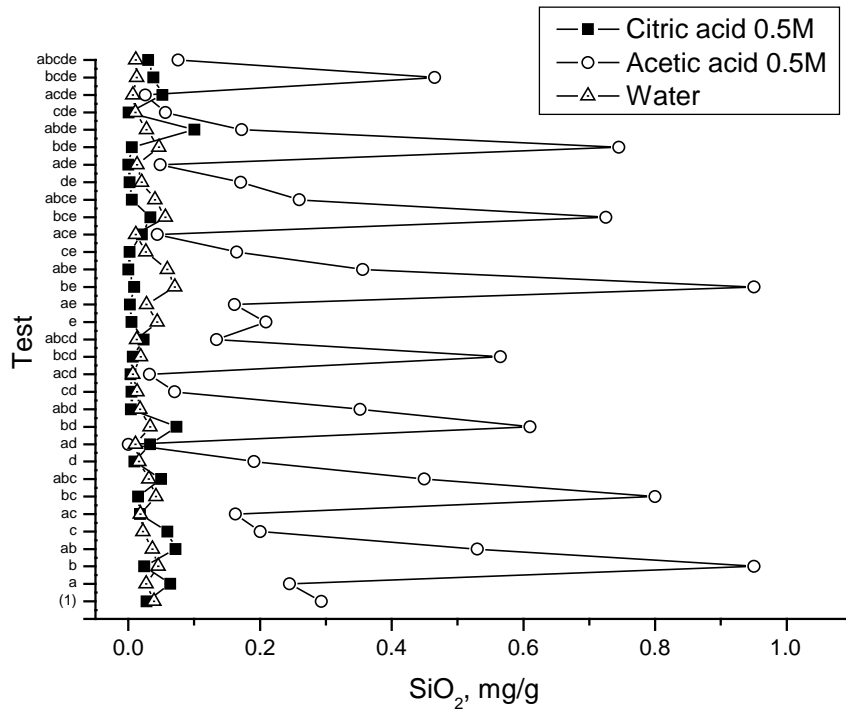
Fig. 4. Leaching of silica in several media and by testing several experimental preparation conditions.

Even the formation of zinc oxide (from the hydroxide at about 870 °C) does not assure a permanent inertness, since it is the most soluble one amongst all the present oxides. Moreover, ZnO slowly converts to the hydroxide in aqueous solution and at room temperature, and the solubility tends to increase [21]. Despite these expectations, water leaching did not remove measurable amounts of Zn, probably because its concentration in the sludge is very low. The formation of stable silicates also explains this result.

Nickel oxide is one of the first to be obtained from the corresponding hydroxide (at 230 °C). Even so, the stability is not very high and the removal by acidic solutions is strongly effective (Figs. 6 and 7). In particular, citric acid tends to
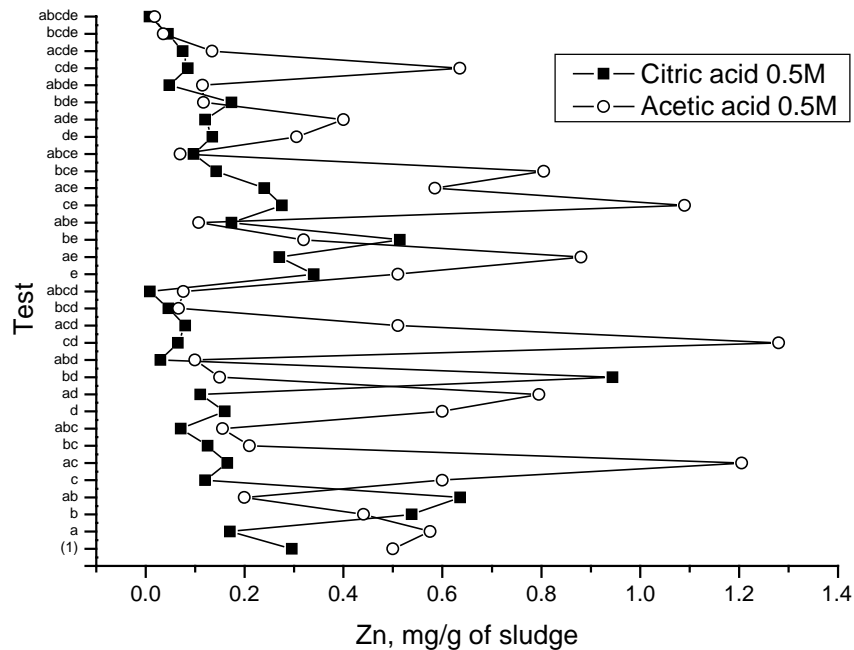

Fig. 5. Leaching of zinc in several media and by testing several experimental preparation conditions.
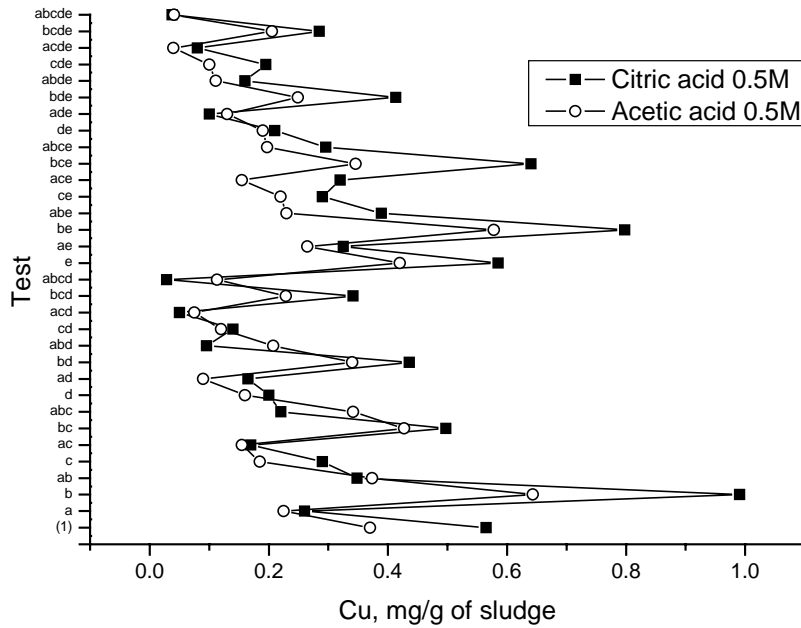
Fig. 6. Leaching of copper in several media and by testing several experimental preparation conditions.

react easily with Ni and Cu species leading to the formation of stable complexes.

3.2. ANOVA statistical test

Table 2 gives the results of the statistical treatment based on the variance analysis (ANOVA). The degree of significance to the response was estimated for each experimental variable and considering different leaching medium. By using water, the solution of most metals is incipient, as

previously mentioned. The effect of the mixing time was found to be insignificant for most species, except for the Cr^{3+} immobilization that tends to be favoured by the use of longer periods. By contrast, the calcination operational parameters (maximum temperature and dwell time) exert relevant effects, irrespective to the leaching media, being less pronounced in the case of Cr and Ca ions. The mentioned high refractoriness of Cr or Ca-based compounds might explain this tendency. This is certainly related with the instability of CaO in room conditions and the quick formation of
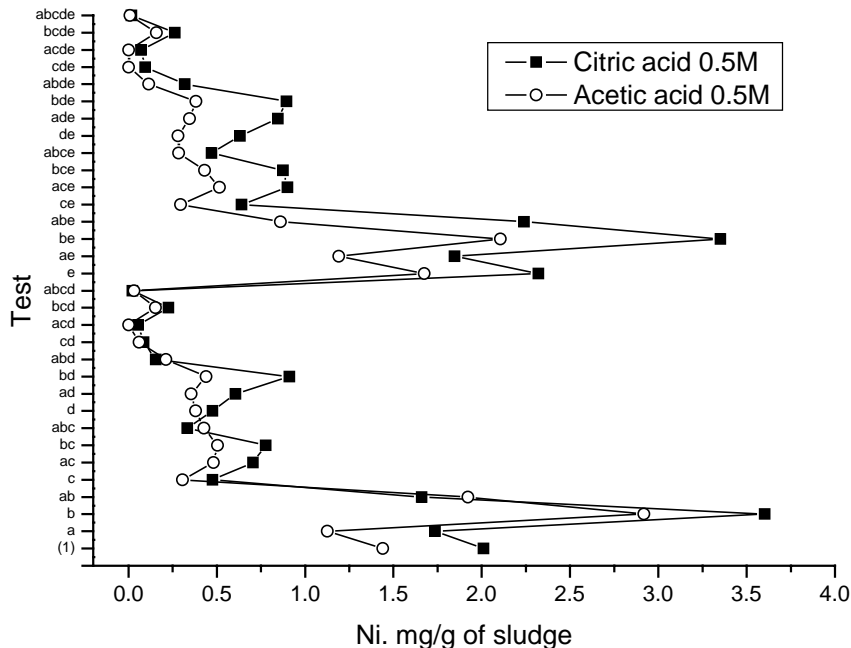

Fig. 7. Leaching of nickel in several media and by testing several experimental preparation conditions.

Table 2
Statistical relevance (ANOVA method) estimated for each variable

Element	Factors				
	TH[a]	TC[b]	tc[c]	PM[d]	EA[e]
Water					
Cr	*	*		**	
Ca		**	*	**	
SiO$_2$		***	**	***	*
SO$_4{}^{2-}$			*	**	**
Acetic acid 0.5 M					
Cr		*		***	
Ca		**		***	***
Cu			**	***	**
Ni	**		*	**	
Zn					
SiO$_2$	***		**	***	****
SO$_4{}^{2-}$		**	*	***	
Citric acid 0.5 M					
Cr					
Ca				***	***
Cu			**	***	**
Ni	**		**	***	
Zn			*	**	
SiO$_2$					
SO$_4{}^{2-}$		**	**	***	**

Significance degree: (****) >99.99%; (***) >99.9%; (**) >99.0%; (*) >95.0%.

[a] Mixing time: 24 h (−), 72 h (+).
[b] Firing temperature: 850 °C (−), 1050 °C (+).
[c] Firing (dwell) time: 3 h (−), 70 h (+).
[d] Relative amount of sludge: 1% (−), 10% (+).
[e] Agglomeration state: powder (−), pellet (+).

soluble Ca(OH)$_2$. Moreover, the presence of the respective non-decomposable sulphates also contributes to this result, since they are somewhat soluble. Relatively high extraction levels of SO$_4{}^{2-}$ species are also related with this presence. In all cases, the effect of temperature is stronger than that of the time, as expected from kinetic-induced effects.

The effect of the agglomeration degree of samples is also relevant, especially in acid leaching and in the removal of sulphates. With acetic acid, the removal of Ca and Cu species is strongly affected by this parameter. Is this case, the calcination variables seem to play a complementary effect, in the sense that one becomes stronger when the other tends to be ineffective. The increasing temperature might change, not only the reaction kinetics but also the nature of prevalent reactions, since the ceramic matrix itself is suffering dramatic changes in that calcination region (>850 °C) [3]. If no strong reactivity between ceramic and sludge components is induced during calcination, the individual sintering tends to promote their physical separation and the final exposure of sludge components might even increase apart the natural diminishing of the specific surface area. Citric acid leaching clearly shows the lower relevance of the calcination temperature and still the beneficial effect of its duration. These effects are more obvious for fluxing agents, such as Ni or Cu-containing species. With this leaching media, both

the agglomeration degree (factor a) and mixing time (factor e) seem to be relevant in the Cr removal, highlighting the potential role of physical encapsulation effects on the immobilization of this specie.

3.3. MANOVA statistical evaluation

Fig. 8 shows the evolution of the significance degree of each experimental variable for the different leaching media. In general, the significance tends to decrease with increasing extraction potential of the leaching media or, in other words, as the extraction is intensified. Even so, some relevant differences might be detected.

In aqueous media all the independent variables exert significant effects on the extraction/immobilization behaviour. Significance degree over 99.999% was estimated for the variables relative amount of sludge (b), calcination temperature (d), and agglomeration state (e). We should remind that with this leaching media, Cr and Ca ions are the main extracted species. In this sense, the optimization of the shape of the material and/or the improving of the sintering process are effective ways to decrease the removal of those extracted species, giving an interesting indication of the prevalence of a macro-encapsulation mechanism.

In acetate media the agglomeration degree is the most effective parameter. Effects due to differences between powdered and pressed samples superimpose those due to changes in the calcination temperature (850–1050 °C).

Citrate media is the most aggressive and the significance degree of variables is generally lower than that observed in acetate leaching. The relative amount of sludge is the most important parameter and the calcination temperature and mixing time are now ineffective. The last variable seems to exert detrimental effects on the immobilization of Cu and Ni (Figs. 6 and 7). As detailed in another work [22], a longer and violent mixing process that might increase the specific surface area, disseminates the sludge-containing metallic species. If combination reactions upon firing are not so extent, their availability during leaching increases. The agglomeration degree (factor a) is still very effective, confirming the importance of macro-encapsulation phenomena. The effect of calcination-related variables is now also very relevant. For example, the dwell time has a significance degree over 99%, while reaches only 95% in acetate leaching. The dwell time has a preferential effect on the species mostly removed in aggressive conditions (citrate media) such as Ca, Cu and Ni (Figs. 3, 6 and 7). An Arrhenius-type dependence should be observed if a pure reactive/kinetic mechanism was observed by changing the temperature and calcinations duration. This is not observed, since changes in the reaction controlling mechanisms might occur and also due to dramatic physical and chemical alterations in the ceramic matrix. Sintering phenomena of clay-based particles might impose diffusional limitations that retard hydroxide decomposition, especially for species lately decomposed such as the Zn.
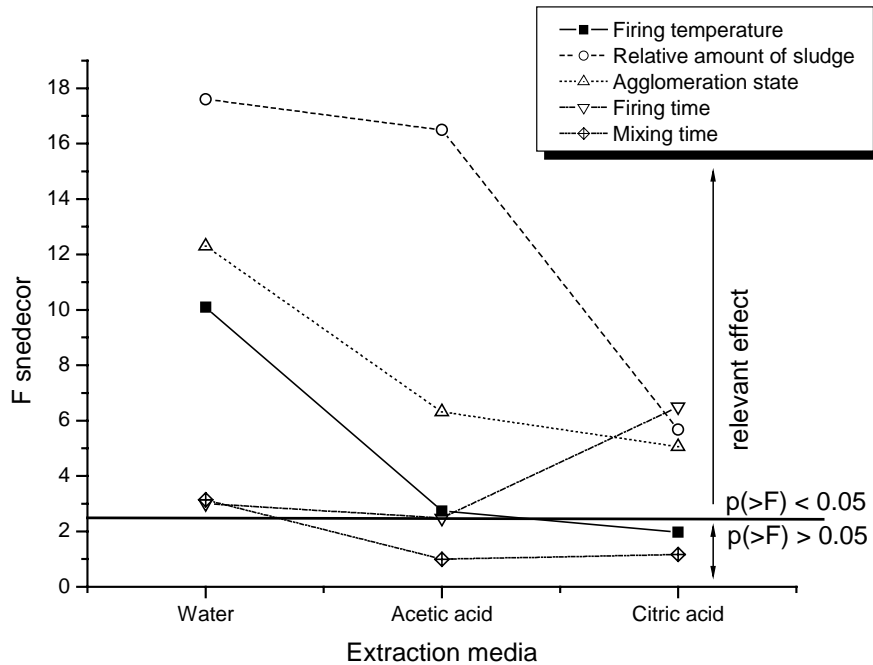
Fig. 8. MANOVA statistical analysis of the relevance of each experimental parameter in the inertization process predicted from leaching results in several media.

4. Conclusions

The incorporation in a clay-based fired matrix is a promising way to immobilize different metals belonging to galvanic sludges. The firing temperature and agglomeration degree imposed by pressing of starting mixtures are the most effective experimental parameters in the inertization process. The relative amount of sludge in the mixture also plays an important role. The dwell time at maximum calcination temperature, and the mixing time during preparation of the mixtures are less relevant. This last parameter seems to affect only the immobilization of Cr and Zn and its beneficial role is only observed after calcination.

The role of the agglomeration degree of samples seems to be important in the immobilization of all the species. On pressed samples the leaching is retarded or inhibited by the creation of a physical barrier that minors the exposing of species to an external removal agent. At the same time, the removal of clay-based constituents tends to increase, diluting the extraction of dangerous species from the sludge.

Amongst all the species, calcium ions is the most difficult to immobilize. It seems necessary to play with three experimental variables at the same time: agglomeration by pressing, and the use of maximum values of calcination temperature and time.

At the tested operation conditions, no severe reactions seem to occur between the two materials (ceramic and sludge) and the inertization is basically assured by a macro-encapsulation mechanism. The use of different ceramic matrixes that can be fired at higher temperature should be attempted to highlight the role of different immobilization mechanisms.

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