



## Stabilization/solidification of an alkyd paint waste by carbonation of waste-lime based formulations

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### ABSTRACT

The application of solvent-based paints by spraying in paint booths is extensively used in a wide range of industrial activities for the surface treatment of a vast array of products. The wastes generated as overspray represent an important environmental and managerial problem mainly due to the hazardous characteristics of the organic solvent, rendering it necessary to appropriately manage this waste. In this paper a solidification/stabilization (S/S) process based on accelerated carbonation was investigated as an immobilization pre-treatment prior to the disposal, via landfill, of an alkyd solvent-based paint waste coming from the automotive industry; the purpose of this S/S process was to immobilize the contaminants and reduce their release into the environment.

Different formulations of paint waste with lime, lime-coal fly-ash and lime-Portland cement were carbonated to study the effect of the water/solid ratio and carbonation time on the characteristics of the final product. To assess the efficiency of the studied S/S process, metals, anions and dissolved organic carbon (DOC) were analyzed in the leachates obtained from a battery of compliance and characterization leaching tests.

Regarding the carbonation of paint waste-lime formulations, a mathematical expression has been proposed to predict the results of the leachability of DOC from carbonated mixtures working at water/solid ratios from 0.2 to 0.6. However, lower DOC concentrations in leachates (400 mg/kg DOC in L/S = 10 batch leaching test) were obtained when carbonation of paint waste-lime-fly-ash mixtures was used at 10 h carbonation and water to solid ratio of 0.2. The flammability characteristics, the total contents of contaminants and the contaminant release rate in compliance leaching tests provide evidence for a final product suitable for deposition in non-hazardous landfills. The characterization of this carbonated sample using a dynamic column leaching test shows a high stabilization of metals, partial immobilization of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$  and limited retention of DOC. However, the obtained results improve the previous findings obtained after the paint waste S/S using uncarbonated formulations and would be a useful pre-treatment technique of the alkyd paint waste prior to its disposal in a landfill.

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### 1. Introduction

The application of solvent wet paint by spraying is extensively used in automobile parts to protect the metallic products [1]. This operation is a significant source of solid (paint sludge) and liquid (boothwater) waste, and it is also a major source of volatile organic compounds (VOCs). Although the generation of paint waste can be reduced by reformulation of the coating material and process modification, high quantities of sludge from boothwater treatments are produced in many manufacturing processes. These sludges represent an important environmental and managerial problem due to the organic solvent content and their hazardous characteristics [2].

Stabilization/solidification (S/S) treatment methodologies have been widely used to treat mainly inorganic hazardous wastes but more recently some organic wastes have also been successfully treated [3–6]; high total organic carbon (TOC) wastes, wastes containing low flash point solvents or inorganic wastes with high concentrations of organic contaminants can be treated by S/S processes before landfill disposal, representing a cost-effective pre-landfill treatment [7,8].

The use of different binders and additives in the S/S processes has proved to be useful in the treatment of wastes and contaminated soils with organic compounds due to the combination of volatilization and immobilization mechanisms. Studies of synthetic cement pastes with various organic solvent additions of toluene, hexanol and cyclooctane [9,10] provide knowledge about interaction between the solvents and the hydrating cement, as well as the solvent retention mechanisms. Karamalidis and Voudrias [6,11]

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show the optimum Portland cement and blended cement (with pozzolanic material) additions to refinery oily sludge, in terms of reducing the leaching of VOCs, alkanes and polycyclic aromatic hydrocarbons (PAHs) for solidified samples. Contaminated dredged sediments with high organic matter contents were used in mixtures of sand, fly-ash, cement and water to obtain a S/S secondary product; this product shows that the dissolved organic carbon (DOC) released concentration plays a significant role in the leaching of metals and metalloids [12]. Wastes such as foundry sludge [13] and petroleum drill cuttings [14] containing a mixture of organic compounds, heavy metals and water-soluble salts were immobilized using different S/S procedures based on Portland cement, lime and pozzolanic binders, in addition to a wide range of additives; in both studies [13,14] the leachability results of the S/S products showed a reduction of the heavy metals and organic pollutants relative to the initial waste and compliance with EU acceptance criteria for non-hazardous landfills.

The mixing of lime with wastes containing VOCs and water causes the exothermic hydration of lime, generating heat energy and the volatilization of VOCs. The emitted VOCs that are not entrapped can be treated in a secondary process (e.g. scrubbers) and may avoid double handling of wastes (e.g. thermal desorption to deal with VOCs followed by stabilization/solidification to deal with metals) [7]. The use of cement or fly-ash as binders in partial substitution of lime contributes to the encapsulation of VOCs promoted by pozzolanic reactions [15,16].

Previous results working with an alkyd solvent-based paint waste showed the effect of using different binders on the release of VOCs and the effect of using uncarbonated formulations of S/S based on lime and mixtures of lime, Portland cement and fly-ash on the DOC and metal leaching [17–19]. These studies have led to lower VOCs contents (0.1%) in the uncarbonated products obtained by S/S using lime and Portland cement. In addition, lower DOC concentrations (2150 mg/kg) have been observed in the batch lixiviation test of the uncarbonated products using lime and fly-ash mixtures with a liquid to solid ratio of 10 ( $L/S=10$ ) [20]. In all S/S studied formulations, significant quantities of Ba (4.8–6.5 mg/kg), Mo (0.1–0.23 mg/kg) and Zn (0.34–1.2 mg/kg) were present in the leachates. Therefore the organic content and metals in the paint waste S/S product are easily released in the  $L/S=10$  leaching test, and the waste is not stable for a long period of time.

In order to fix the content of the inorganic and organic components and to reduce the organic matter leaching release from the paint waste, accelerated carbonation technology is proposed in this work, since this process can aid the immobilization of contaminants in waste forms [21,22]. In the process,  $\text{CO}_2$  consumes the Ca of the binders to produce  $\text{CaCO}_3$ , lower the pH, produce physical and microstructural changes and lead to a general improvement of contaminant immobilization. However, the reduction of the buffering capacity and the final pH obtained could increase the leachability of some species, making it necessary to study the carbonation influence with each particular waste matrix in each management scenario [23–25]. Previous waste carbonation studies [21,25,26] show that the water to solid ratio (W/S) is crucial for carbonation to proceed at an optimum rate when lime, different cement types and pozzolanic admixtures (fuel ash, blast furnace slag, metal hydroxide filter cakes) are used. Different water contents have been used in the accelerated carbonation of wastes; values of the water/solids ratio in the range of 0.05–0.6 (w/w) [26,27] have been proposed for carbonation in the thin water film near the gas–solid interface, being necessary in each particular case for the optimization of this operational parameter. In this work, the accelerated carbonated process is used for paint waste treatment of S/S with lime and mixtures of lime, Portland cement and fly-ash.

To assess the efficiency of S/S processes, various test methods have been adopted. In particular, the leaching tests may be used for understanding contaminant-release mechanisms or to assess compliance with landfill waste acceptance criteria or guidelines for secondary material reuse. The extraction test as the digestion procedure for total heavy metals determination [28], the availability leaching test NEN 7341, the static pH test and the dynamic column test CEN/TS 14405 can be used as characterization tests in order to study the key parameters controlling the contaminants release [29,30]. The compliance tests are aimed at a direct comparison with regulatory thresholds and have been developed for several materials and different utilization or management scenarios of landfill or reuse [31,32]. In the EU legal framework, limiting values of the total content and chemical concentrations in the batch tests EN 12457-1,2 and percolation test CEN/TS 14405 at  $L/S=0.1$  are considered as the acceptance criteria for different classes of landfill [33].

The aim of this study is to evaluate the results of the accelerated carbonation of an alkyd organic solvent-based paint waste with a mixture of lime and mixtures of lime, Portland cement and fly-ash as a pre-treatment prior to disposal in a landfill. At first, the influence of time and the water content of the carbonation reaction of waste-lime mixtures on the leachability of organic matter measured as DOC, was analyzed and modeled. Then, carbonation of waste-lime and mixtures of waste-lime-fly-ash and waste-lime-Portland cement were also studied in order to reduce the leachability of DOC under the EU landfill waste acceptance criteria. Finally, the carbonated mixture with the lowest release of DOC was characterized under two approaches: (i) compliance testing of release concentrations under EU landfill regulation using batch and percolation leaching tests and (ii) characterization of the contaminants release behavior using a total contents analysis, the availability test, and the mobility through dynamic column leaching test at different liquid to solid ratios.

## 2. Materials and methods

### 2.1. Materials

The paint waste (Table 1) is generated from a water booth, where an alkyd solvent-based paint is applied via spraying. It is highly inflammable, contains high dissolved organic carbon (DOC) contents in the  $L/S=10$  leachates, and non-ecotoxic according to Spanish regulations [2]. Commercial lime (CaO) from Calcinor S.A., Cantabria, with 96% purity, coal fly-ash (FA) ASTM C618 Class C from an electrostatic precipitator of the Pasajes Power Plant (Guipuzcoa, Spain) and Portland cement (PC) ASTM Type I, 42, 5 R from Cementos Alfa, S.A. (Cantabria, Spain) were used as binders.

### 2.2. Preparation of carbonated formulations

The waste and binders were mixed with water at different water to solid ratios (W/S) and the mixture was exposed to accelerated carbonation by continuous circulation of pure  $\text{CO}_2$  (L'Air Liquide, Spain) through the laboratory scale solid mixer IKA HKD-T0.6 under the conditions shown in Fig. 1; the continuous mixing maximizes the liquid–solid and solid–gas contact, thereby improving the hydration and carbonation reactions. The gas output flowed to a water scrubber and an active carbon adsorption tower to retain solids and VOCs.

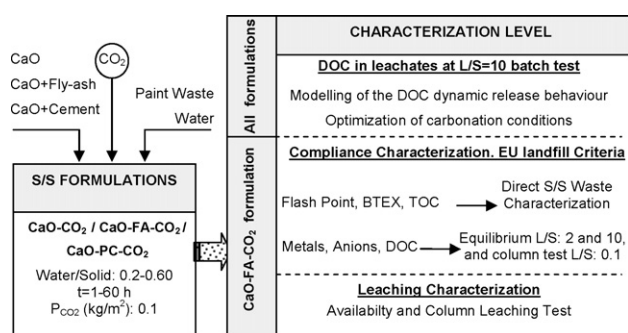
The total amount of solid was constant (178 g) in all the carbonation experiments. The waste/binder ratio was selected to be constant and equal to 1.3 based on previous work where this ratio produced an uncarbonated product with the lower contaminants release in leaching tests [17–19]. The amount of added

**Table 1**  
Paint specifications and paint waste contents and characteristics.

Paint specifications (% d.w.)					
Carbon black	3.15	Toluene	19.92	Polycarboxylic acid	0.54
Calcium carbonate	8.97	Drying agents	1.59	Alkyd resin (60% xylene)	41.64
Thickener	2.97	Barite	9.76	Methyl-ethyl-cetoxime	0.16
Triethylamine	0.32	Talc	9.98	Bonding agent	1.00
Paint waste contents (% d.w.)					
BTEX <sup>a</sup>	14	Cu	0.01	Sb	0.01
As	0.01	Fe	1.58	Se	0.01
Ba	6.24	Hg	0.01	Si	1.43
Ca	6.77	Mg	0.32	Sr	0.97
Cd	0.01	Mo	0.11	Ti	0.52
Co	0.23	Ni	0.54	Zn	0.30
Cr	0.33	Pb	0.10		
Paint waste characteristics					
Flash point (°C)	22	DOC <sup>b</sup> in leachates (mg/l)	3700	Microtox EC <sub>50</sub> (mg/l)	4132

<sup>a</sup> BTEX: benzene, toluene, ethylbenzene, xylenes.

<sup>b</sup> DOC: dissolved organic carbon.



**Fig. 1.** Materials, design of the accelerated carbonation experiments and characterization levels to evaluate the carbonated products.

water was changed over a range representative of waste carbonation processes from 0.2 to 0.6 (w/w) water to solid ratio [26,27]. Table 2 reports the studied formulations and treatment conditions to obtain the carbonated products.

### 2.3. Leaching tests

The value of pH and DOC concentration of the equilibrium leaching tests at L/S = 10 l/kg obtained after different carbonation times (1, 2, 4, 8, 12, 24, 36 h) were used to determine the optimum reaction time. The carbonated mixture with the lower release values of DOC was characterized through compliance leaching tests (batch extraction tests EN 12457-1, 2 with distilled water for 24 h with an L/S = 2 and 10, and percolation test CEN/TS 14405 at L/S = 0.1), availability test NEN 7341 and column test CEN/TS 14405 at different L/S ratios (Fig. 1). The leaching tests used were previously described by Coz et al. [34].

**Table 2**  
Formulations and treatment conditions to obtain the carbonated products.

Sample code	Waste	CaO	Additive	H <sub>2</sub> O	Waste/binder (wt/wt)	Water/solid (wt/wt)	Process conditions
		% total weight					
CaO-CO <sub>2</sub>	47	36	0	17	1.3	0.2	Contact time solid mixture-water-CO <sub>2</sub> (h) = 1, 4, 8, 12, 24, 36, 60
	43	34	0	23	1.3	0.3	
	35	27	0	38	1.3	0.6	
CaO-FA-CO <sub>2</sub>	47	20	16	17	1.3	0.2	<i>p</i> <sub>CO<sub>2</sub></sub> (kg/cm <sup>2</sup> ) = 0.1
CaO-PC-CO <sub>2</sub>	43	18	16	23	1.3	0.3	Contact at laboratory scale solid mixer
	35	15	12	38	1.3	0.6	

CaO: lime; CO<sub>2</sub>: carbon dioxide; FA: fly-ash; PC: Portland cement.

### 2.4. Analytical methods

Benzene, toluene, ethylbenzene and xylenes (BTEX) content, flammability and total organic carbon (TOC) were determined on the solid matrices of waste and carbonated formulations. Analysis of BTEX was performed by GC/FID on a CE Instruments GC 8000 Top by the equilibrium headspace method for analysis in solid matrices (US EPA 5035). The flammability was determined by the ISO 3679:2004 Method in a Setafash Closed Tester 13740-4. TOC on the solids and DOC on the leachates were determined by the European EN 13137:2002 and EN 13370:2004 standard methods respectively, using TOC-V CPH Shimadzu equipment.

The chemical analytes regulated in the EU landfill Directive [33] and present in the paint waste, namely As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn, the total dissolved solids (TDS) and the anions F<sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, were analyzed in the leachates obtained from the different lixiviation test previously described. The TDS concentration was determined by gravimetric Standard Method APHA 2540C. Analytical evaluations of metals were performed by the ISO 11885:1996 method using an ICP/OES Perkin Elmer 400. Anion concentrations were evaluated by the ISO 10304-1:1992 method using a Dionex DX-120 Ion Chromatograph with a conductivity detector.

### 2.5. Quality assurance/quality control

A 5-point calibration curve was made for BTEX, using a range of concentrations from 10 µg/l to 500 µg/l of US EPA 8020/8240 Aromatic Volatiles Mix (Supelco), with an internal standard calibration method based on the compound o-fluorotoluene (100 µg/l). The correlation coefficients (*r*<sup>2</sup>) for toluene, xylenes, benzene and ethylbenzene compounds ranged from 0.98 to 0.99 with a relative standard deviation (%RSD) < 20%. The limit of detection was deter-

mined according to the US EPA Method 8000, by tripling the average signal-to-noise (S/N) at low concentrations, and the limit of quantification was calculated to be 10 times the S/N. The quantification limit was 10 µg/l for all compounds. The precision was evaluated using duplicates (10% of the samples), and the %RSD < 30% between duplicate samples. Concentrations for all calibrated compounds in method blanks were lower than the reporting limit.

Multi-point calibration standards were used in the TOC analysis in solid matrices; a calibration blank, five TOC calibration standards of 1–50 mg C/l TOC as potassium hydrogen phthalate (KHP) and five IC calibration standards of 1–50 mg C/l IC as Na<sub>2</sub>CO<sub>3</sub>. The correlation coefficients (*r*<sup>2</sup>) were 0.99 with %RSD < 20%. A 5-point calibration curve was made for DOC analysis in leachates with a Merck calibration stock solution of KHP. The calculated average over 3 replicates shows a %RSD < 20%. ICP-OES was calibrated by standard addition methods and freshly prepared metal salt (Merck multi-element ICP standard Certipur) solutions, with the obtained *r*<sup>2</sup> ranging from 0.98 to 0.99 and %RSD < 10%. Practical minimum detection limits against replicated procedural blanks were 0.686 mg/l for As, 0.013 mg/l for Ba, 0.054 mg/l for Cd, 0.074 mg/l for Cr, 0.062 mg/l for Cu, 0.056 mg/l for Hg, 0.040 mg/l for Mo, 0.129 mg/l for Ni, 0.081 mg/l for Pb, 0.591 mg/l for Sb, 0.375 mg/l for Se, and 0.076 mg/l for Zn. Ion chromatography was calibrated by freshly prepared metal salt (Merck multi-element IC standard Certipur) solutions obtaining *r*<sup>2</sup> = 0.99 and %RSD < 10%. Practical minimum detection limits against replicated procedural blanks were 0.09 mg/l for F<sup>-</sup>, 0.10 mg/l for Cl<sup>-</sup> and 0.16 mg/l for SO<sub>4</sub><sup>2-</sup>.

### 3. Results and discussion

#### 3.1. Carbonation of paint waste-lime mixtures

Previous results of the solidification/stabilization of the alkyl paint waste without carbonation [17–19] show that the dissolved organic compound concentration (DOC) in the leachates is the critical parameter in obtaining an S/S final paint waste that fulfils the EU landfill waste acceptance criteria [33]. For this reason, the results of the DOC obtained in the L/S = 10 batch compliance leaching test were used to select the water/solid (W/S) ratio and carbonation time conditions of the accelerated carbonation of paint waste-lime mixtures. The paint waste-lime mixtures were carbonated (CaO–CO<sub>2</sub> code samples, Table 2) during different reaction times using water/solid ratios of 0.2, 0.3 and 0.6 in order to determine the carbonation conditions that lead to a final product with low DOC concentration in the leachates. Equation 1 represents the carbonation of the hydrated lime produced in the paint waste-lime mixtures:



Fig. 2 shows the behavior of pH and DOC with time when mixtures of paint waste-lime are carbonated at different water/solid ratios. The pH of the leachates for samples subjected to accelerated carbonation shows an important decrease from about 12.8 to 8.5–7.2 within the first 12 h with higher pH decreasing at higher W/S ratios; the pH then continues to slowly decrease to 8–7 (Fig. 2a). The carbonation rate is limited by diffusion and among others factors is dependent on the water content [21,26]; in the studied water/solid ratios the reaction is absent without water (Blank in Fig. 2) and the reaction time decreases as W/S ratio increases, without limitation of carbonation rate at high W/S ratios [26]. The same behavior is also observed in the dependence of DOC with time obtained from the leachates of selected samples (Fig. 2b); the lowest value of DOC of 490 mg/kg is obtained at W/S = 0.6 for a carbonation time higher than 4 h. However, the rest of the DOC obtained values are higher than the EU landfill waste acceptance

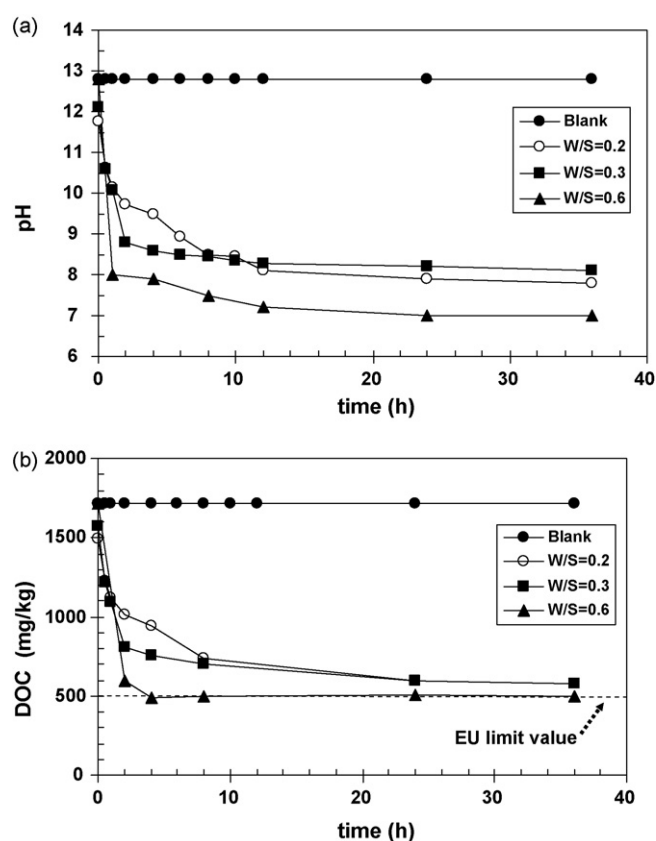


Fig. 2. Carbonation of paint waste-lime formulations at three different water/solid ratios. (a) Behavior of the pH with time; (b) behavior of the dissolved organic carbon (DOC) with time.

criteria of 500 mg/kg.

In Fig. 3a the DOC concentration in leachates as a function of pH for paint waste-lime carbonated mixtures is given. The DOC concentrations decrease toward lower pH values according to the linear relationship  $\text{DOC} = 232.6 \text{ pH} - 1236$ , with a regression coefficient of  $r^2 = 0.96$ . Previous literature shows that DOC generally is strongly dependent on pH, with DOC concentrations increasing with pH values where the colloidal properties, ionic strength and polyvalent cations are referred to as the main factors in the mobility of the DOC [35,36]. The DOC leaching concentration is a parameter with an associated limit value established as a criterion for the acceptance of waste at different classes of landfills [33] due to their pollutant impact; additionally the role of DOC is one of the most dominant factors controlling release of metals and organic contaminants from the waste [35,37]. Therefore the modeling of the evolution of DOC with time when the paint waste-lime mixtures carbonation process is used would help in the decision-making process from an operational point of view. Jund et al. [38] use Eq. (2) for the simulation of the concentration of OH<sup>-</sup> with time during the carbonation of lime in presence of water:

$$C = \frac{C_0}{(1 + tkC_{\text{CO}_2})^j} \quad (2)$$

where *t* is the reaction time, *C*<sub>CO<sub>2</sub></sub> is the concentration of CO<sub>2</sub> in the interface and *k* and *j* are adjustable parameters. As can be seen from Fig. 3a, the relation obtained between the experimental values of pH and DOC is linear; therefore, in the present work, the equation presented by Jund et al. [38] was used to simulate the evolution of DOC. Eq. (2) requires the concentration of CO<sub>2</sub> at the gas-liquid interface, and in the present work this was not measured directly. Instead, the W/S was used since it is directly related to the CO<sub>2</sub> at

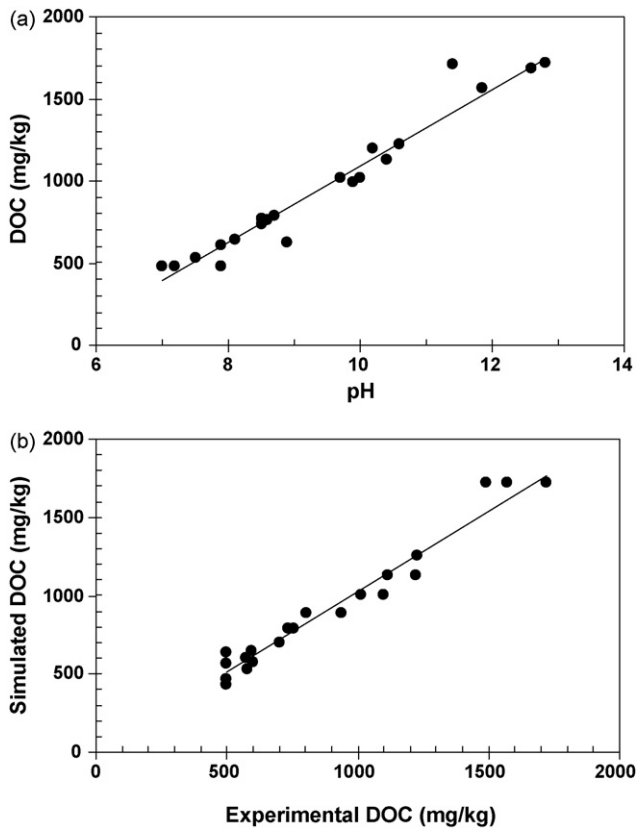


Fig. 3. Relation between pH and DOC in the  $L/S = 10$  leachates of the carbonated paint waste-lime formulation in (a) and the parity graph of experimental and simulated DOC values for Eq. (2) in (b).

the gas-liquid interface. The final expression is given by Eq. (3):

$$DOC = \frac{DOC_0}{[1 + tk(W/S)^a]^j} \quad (3)$$

where  $t$  is the reaction time, DOC and  $DOC_0$  are the concentration of dissolved organic carbon at  $t$  and  $t_0$  respectively,  $W/S$  is the water to solid ratio used in the carbonation reaction, and  $k$ ,  $a$ ,  $j$  are adjustable parameters. The adjustment of the experimental data to Eq. (3) was carried out using the mathematical program Table Curve 3D SYSTAT®, and the values obtained for the adjustable parameters are  $k = 124$ ,  $a = 1.70$  and  $j = 0.18$  with a correlation coefficient of  $r^2 = 0.95$ . The parity plot presented in Fig. 3b shows the measured DOC data and the simulated DOC values, with good agreement and an error range lower than  $\pm 8\%$ . Therefore, under the carbonation conditions and for the studied  $W/S$  ratios, the proposed expression predicts satisfactorily the results of the DOC in leachates, helping predict the degree of compliance with the EU landfill waste acceptance criteria.

Eq. (3) was obtained for the carbonation of lime paint wastes mixtures. Although the carbonation takes place mainly in the lime matrix, the complexity of industrial wastes including a wide range of metals, anions and organics can have a strong influence on the carbonation extension and results. For this reason the applicability of expression 3 must be checked when other wastes-lime mixtures would be treated by carbonation.

### 3.2. Carbonation of paint waste-lime-Portland cement and paint waste-lime-fly-ash mixtures

According to the EU landfill waste acceptance criteria, limit values for dissolved organic carbon concentrations in compliance

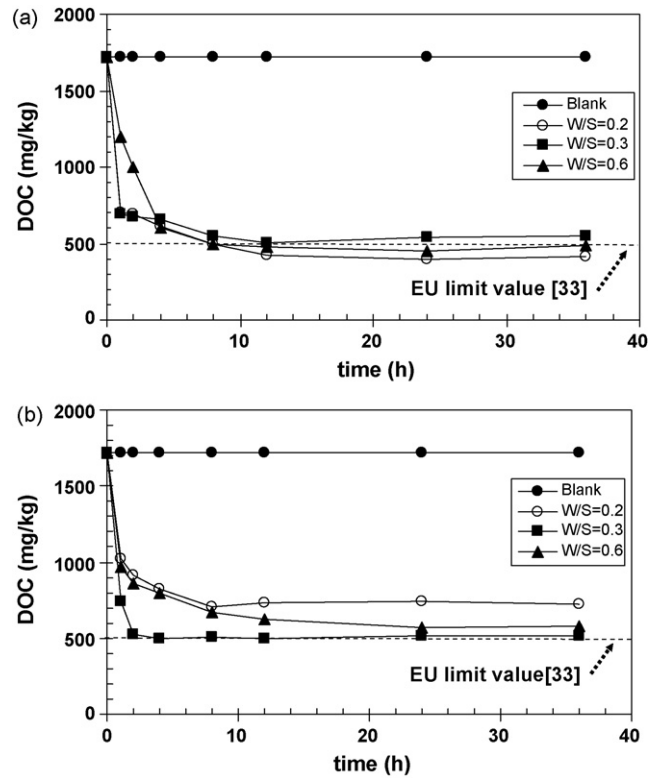
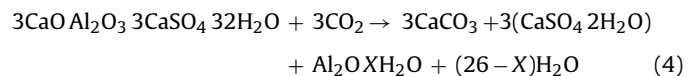


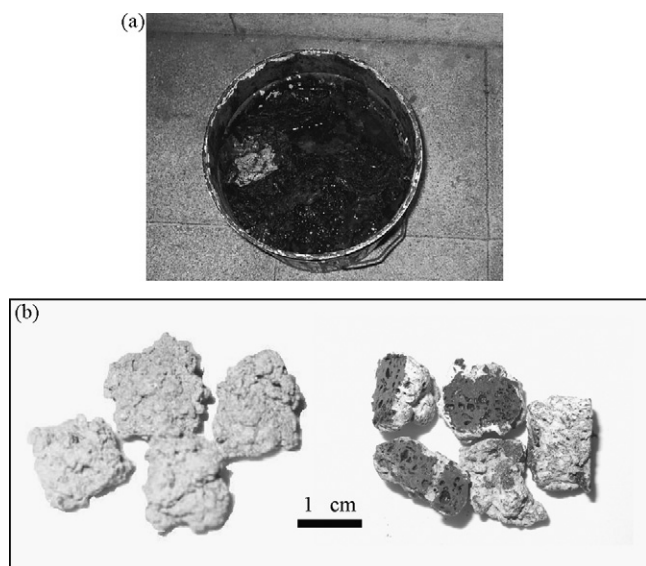
Fig. 4. DOC of  $L/S = 10$  leachates as a function of carbonation time at different water to solid ratios (a) CaO-FA- $CO_2$ ; (b) CaO-PC- $CO_2$  mixtures.

leaching tests using the batch test EN 12457:2002-2 at  $L/S = 10$  are 500 mg/kg, 800 mg/kg and 1000 mg/kg for inert, non-hazardous and hazardous waste, respectively [33]. For all the carbonated paint waste-lime samples (CaO- $CO_2$  code samples) studied, the DOC leachate concentrations exceeded the limit value for inert waste (Fig. 2b). Carbonation of mixtures of paint waste with lime and fly-ash (CaO-FA- $CO_2$  code sample) and Portland cement (CaO-PC- $CO_2$ ) were tested to assess their ability to treat the paint waste (Table 2). The released concentrations of the analyzed metals (metals in paint waste that are regulated in the EU landfill directive [33]) in the leaching test from the carbonated formulations are below the detection limit. Carbonation of cement based-waste formulations [24,26], involves reaction with phases like hexacalcium aluminoferrite trisulphate (AFt) and tetra calcium aluminate monosulphate (AFm), calcium silicate hydrate (CSH) and calcium hydrate (CH); carbonation of CSH produces silica gel and  $CaCO_3$ ; carbonation of portlandite produces  $CaCO_3$ ; carbonation of ettringite, present in abundance within hydrated cement-containing materials, to produce calcite is presented in Eq. (4):



This reaction may lead to the precipitation of calcium metal double carbonates such as calcium zincate when certain toxic species are present in solution and can aid the immobilization of certain metals in waste forms [26].

Fig. 4 shows the behavior of DOC leaching concentrations with time, when formulations CaO-FA- $CO_2$  (Fig. 4a) and CaO-PC- $CO_2$  (Fig. 4b) were carbonated at different water/solid ratios. The values of DOC obtained after carbonation ranged from 400 to 1200 mg/kg depending on the carbonation time; these values are lower than DOC values (2150 mg/kg) obtained in previous works [17–19] where Portland cement and fly-ash were used as binders in uncar-



**Fig. 5.** Photographs of (a) raw paint waste and (b) carbonated paint waste-CaO-fly-ash formulations.

bonated formulations. The DOC concentration reduction obtained with carbonation would indicate a DOC fixation into the solid matrix during the accelerated carbonation process. The carbonation produces significant reductions with time in the DOC leachates concentrations since the  $\text{CO}_2$  reacts with the lime and pozzolanic compounds from fly-ash and Portland cement causing carbonation; this not only affects the pH dissolution and therefore the sorption-precipitation processes [30,39], but also affects the solid microstructure with a decrease in porosity [40]. The best results of DOC mobility (400 mg/kg), with values lower than the limit value of the EU landfill waste acceptance criteria for inert landfills (500 mg/kg), was obtained when paint waste-lime-fly-ash mixtures were used after 10 h carbonation and a W/S ratio of 0.2.

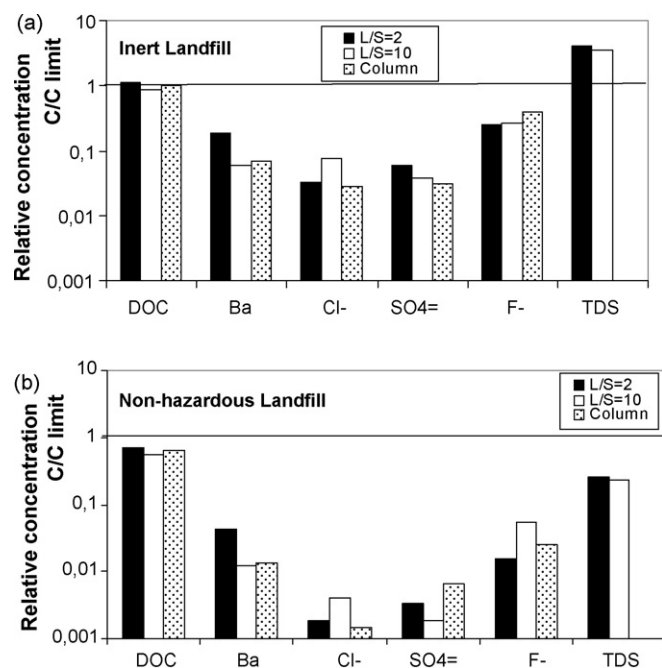
### 3.3. Characterization of the paint waste-lime-fly-ash carbonated mixtures

A battery of compliance and characterization leaching tests consisted of a set of batch and dynamic tests were applied to the carbonated paint waste obtained after 10 h carbonation at W/S = 0.2 (Code sample CaO-FA- $\text{CO}_2$ , Table 2). The compliance tests determine the degree of compliance with the EU landfill waste acceptance criteria using batch leaching tests EN 12457-1, 2 at L/S = 2 and L/S = 10 and the column leaching test CEN/TS 14405 at L/S = 0.1; furthermore, the characterization tests study the parameters and factors which control the lixiviation of the contaminants from the samples to obtain information about the leaching behavior at short and long times.

Besides the reduction of the DOC, the carbonation process leads to a dry and hard product that improves the manageability of raw paint waste and obtains a non-flammable solid with pH = 8.5, contents of 6% of LOI, 5.65% of TOC, 420 mg/kg of COD at pH = 7 and 0.18% of BTEX. Fig. 5a shows a photograph of the raw waste and Fig. 5b shows a photograph of the CaO-FA- $\text{CO}_2$  carbonated mixture. From Fig. 5b it can be seen that a low thickness (0.1 mm) of new mineral, probably calcium carbonate, from the carbonation of the CaO-FA- $\text{CO}_2$  mixtures is formed; this layer covers all the surface of the irregular particles (14 mm × 10 mm) generated during the carbonation process. The use of spectroscopic techniques as well as Unconfined Compressive Strength (UCS) and microstructure, would be useful in additional studies of characterization, especially in a reuse framework.

The results of the present study show that the released concentrations of the analyzed metals (metals in paint waste that are regulated in the EU landfill directive [33]) in the leaching test from the carbonated formulations are below the detection limit. The only detected species in the leachates were Ba, anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{F}^-$ ) and the DOC and TDS concentrations that became significant in this product due to their potential environmental implications in a landfill management framework. Fig. 6 shows the relative concentration of the detected chemicals in the compliance leaching tests; the relative concentration is the ratio between the experimental concentration in different leaching tests (L/S = 10, L/S = 2 and column at L/S = 0.1) and the limit value concentration for acceptance of the waste in inert landfills (Fig. 6a) and for acceptance in non-hazardous landfills (Fig. 6b). A value of 1 in both cases exceeds the limit concentration for each chemical in each scenario of deposition. The concentrations of DOC and TDS do not comply with the EU landfill waste acceptance criteria in inert landfills (Fig. 6a), but all the concentrations are actually below the EU limit value for deposition in non-hazardous landfills (Fig. 6b). The flammability characteristics, the total contents of contaminants and the contaminants released in the compliance leaching tests show that the CaO-FA- $\text{CO}_2$  formulation is suitable for deposition in non-hazardous landfills as a management option.

The availability test and column leaching test at different L/S ratios were used to characterize the CaO-FA- $\text{CO}_2$  formulation in order to obtain better knowledge of the leaching behavior and the processes controlling long-term release. Fig. 7 shows the availability/total and mobility/total ratios for the analytes detected in leachates, showing a wide variation depending on the analytes (Ba, anions and DOC). The availability amounts increased in the order  $\text{F}^- < \text{Ba} < \text{DOC} < \text{Cl}^- < \text{SO}_4^{2-}$  as shown in Table 3; however, in relation to availability/total concentration ratios, Fig. 7 shows that sulfates, fluorides and chlorides a similar value with high availability/total ratios (45%), and these values decrease one order of magnitude in mobility/total ratios at L/S = 10 (3%) and at L/S = 2 (1.5%). The ratio of availability/total for Ba is 3% with a strong decreasing of the mobility/total ratio at values of 0.013%.



**Fig. 6.** Relative concentration of chemicals under application of the EC acceptance criteria based on compliance leaching tests for different classes of landfill: (a) inert and (b) non-hazardous.

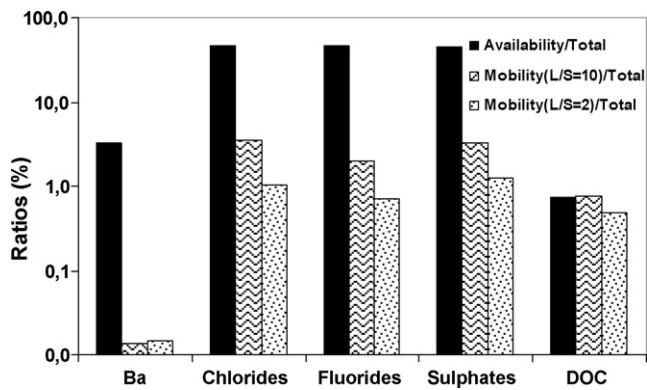


Fig. 7. Fraction (%) of the total concentration which is potentially leachable under worst-case conditions (availability test) and under mobility conditions at  $L/S = 10$  and  $L/S = 2$  from carbonated CaO-FA-CO<sub>2</sub> formulation.

The DOC concentration in Fig. 7 shows low availability/total and mobility/total ratios in the same order of magnitude (0.5–0.8%), with large differences between total (TOC) and leached values (DOC) of organic carbon and small differences between availability and mobility. The values of the availability constant defined as  $k_{avail} = [(Total\ content - Availability)/Availability]$ , are calculated to be 1.2 for anions, 30.1 for Ba and 132.6 for DOC. These values make possible the comparison of the availability characteristics of each chemical compound in other stabilized and carbonated matrices [29].

Besides the equilibrium test, a dynamic test in column was also carried out for the basic characterization of the carbonated mixture. Results obtained from the dynamic column leaching test are shown in Figs. 8 and 9 and simulate the short, intermediate and long leaching behavior, relating the mobility to  $L/S$  at  $L/S$  ratios of 0.1/0.2/0.5/1/2/5/10.

During the column tests, the pH of the extract was observed to be in the range of 7.9–9.1, with a minimum value at  $L/S = 2$  as shown (Fig. 8a). The changes in pH could modify the organic mat-

ter and inorganic element release, playing an important role in the observed differences between equilibrium and dynamic lixiviation tests of other contaminants. A decrease in electrical conductivity was observed with increasing  $L/S$  ratio (Fig. 8b), while the redox potential (Eh) of the leachates obtained from the dynamic column leaching tests remain constant at an average value of  $107 \pm 36$  mV without any defined trend with  $L/S$ ; therefore, the Eh should not be a key factor in the variation with time of the leaching concentrations of the studied analytes.

The cumulative leaching profiles of DOC, Ba, Cl<sup>-</sup>, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> as a function of  $L/S$  ratio are given in Fig. 9. In these profiles, the total content, availability and equilibrium mobility at  $L/S = 2$  and  $L/S = 10$  for each studied element are also shown. For the case of Cl<sup>-</sup>, two different behaviors are observed at low and high  $L/S$  ratios. At low  $L/S$  ratios ( $L/S = 0.1$ – $0.5$ ), approaching typical pore water solutions, the observed cumulative column leached amount is controlled by dissolution mechanisms (slope 1 in cumulative release-Log  $L/S$  plot) [41], and at high  $L/S$  ratios, the equilibration of the leaching profile for Cl<sup>-</sup> can be attributed to the reduced availability of the chlorides after their initial dissolution in column test [42].

The cumulative leaching profiles for the remaining analytes (DOC, Ba, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) in Fig. 9 show a semilogarithmic increase in the release with  $L/S$  ratio. In these analytes the difference between the availability value and the maximum cumulative column value released at  $L/S = 10$  [ $Availability - E_{L/S=10}/Availability$ ] (%) is 69% in DOC and between 98.3% and 99.9% in SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup> and Ba. These high values can also be attributed to a reduction of the mobility of these species [29].

A comparison between the batch tests and the column test showed that the measured release of analytes from batch tests at  $L/S = 2$  and  $L/S = 10$  are higher by a factor of 1.8 (at both of the  $L/S$ ) for SO<sub>4</sub><sup>2-</sup> and a factor of 20 (at  $L/S = 10$ ) for Cl<sup>-</sup> than the release measured in the column test. Agreement of the release of tank and column leaching tests was reported to be better for anions because leaching is controlled mainly by solubility and/or availability [43]; however, similar and larger differences than in the present work were observed in the metal and organic release from different waste solid matrices due to the difference in experimental proce-

Table 3

Results of the total contents, detected parameters in the leaching test and retention factor of the detected parameters in the leaching column test.

Parameter test	Ba	Cl <sup>-</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	DOC
Total content (mg/kg)	8900	1761	138	2690	56500 <sup>a</sup>
Availability (AVB) (mg/kg)	286	808	64	1.203	423
Mobility					
$L/S = 2$ (mg/kg dw)	1.3	18.3	1.0	33.7	271
$L/S = 10$ (mg/kg dw)	1.2	61.2	2.7	38	440
Column (mg/l)	0.27	12.6	1.0	46	160
Matrix retention factor, $k$ (l/kg) (Eq. (5))	2367	1056	341	146	7.5
$r^2$ of Eq.5	0.87	0.73	0.99	0.95	0.97
Retention degree [30]	High	Medium	Medium	Medium	Low

<sup>a</sup> Total content of the carbonated matrix as total organic content (TOC).

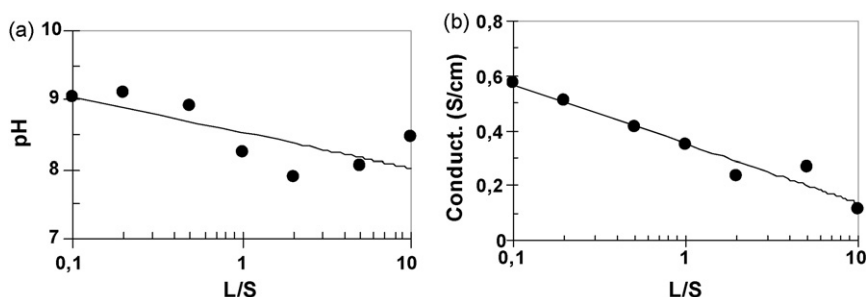
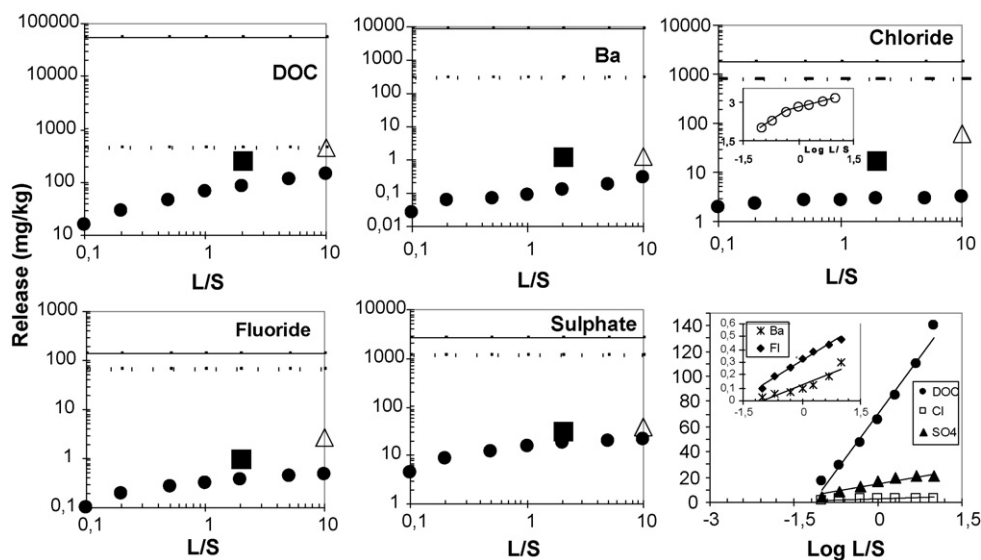


Fig. 8. pH and conductivity in the successive leaching fractions of carbonated CaO-FA-CO<sub>2</sub> formulations obtained after application of the column test CEN/TS 14405.



**Fig. 9.** The cumulative leaching of DOC, Ba,  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  during the column test (R) is shown as well as total concentration (—), availability (---) and equilibrium mobility at  $L/S=2$  (■) and  $L/S=10$  (▲) of the respective chemical species.

dures and controlling mechanisms influenced by changes of pH, organic matter content and redox potential [44].

According to Van der Sloot et al. [29], Eq. (5) describes the cumulative release of an element as a function of  $L/S$  ratio. This equation can be used to obtain the matrix retention parameter ( $k$ ) for the different species and provides comparison criteria for different materials [30,42]:

$$R = AVB(1 - e^{-(\log LS/k)}) + C_0 \quad (5)$$

where  $R$  is the release in mg/kg,  $AVB$  is the availability NEN 7341 in mg/kg,  $k$  is the matrix retention factor in l/kg,  $LS$  is the liquid over solid ratio in l/kg and  $C_0$  is a constant representing the average cumulative release value. Eq. (5) was solved with Table Curve 3D SYSTAT®, obtaining values of the  $k$  parameter that increase in the following order:  $\text{DOC} < \text{SO}_4^{2-} \cong \text{F}^- < \text{Cl}^- < \text{Ba}$  as shown in Table 3, indicating a low degree of retention for DOC, medium for  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  and high for Ba.

#### 4. Conclusions

The present work studies the carbonation of lime, Portland cement and fly-ash mixtures with paint wastes generated from an automotive industrial activity that uses a solvent-based alkyd paint. The dissolved organic carbon obtained in the  $L/S=10$  batch compliance leaching test was used to optimize the conditions of the accelerated carbonation of the different formulations. In the carbonation of paint waste-lime formulations, it is observed that the amount of water in the mixtures is important for the rate of the carbonation process and for the reduction of the dissolved organic carbon concentration in the leachates. The DOC concentrations obtained in the leachates range from 500 mg/kg to 1800 mg/kg and are above the UE limit acceptance criteria of wastes in inert landfill. In addition, for this matrix an expression has been proposed to predict the results of the leachability of DOC from carbonated mixtures working with pure  $\text{CO}_2$  at water/solid ratios from 0.2 to 0.6; this expression can help predict the degree of DOC compliance with EU landfill waste acceptance criteria of the paint waste-lime carbonated samples.

Other matrices using mixtures of lime and fly-ash and lime and Portland cement were also carbonated in order to reduce the DOC concentrations in leachates below the limit value of 500 mg/kg DOC for waste disposal at inert waste landfills. These values are lower

with fly-ash than with Portland cement, and the best results of DOC mobility have been obtained when the carbonation of paint waste-lime-fly-ash mixtures was set to be 10 h carbonation and a the water to solid ratio was 0.2.

The flammability characteristics, the total contents of contaminants and the contaminants release in the compliance leaching tests show a final product obtained after carbonation of paint waste-lime-fly-ash mixture suitable for deposition in non-hazardous landfills. The characterization of this carbonated sample using availability and a dynamic column leaching test shows a high stabilization of Ba; however, the anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{F}^-$  are only partially retained and DOC shows a low degree of retention.

The use of accelerated carbonation of paint waste-lime-fly-ash mixtures is a viable immobilization pre-treatment prior to the landfill of paint waste; the process produces the volatilization of VOCs and a variable degree of volatile organic compound encapsulation depending on the carbonation formulation. The final carbonated product obtained is suitable for landfill disposal making the study relevant when landfill disposal is the management option for this waste; however, restrictions on the organic matter content in the wastes to be landfilled and the organic matter released from the waste suggest that additional studies should be undertaken to improve the properties of organic matter retention.

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