Toxicity test with ceramic sludges

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Abstract

The toxicity of the leachates of four ceramic sludges was studied. An extraction method similar to the EP method was used. The evolution of boron, lead, zinc, calcium and sodium during the extraction process was measured over a 72 hs duration. For each sludge, three tests were carried out: (a) at 25 °C with the non-ground sample, (b) at 25 °C with the ground sample, and (c) at 40 °C with the non-ground sample. The toxicity of the leachates was also evaluated by a luminiscence bioassay with Photobacterium Phosphoreum.

1. Introduction

At present, one of the major environmental problems associated with glazed ceramic tile manufacturing processes is the correct removal of sludges arising from wastewater treatment [1,2]. In this study, the toxicity of sludges from the ceramic industry was characterized and evaluated.

The extraction procedure (EP) is a test specified by the United States Environmental Protection Agency (US EPA) in which a sample of the solid waste is extracted with a volume of deionized water adjusted to a pH of 5.0 ± 0.2 with acetic acid (no more than 4 ml per gram of solid) for 24 h at a temperature between 20 and 40 °C. The total volume in ml added is 20 times the weight in grams of the sample. If the sample is a sludge, a wet solid fraction is separated from the liquid fraction. After having carried out the solubilization test with the wet solid fraction, the leachate is diluted to a volume in ml 20 times the wet solid weight in grams, and mixed with the fraction liquid. For the analysis of metals, the samples were stabilized by adding HNO_3 to a 2 wt.%. If any of the contaminants present in the liquid is greater than the corresponding top levels fixed by the US EPA, the sample is considered hazardous. Considering the toxic elements analyzed in this paper, only Pb is present in the list with a top level of 5.0 mg/l.

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The extraction procedure (EP) is also considered in the Spanish Regulations for the characterization of toxic and hazardous wastes. The waste is considered hazardous if the leachates have a EC_{50} less than 3000 ppm in the luminiscence bioassay with Photobacterium Phosphoreum [3].

On the other hand, another method, the toxicity characteristic leaching procedure (TCLP) was proposed by the EPA to determine the mobility of both organic and inorganic contaminants present in liquid, solid and multiphasic wastes. Two extraction fluids are used: (a) acetic acid/sodium acetate solution with pH equal to 4.93 ± 0.05, and (b) acetic acid solution with pH equal to 2.88 ± 0.05.

In accordance with the Proposal of the European Community with respect to disposal, wastes can be considered as hazardous, non-hazardous or inert (COM (91) 102 end -SYN 335). The analytical method proposed is DIN-38414-54 with some small modifications. In this method, a sample with 100 g of dry solids is diluted with 1 l of water and the leaching time is 24 h. In accordance with the Proposal of the European Community, a waste is considered hazardous when the content of Pb in the leachates is in the range 0.4–2.0 mg/l and the content of Zn is in the range 2–10 mg/l.

The ceramic industry, which is very important in the Valencian Community, produces sludges containing boron and heavy metals, such as Zn and Pb.

The objective of this paper has been the study of the solubilization of four sludges, which correspond to different ceramic industries. The study of solubilization was carried out in conditions similar to the EP toxicity test. No information about the solubilization process in ceramic sludges has been found in literature.

2. Materials and experimental procedure

Four sludges of the ceramic industry have been studied. They were provided by the Environmental Agency of the Valencian Government and correspond to sludges produced in glazed ceramic tile manufacturing processes. They are called Sludge 1, Sludge 2, Sludge 3 and Sludge 4 in this paper. Sludges 1, 3 and 4 are quite homogeneous with fine particles whereas, Sludge 2 has coarse and fine particles.

The experimental procedure was the following:

An amount of sample greater than 100 g was taken. The sample was centrifuged to separate the solid and liquid fractions. The liquid fraction was passed through a 0.45 μm filter. The solids retained on the filter were mixed with the centrifuged solids, and this mixture was the solid fraction used for studying its solubilization. The water content of the sludges was determined by drying the sludge at 80 °C until constant weight.

The solid fraction (wet solid fraction) was weighed and placed in a bottle with an amount of de-ionized water, 16 times the wet solid fraction. The stirring was intense enough to favor a good solid–liquid contact and avoid external diffusional resistances. The pH was measured and 0.5 N acetic acid was added until the pH value was 5. The control of the pH and the addition of the 0.5 N acetic acid solution in the experimental runs carried out in this work were slightly different from those proposed in the EP method. The control of pH was done when extracting a sample for analysis. This was

done each hour for the first period (until the 5th hour) and afterwards less frequently (in the EP method, the pH must be controlled continuously or at least every 15 min when there is a change greater than 0.5 units of pH value). Nevertheless, as can be deduced from the experimental data presented in the following sections, similar results of solubilization after 24 h would probably have been obtained if the EP method had been used. In addition, the test carried out in this work continued until the 72nd hour. After each control, the pH value was lowered to 5.0.

In all of the cases, the amount of acetic acid added was lower than 4 ml/g of solid. The bottle had a volume of 2.5 l and was sunk in a thermostatic bath of constant temperature (25 °C or 40 °C).

The analytical techniques used were the following: (1) electron microscopy with X-ray analyzer for determining the elements present in the solid (EDX); (2) atomic absorption spectrophotometry or inductively coupled plasma atomic emission spectrometry, for determining solubilized metals in leachates of sludges and extracted fractions; (3) colorimetry for boron determination with azomethine H; (4) X-ray diffraction for determining the most abundant compounds; (5) microtox equipment for toxicity determination with Photobacterium Phosphoreum; (6) Laser diffraction, based on the Fraunhofer theory, for determining particle size distribution, and (7) micromeritics, for determining specific surface in porous solids.

3. Characterization of the sludge

Table 1 shows the percentage of the dry sludge and the wet sludge obtained in the experimental method used. Sludges 1, 3 and 4 had a water percentage within the normal range 35–60% corresponding to sludge that have been thickened, whereas sludge 2 had a high water content.

Table 2 shows the percentage of Na, Al, Si, K, Ca, Ti, Zn, Fe, Zr and Pb determined by electron microscopy (EMX). Although the analysis may not be accurate by using this technique, an estimation of compounds and relative abundance can be obtained. The composition of the sludges is in the normal range of ceramic sludges [2, 4, 5].

Table 3 shows the quantity of some elements in the liquid fraction of the sludges. By X-ray diffraction, the compounds detected were the following for each sludge: (a) for Sludge 1, portlandite, calcite, quartz, feldspat and zircon; (b) for Sludge 2, quartz,

Table 1
Percentage of solids in sludges

Sludge	Dry solids (%)	Wet solids (%)
Sludge 1	55.8	82.0
Sludge 2	23.6	32.7
Sludge 3	57.2	80.0
Sludge 4	52.3	84.5

Table 2
Analysis of a fraction solid (wt. %)

Element	Sludge 1	Sludge 2	Sludge 3	Sludge 4
Na	s.q.	s.q.	3.8	3.8
Al	16.5	19.1	12.2	12.2
Si	48.1	42.1	51.2	46.7
K	5.8	4.4	5.0	4.8
Ca	10.7	10.9	10.9	14.9
Ti	1.1	1.1	n.d.	n.d.
Zn	5.5	8.3	7.2	5.9
Zr	6.4	7.5	4.6	5.5
Pb	5.7	6.4	0.4	1.2
Fe	n.d.	n.d.	1.9	2.07
Mg	n.d.	n.d.	2.6	2.83
Ba	s.q.	n.d.	n.d.	n.d.

s.q.: small quantity; n.d.: not detected.

Table 3
Analysis of the liquid fraction

	Sludge 1	Sludge 2	Sludge 3	Sludge 4
pH	8.50	8.56	8.60	8.76
Conductivity	—	1714	1722	2250
Sulfates (ppm)	155.50	226.2	206	293
Sodium (ppm)	440	104	—	—
Calcium (ppm)	178	176	—	—
Silicon (ppm)	46.6	39.7	—	—
Amonium (ppm)	4.70	1.35	1.27	2.24
Boron (ppm)	443	109.7	114	55.2
Iron (ppm)	1.81	1.76	1.68	1.75
Aluminium (ppm)	0.95	1.47	n.d.	0.91
Zinc (ppm)	n.d.	0.1	n.d.	n.d.
Lead (ppm)	0.98	1.08	n.d.	n.d.
Titanium (ppm)	0.25	n.d.	0.12	n.d.
Zirconium (ppm)	0.47	0.64	0.51	1.13

—: not determined. n.d.: not detected.

zircon and calcite (very weak), (c) for Sludge 3, zircon, quartz and dolomite (very weak), and (d) for Sludge 4, quartz, zircon and dolomite and calcite (very weak).

Figs. 1–4 show the particle size distribution of the Sludges 1–4, respectively. It can be observed that the particles of Sludge 1 have diameters less than 40 μm, whereas Sludge 3 and 4 have particles with diameters less than 15 μm. Sludge 2 has about 5% of coarse particles (ca 1 mm) and the size of the remaining particles varies between 2 and 50 μm, as indicated in Fig. 2.
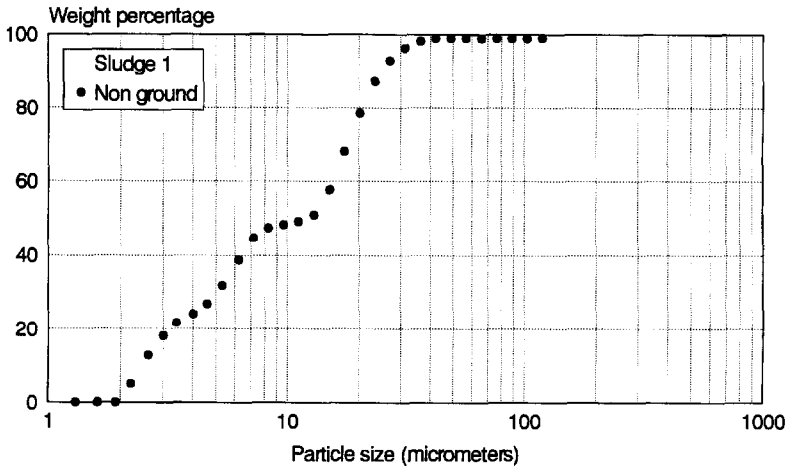
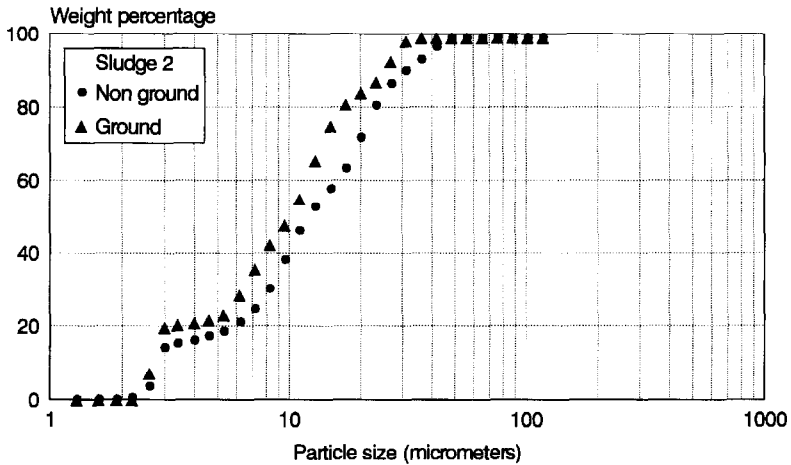Fig. 1. Particle size distribution of Sludge 1.

Fig. 2. Particle size distribution of Sludge 2.

The specific surfaces for Sludges 2, 3 and 4 are 4.2, 5.1 and 6.2 m^2/g, respectively. Although for Sludge 1, it was not possible to determine this value, a similar surface could be expected. The specific surface was also measured for 0.2 mm sand particles, obtaining in this case a nil value. The values around 4–6 m^2/g for solids, where all the particles are greater than 2 μm, indicate that these solids are porous but their porosity is not great.
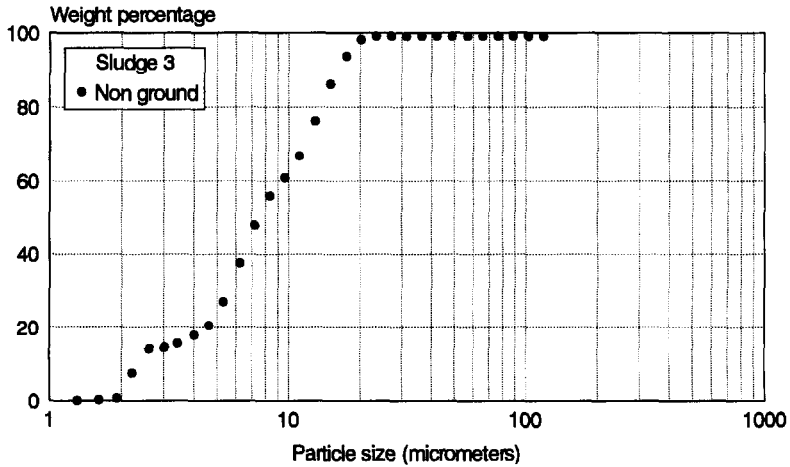
Fig. 3. Particle size distribution of Sludge 3.
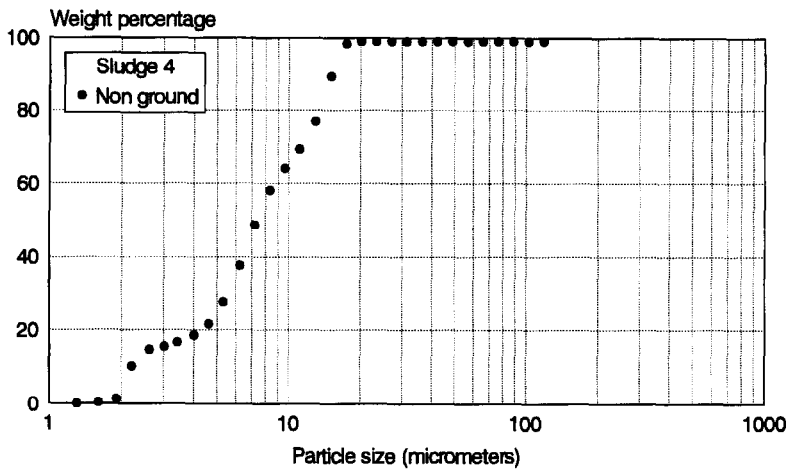
Fig. 4. Particle size distribution of Sludge 5.

4. Solubilization of the solid fraction by acid solution

For each of the four sludges studied, three runs of solubilization were carried out as indicated previously for (a) normal sample extracted at 25 °C, (b) normal sample extracted at 40 °C, and (c) ground sample extracted at 25 °C. The temperatures selected, 25 and 40 °C correspond to the extreme temperatures proposed in the EP test.
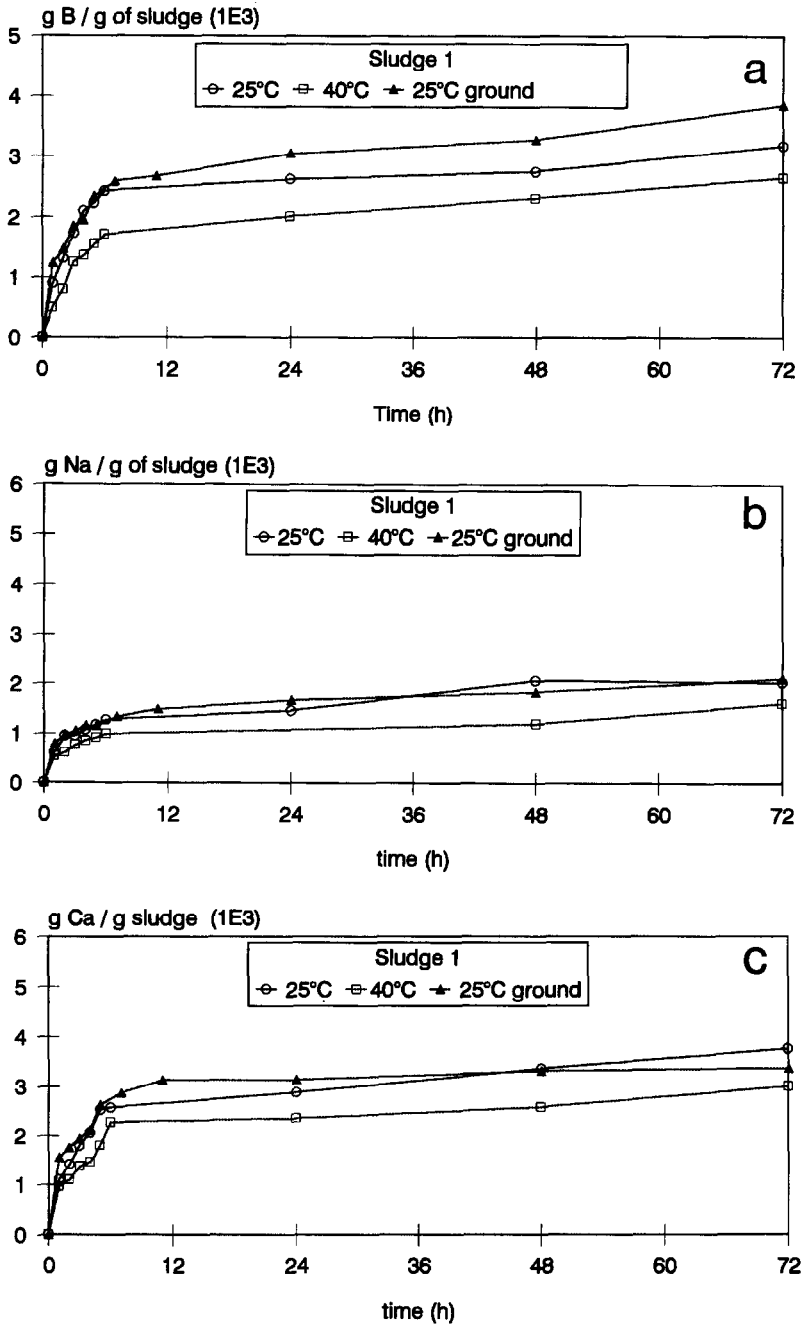
Fig. 5. Solubilization of Sludge 1: (a) boron, (b) sodium, (c) calcium, (d) zinc, (e) lead, (f) pH and (g) 0.5 N acetic acid solution.
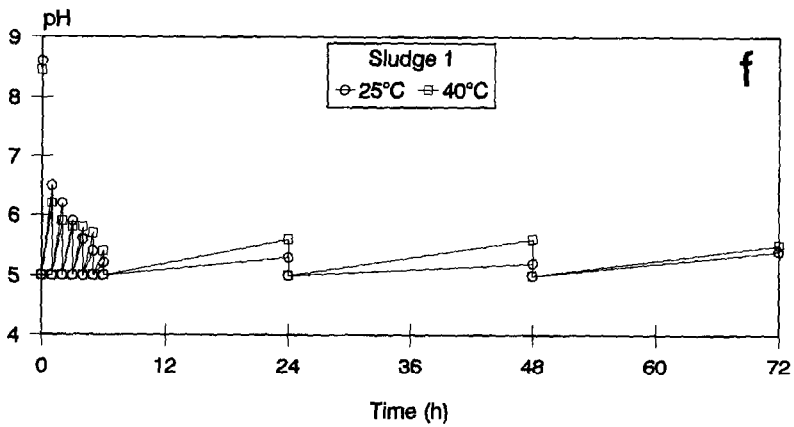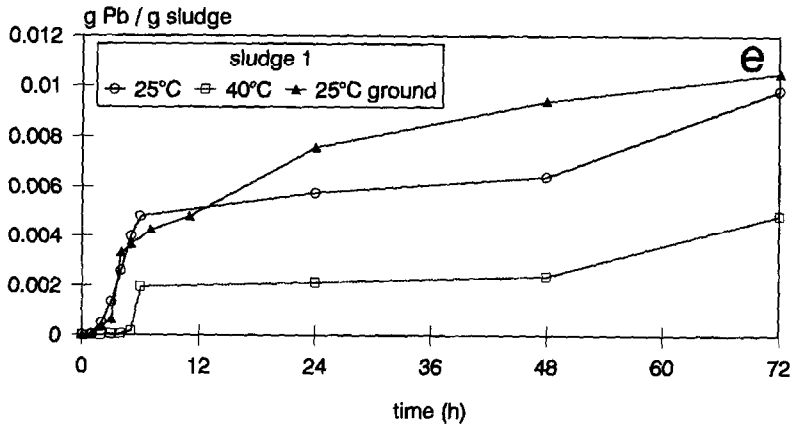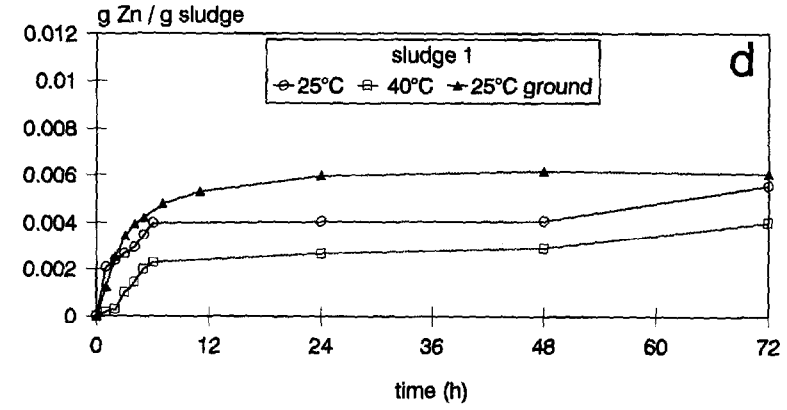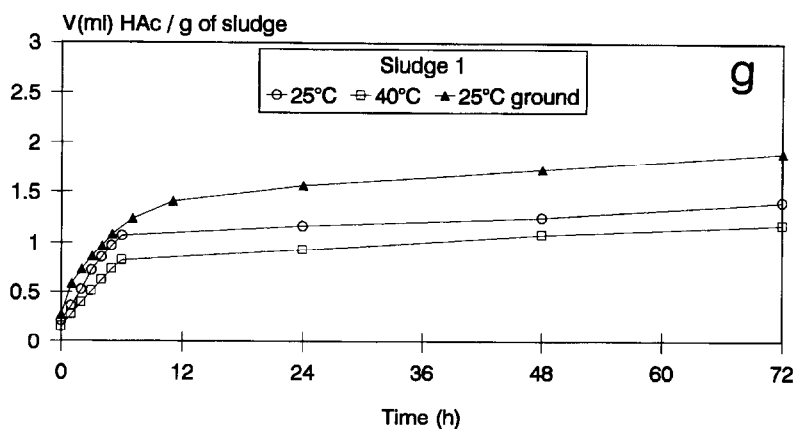
Fig. 5d–f.

Fig. 5g.

The grinding of small samples of the wet sludge was carried out manually. The only reason for performing this operation was to deduce if the internal diffusion/migration of some ionic compounds influenced the overall solubilization process. When the controlling step in fluid–solid reactions and solubilization processes, is the internal diffusion through the particle, the reaction rate can be increased by decreasing the particle size. Although the size distribution of the Sludges 1, 3 and 4 after grinding was similar to the non-ground samples, grinding favors the solubilization process, as can be seen in this section. The coarse particles of Sludge 2 were broken in the grinding. Fig. 2 also presents the particle size distribution after grinding Sludge 2, showing a decrease in the particle diameter range (from 2–40 μm to 2–30 μm).

Figs. 5–8 show the variation of analyzed elements solubilized per gram of wet solid for the four wet sludges studied. In each figure, the three runs carried out at different conditions can be distinguished. The solubilization data have been presented taking into account that the initial volume of the liquid (around 1 l) decreased during the run as a consequence of the volume taken for analysis (≈ 10 ml). Each figure shows the solubilized amount of B, Ca, Na, Pb and Zn per gram of wet solid, the variation of pH and the amount of acetic acid added per gram of wet solid vs. time (data of pH for ground samples of Sludges 1 and 2 are not available, although values of pH can be considered close to the corresponding values of the runs carried out at 25 °C with non-grounded samples). Initial values of pH are those obtained after five minutes of dispersing the wet solids in water. The estimated errors in the determination of the degrees of solubilization depend on the relative abundance of each element. When the g. element solubilized/g. sludge is greater than 5×10^{-4}, the relative error is less than 5%, whereas for small degrees of solubilization (around 10^{-5} g. element/g. sludge), the error can be around 25%.

From Figs. 5–8, the following can be observed:
– There is a significant level of solubilization of Pb, Zn and B in Sludges 1, 2 and 4. Table 4 presents the values of EC_{50} of Photobacterium Phosphoreum of the
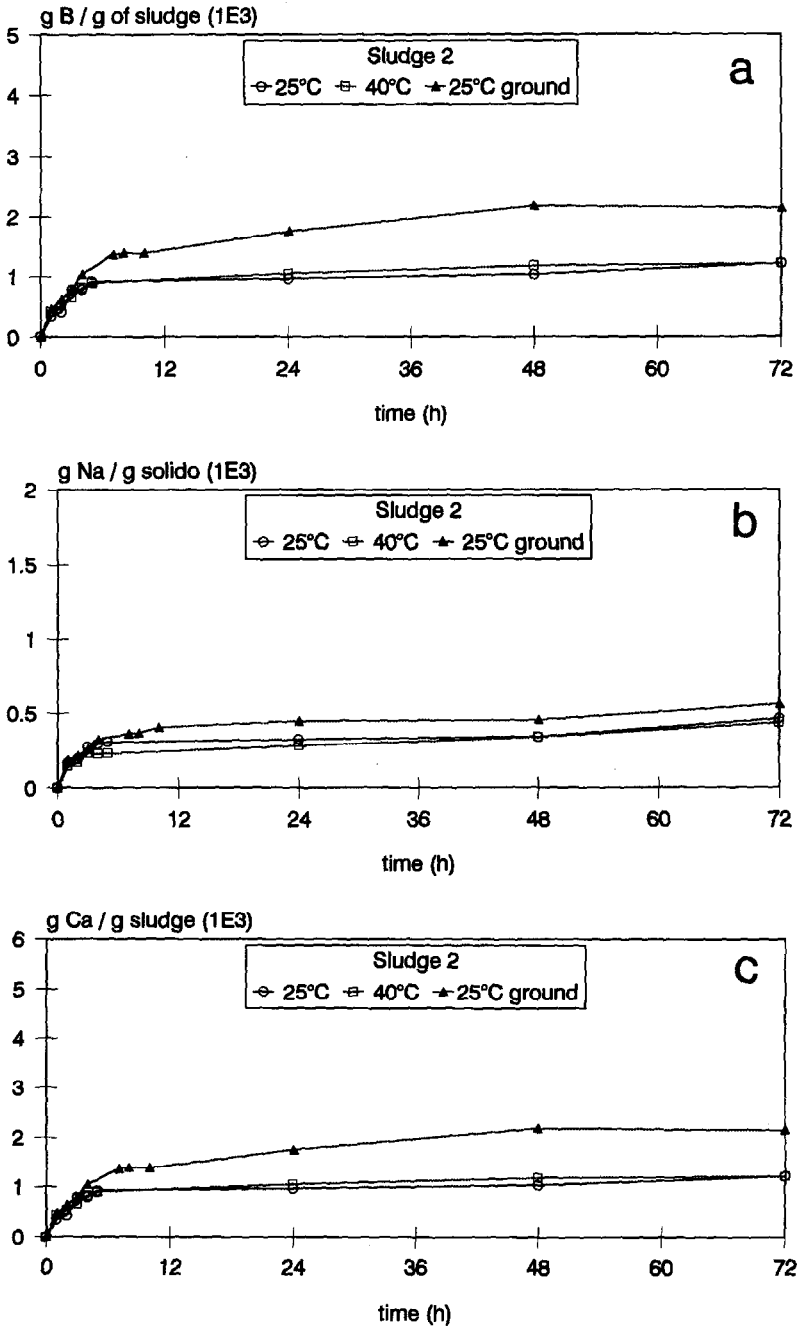
Fig. 6. Solubilization of Sludge 2: (a) boron, (b) sodium, (c) calcium, (d) zinc, (e) lead, (f) pH and (g) 0.5 N acetic acid solution.
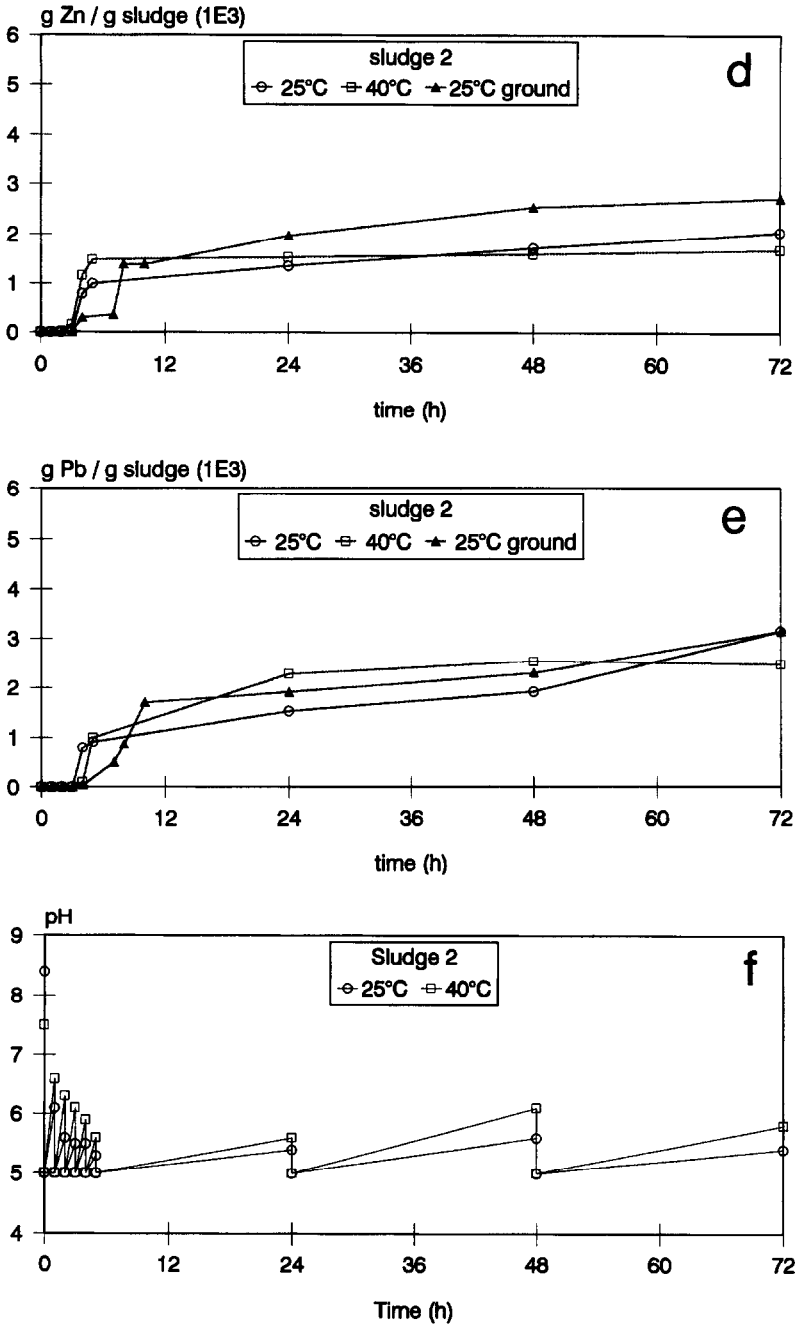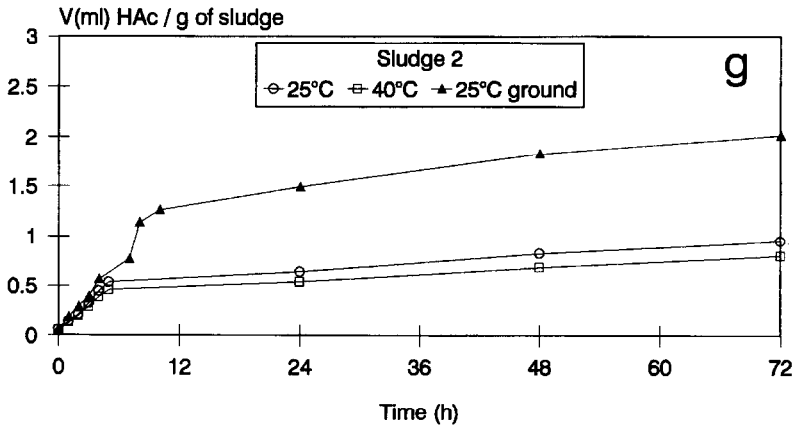
Fig. 6d–f.

Fig. 6g.

leachates obtained after the period of 24 h. It can be observed that the leachates of Sludges 1, 2 and 3 show a considerable toxicity. The values of EC_{50} and toxicity units can have an error of 30%. Due to this fact, no correlations have been proposed and only the correspondance between the Pb contents and the toxicity can be observed, within the determination error. The influence of the toxicity of this compound is much greater than the remaining ions.

— In general, the solubilization takes place for the first 24 h and therefore, this period of time is apparently long enough to determine the fraction which is easily solubilized. Nevertheless, in some cases, as it occurs with Pb in Sludge 1, the solubilization can increase significantly after the 24 h period.

— The solubilization of B, Ca and Na takes place mainly in the first 8 h, whereas the solubilization of Pb and in some cases the solubilization of Zn is delayed with respect to the remaining elements analyzed (≈ 2–6 h).

— When grinding Sludges 1, 2 and 4, the extraction of some elements is favored. In Sludge 3, where the solubilization is small, there is no significant difference in all the elements considered.

— In Sludges 1, 3 and 4, the solubilization process at 40 °C is slower than at 25 °C. When the amount solubilized is small, as it occurs with B in Sludge 3 and Sludge 4 and Na in Sludge 4, the differences between solubilization at 25 °C and 40 °C are very small. Nevertheless, in Sludge 2 the solubilization at 40 °C is similar to that at 25 °C.

The operational procedure was not exactly as that indicated in the EP method. Nevertheless, taking into account that the solubilization rate after the 24th hour was very small and that after the first period (4 or 5 h) the pH values are always between 5.0–5.2 and 5.5–5.7, it can be deduced that similar results would have been obtained if the EP method had been applied. With the method used in this research, the hourly variation of the pH could be observed.
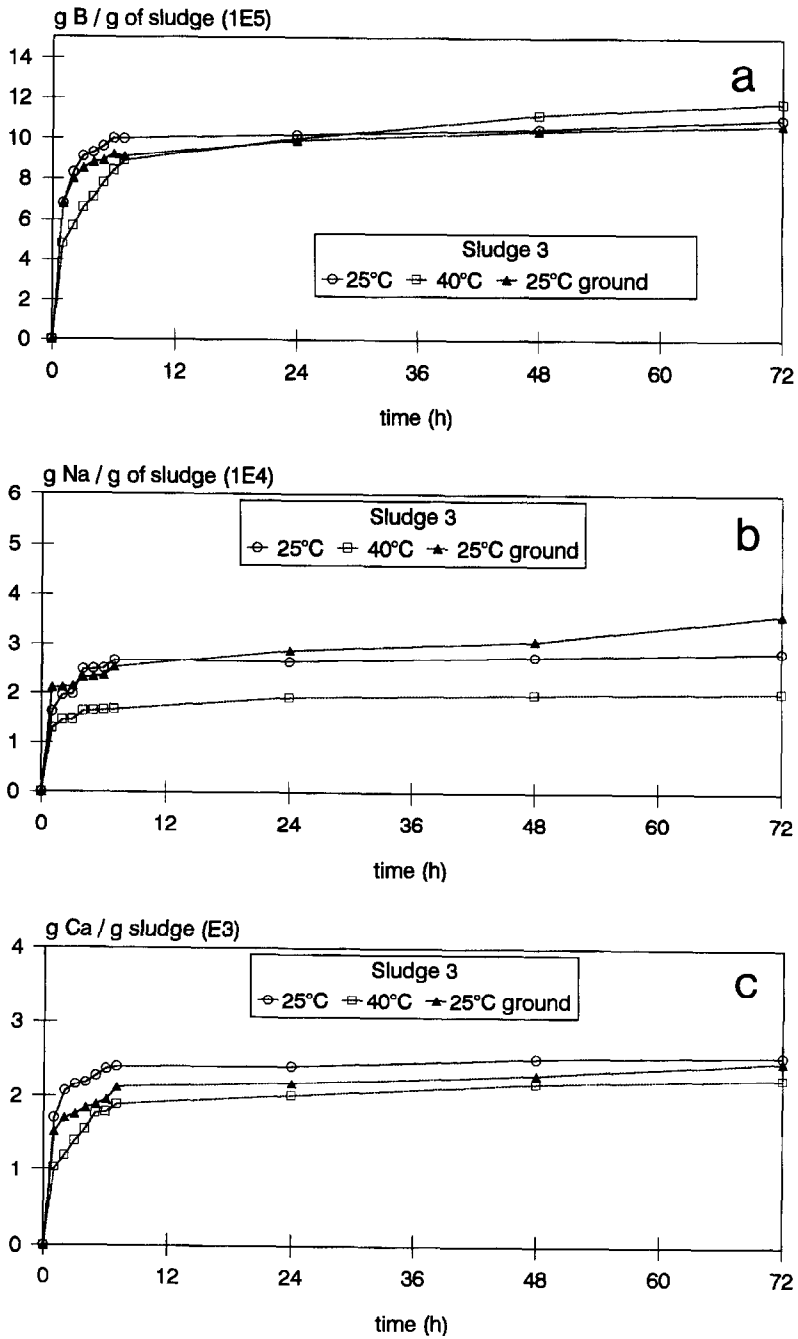
Fig. 7. Solubilization of Sludge 3: (a) boron, (b) sodium, (c) calcium, (d) zinc, (e) pH and (f) 0.5 N acetic acid solution.
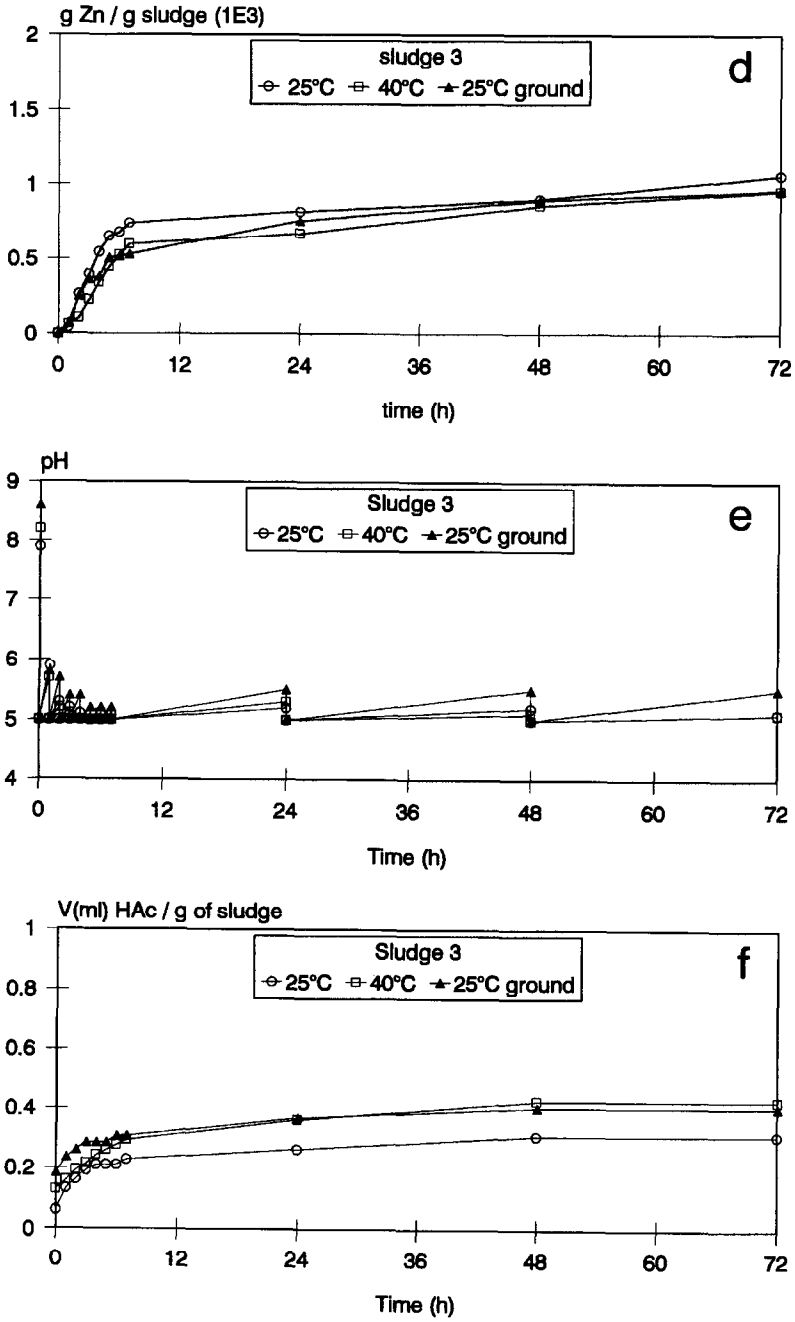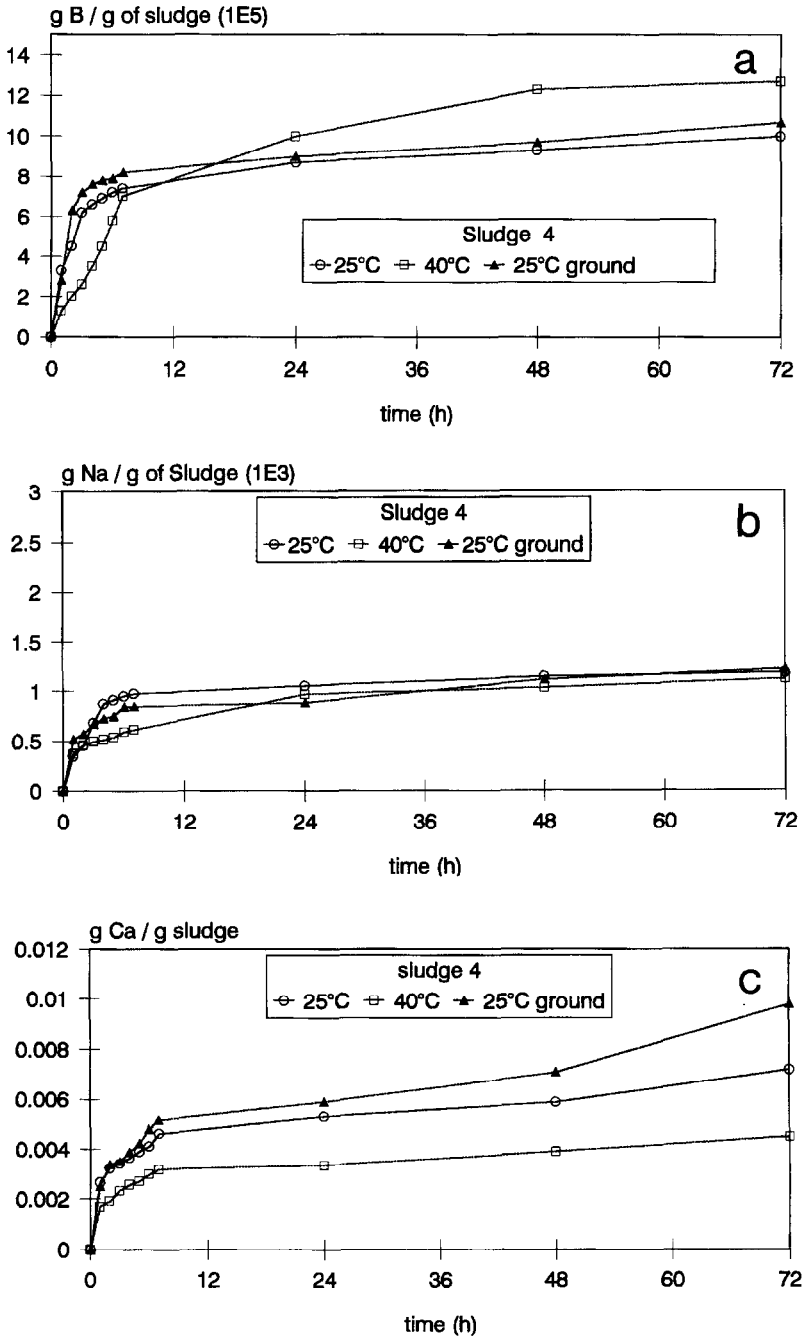
Fig. 7d–f.

Fig. 8. Solubilization of Sludge 4: (a) boron, (b) sodium, (c) calcium, (d) zinc, (e) lead (f) pH and (g) 0.5 N acetic acid solution.
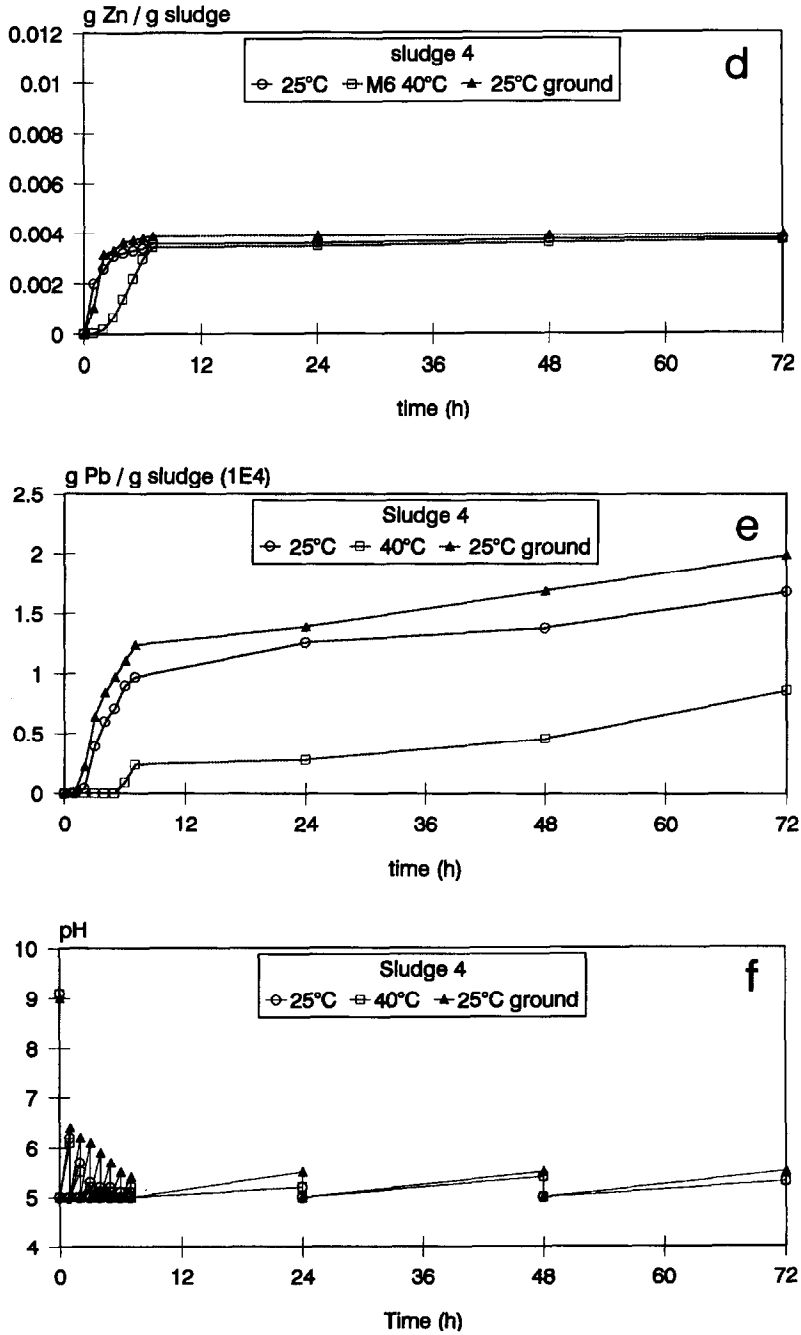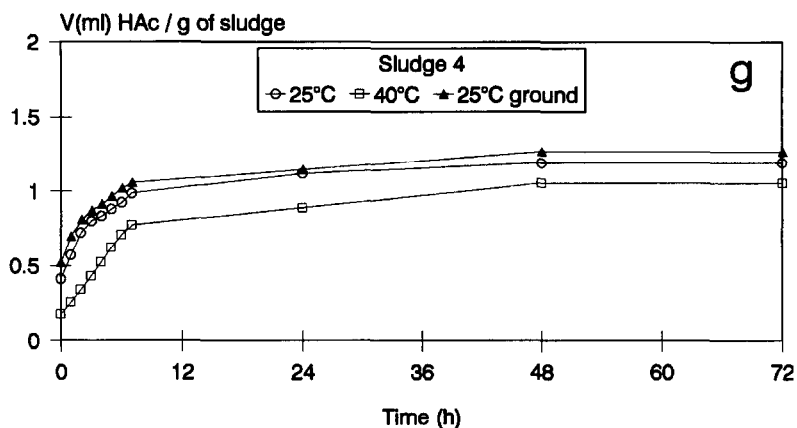
Fig. 8d–f.

Fig. 8g.

Table 4
Values of EC_{50} for leachates obtained after 24 h

Sample	EC_{50} at 5'	Toxicity units	EC_{50} at 15'	Toxicity units
Sludge 1				
25 °C non-grounded	8775	114	1226	816
40 °C non-grounded	9291	108	3870	258
25 °C grounded	6279	159	955	1047
Sludge 2				
25 °C non-grounded	7300	137	3017	331
40 °C non-grounded	4193	239	1271	787
Sludge 3				
25 °C non-grounded	203 566	5	44 799	22
40 °C non-grounded	351 024	3	65 733	15
25 °C grounded	392 250	3	93 755	11
Sludge 4				
25 °C non-grounded	17 740	56	4038	248
40 °C non-grounded	10 671	94	3857	260
25 °C grounded	20 055	50	1845	542

If only the wet sludge, after separating the liquid, is considered as the waste, the composition of any element in the leachate at any time in accordance with the EP method is :

$$C(\text{ppm}) = 5 \times 10^4 A, \tag{1}$$

where A is the ratio: amount solubilized/amount of wet sludge.

If the sludge with the initial content of water is considered as the waste, the composition of any element is:

$$C \text{ (ppm)} = \frac{20W \times 5 \times 10^4 \times A + BD}{20W + B},$$ (2)

where W is the solid percentage (including the water retained), B the supernatant liquid percentage and D is the concentration of the supernatant (in ppm).

If value D is not very high and B is much less than $20W$, Eq. (2) becomes:

$$C \text{ (ppm)} = 5 \times 10^4 A.$$ (3)

On considering the data presented in Figs. 5–8 and Tables 1 and 3, for each case the Pb contents (in ppm) in the leachates at the 24th hour for the four sludges are shown in Table 5. It can be observed that the concentration of Pb is very high for Sludges 1 and 2, exceeding the limit of 5 ppm considered in the US EPA regulations. Nevertheless, considering the test carried out at 25 °C with Sludge 4, the concentration of Pb is greater than the limit of 5 ppm, whereas for the test carried out at 40 °C, the concentration of Pb (1.7 ppm) is less than 5 ppm. Note that the samples containing a great or considerable amount of solubilized Pb (Sludges 1, 2 and 4) are those with values of EC_{50} close to or below the 3000 ppm limit, considered in the Spanish Regulations (Sludges 1, 2 and 4).

The sludges studied are heterogeneous compounds, formed by different materials. A satisfactory interpretation of all the data obtained would require detailed information about the reactivity of the different materials and their size distribution in the particle, solubility at different values of pH and temperatures of the materials, etc. These studies are normally done with pure compounds or mixtures of compounds with known composition and distribution. Nevertheless, in spite of the heterogeneity of the samples formed by frits and raw materials, some interpretations can be proposed:
- The fact that grinding favors the solubilization of some elements in Sludges 1, 2 and 4 indicates the great influence of the internal liquid phase migration/diffusion, corresponding probably to the ion $H_3O^\cdot$ and acetate ion (from the acetic acid), and perhaps also to the solubilized compounds.

Table 5
Concentration of Pb in the leachates (ppm)

	25 °C; non-ground	25 °C; ground	40 °C; non-ground
Sludge 1	276	363	102
Sludge 2	65	82	98
Sludge 3	0	0	0
Sludge 4	5.9	6.6	1.7

– The delay in the solubilization of Zn and Pb in the four sludges with respect to the remaining compounds can be explained by two facts:

(a) For the first 5–6 h, the pH values of the suspension oscillated between 5 and 5.7–5.8, and consequently the solubilization of basic compounds such as those containing Zn and Pb (PbO and ZnO used in glazed ceramic tile manufacturing processes) is slow. Afterwards, when the pH values were close to 5.0–5.2, the solubilization of Zn and Pb increased. Nevertheless, this effect alone cannot explain the delay in the solubilization, in runs in which the pH value was close to 5 (Sludge 4, 25 °C; Sludge 4, grounded sample).

(b) It is also possible that the internal diffusion played an important role in the solubilization process. At the begining of the test, when an acetic acid solution was added to lower the pH value, the solution of basic compounds (calcium hydroxide and others) took place maintaining the pH above 5 inside the pores. The solubilization of Pb and Zn was much less and later on, when a great fraction of the basic compounds was solubilized, the pH inside the pores could be close to 5 and the solubilization of Pb and Zn could take place.

In Sludges 1 and 4, the solubilization of all the elements was slower at 40 °C than at 25 °C, at least for the first period of time, and the differences were greater with the solubilization of Pb and Zn. This could be due to two effects:

(a) The compounds, the solubility of which decreases with temperature (calcium hydroxide and others) are solubilized more slowly. On the other hand, the decrease in the solubilization of some compounds can also provoke the decrease in other elements due to the decrease in the internal porosity. Note that portlandite (calcium hydroxide) was clearly detected in Sludge 1 by X-ray. For Sludge 4, calcite was weakly detected and perhaps a part of the calcite detected formed by carbonation of calcium hydroxide.

(b) During the run and after an initial period, the pH inside the pores can be higher at 40 °C than at 25 °C. Probably the presence of compounds, the solubilization of which, decrease when temperature increases, is responsible for the solubilization of these compounds taking place for the first period when operating at 25 °C and allowing the pH inside the pores to be higher after this initial period. When operating at 40 °C, the solubilization process takes place slowly due to the low solubilization of compounds such as calcium hydroxide, and the pH inside the pores can be high even during long runs.

In Sludge 2, where calcite was weakly detected, there was a delay in the solubilization of Zn and Pb with respect to the remaining ions, but there were no differences between the solubilizations of all the other elements at 40 °C and those at 25 °C. These results could be explained considering that the basic compounds containing the elements analyzed have similar solubility at 25 °C and at 40 °C in this case. Nevertheless, for the first period of time, the pH value inside the pores could be greater than 5.0 and the solubilization of Zn and Pb was delayed.

In Sludge 3, where calcium carbonate was not detected by X-ray diffraction and Pb was not present in the solubilized fraction, there were no great differences between the solubilization of the three samples.

Taking into account the heterogeneity of the sludges considered, with a high percentage of quartz and a wide particle size distribution without the possibility of
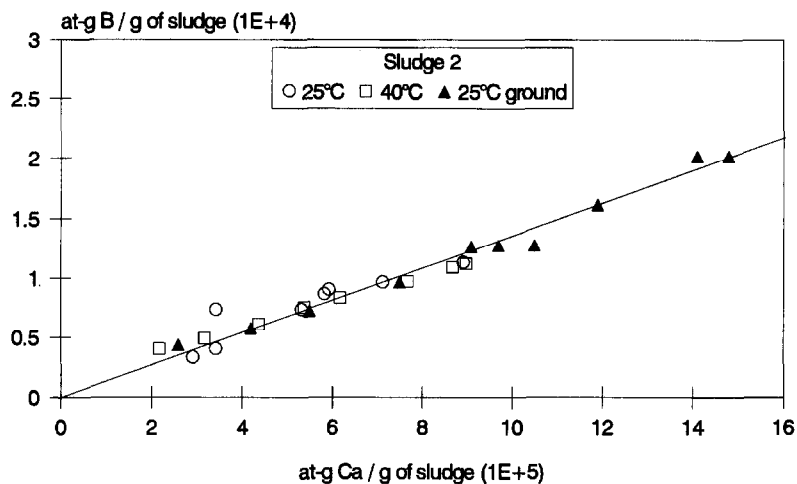
Fig. 9. Solubilization of boron vs. solubilization of Ca in Sludge 2.

differentiating inert material from reactive material, the choice of kinetic models is not useful. Nevertheless, the shapes of the convex curves obtained for Ca, B and Na in the four sludges can correspond to the case when internal diffusion/migration is the controlling step in solids with uniform size or a wide particle-size distribution. Nevertheless, it can also correspond to the case when the solubilization reaction is the slowest step.

From the comparison between the amounts solubilized in all the runs, only good correlations between the amount of B and Ca can be observed in Sludges 1, 2 and 3. Fig. 9 shows the correlation for one case (Sludge 2). Similar correlations can be obtained for Sludges 1 and 3. Nevertheless, taking into account the heterogeneity of the samples, this fact is not important for obtaining information about the compounds that are solubilized in the process.

5. Conclusions

The toxicity of the ceramic sludges is due to the presence of Pb. The operating temperature plays an important role in the solubilization process of the EP test and different degrees of solubilization can be obtained at 25 °C than at 40 °C. The solubilization of Zn and Pb, and in some cases Ca, are delayed with respect to other elements such as B and Na probably due to the internal diffusion/migration of the ions inside the pores of the solids. The 24 h period considered in the EP test has been sufficient in most cases in order to obtain information about the elements that are solubilized easily. Nevertheless, a considerable amount of Pb was solubilized in a sludge, from the 24th hour to the 72nd hour.

Acknowledgements

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