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Accelerated carbonation of sewage sludge–cement–sand mortars and its environmental impact

S. Valls*, E. Vàzquez

Department of Construction Engineering, Universitat Politècnica de Catalunya, ETSECCPB, C/Jordi Girona, 1-3 Campus Nord Building B1-004, E-08043 Barcelona, Spain

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Abstract

One of the main objectives of this work is to present an effective alternative for the final destination of sludge from urban waste water treatment plants by its use as a component of mortar or concrete. Assessment of the environmental quality of the final product and the consequent guarantee of its use in the building industry demand that it meets a number of requisites, one of which is that the effluents extracted by water action should be contamination-free or at least that the concentration of contaminants should be below certain preset limits. To this end, a durability study was performed on the system. The study consisted in subjecting the mortar samples to a process of accelerated carbonation and subsequently assessing the products of the carbonation by ^{29}Si RNM-MA nuclear magnetic resonance of solids and its environmental impact by the NEN-7345 monolithic leaching test. Carbonation at very high concentrations of CO_2 favours the polymerization of the C–S–H and the breakdown of the ettringite, which affects the leaching processes and the concentration of heavy metals and other pollutants in the leachates obtained from the NEN 7345 leaching test. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sewage sludge; Accelerated carbonation; ^{29}Si RNM-MA; Leaching process; Environmental impact

1. Introduction

There is a need of consistent measurements of the environmental impact of sewage sludge and other residues so that decisions can be made on the use, treatment or disposal. In Catalonia, the sewage sludge production is very high, and immediate solutions are needed. The recovery of waste material has priority over disposal.

Wastewater sewage sludge is a waste product with toxic potential, therefore, we have considered a stabilisation process of sewage sludge with Portland cement. Once checking the compatibility of both, Portland cement and sewage sludge, it is therefore necessary to make an environmental assessment of the material before and after subjecting it to a durability test such as carbonation.

Assessment of the environmental quality of the final product and the consequent guarantee of its use in the building industry demand that it meets a number of requisites, one of which is that the effluents extracted by water action should be contamination-free or at least that the concentration of contaminants should be below certain preset limits. For this purpose, a number of leaching tests must be carried out, such as the Netherlands Tank Leaching Test (NTLT) [1].

1.1. Characterisation of the sludge

The sewage sludge used is a biological sludge from the waste waters generated in the surroundings of Manresa, close to the city of Barcelona. The sludge was treated by the classic process of anaerobic digestion. In general, the pH was fairly constant, with a moderately basic value between 7 and 8. Part of the chemical characterisation corresponds to the determination of the total heavy metals.

1.1.1. Total heavy metal content of the sludge

Determining this is of fundamental importance since it enables us to compare and establish the degree of suitability of the materials produced according to the leaching test and thereby ascertain what proportion of the total has been extracted. The solutions obtained are analysed by plasma source atomic emission spectrometry (ICP). The results

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* Corresponding author. Tel.: +34-93-401-70-84; fax: +34-93-401-72-62.

E-mail address: susanna.valls@upc.es (S. Valls).

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Table 1
Heavy metal content of the Manresa Treatment Plant sludge by total sample digestion

Cd	Cu	Mn	Ni	Pb	Cr	Zn	Ba
< 0.58 ± 0.05	157.43 ± 14	391.65 ± 2.7	60.61 ± 5.75	116.18 ± 3.0	202.11 ± 6.4	4130 ± 353	618.8 ± 72.2

The results are expressed in milligrams of metal per kilogram sample of dry waste analysed.

obtained for the sludge from the waste water treatment plant are set out in Table 1.

The remaining toxic contaminants: sulphates, chlorides, phosphates and total organic carbon (TOC) were determined according to the leaching test for German standard DIN 38414 S4 [2] (see Table 2).

1.2. The sludge mortar mixes

The mortar was composed of: wet sludge, calcareous sand, Portland I 45/A cement and tap water, the quantity of which was determined with the flow table test [3]. The conditions of mortars processing are according to standard UNE 80-101 [4]. In some of the mortar mixes, calcium chloride was added as an accelerator and Escucha coal fly-ash was used as a partial cement replacement, in order to obtain a economic system of stabilisation. The calcium chloride (at 3% of the cement content and in a 33% solution) was added with the aim of improving the cement's hydration to counteract the effects of the *organic material* contained in the sludge. The amount of organic matter content in sludge is approximately 45%.

The sludge mortar mixes complied with the results of another study on physical stabilisation/solidification in cement pastes containing sludge, in which 35–25% wet sludge in the mixture was found to be the maximal amount compatible with strength requirements. The mixes studied are set out in Tables 3 and 4.

2. Durability: accelerated carbonation

Previously to the durability test, all mortars were evaluated by the leaching test, with the purpose of knowing the leaching potential of the created system.

After a 60-day curing process in a damp chamber (95% relative humidity), the test specimens in different dosages were dried to a relative humidity of 63 ± 2%. At this humidity, the depth of the initial carbonation front was determined with a 1% phenolphthalein solution in 70% ethanol. Later on, five faces of the test specimens were impermeabilised to get a one-directional carbonation. The application of the indicator and the measurements of the carbonation front were made following the recommendations in RILEM CPC-18 [5].

The test consisted of an accelerated carbonation based on the process by Ho and Lewis [6]. It consists of eight cycles. Each cycle is of 192 h in a climatic chamber at a temperature of 20°C, a relative humidity of 65% and a 1 atmosphere pressure of 99.99% pure CO_2. The CO_2 injections were up to saturation point. The carbonation process is very aggressive. After undergoing the eight cycles, the mortars displayed large carbonation fronts, between 54% and 100%, since these mortars are characterised by their high porosity.

2.1. Products of carbonation

The carbonation products were studied by ^{29}Si RNM-MAS nuclear magnetic resonance of solids. The ^{29}Si RNM-MAS spectra indicate the degree of polymerisation of the hydrates in the cement paste, and thus the evolution of the C–S–H. The degree of polymerisation is shown according to the chemical environment or displacement band. If we find Q^0 in the sample spectrum, this indicates the presence of monomeric units corresponding to anhydrous calcium silicates. On the other hand, the Q^1 (− 80 ppm) and Q^2 (− 85, − 90 ppm) bands correspond to the hydration of calcium silicates and the formation of C–S–H. The presence of the Q^3 (− 94 ppm) and Q^4 (− 101.6 ppm) displacement bands correspond to the polymerisation of the C–S–H [6], which occurs in the formation of silica gel when this is carbonated (Eq. (1.1)).

$$3CaO\cdot 2SiO_2\cdot 2H_2O + 3CO_2 \rightarrow 2SiO_2\ (\text{gel}) + 3CaCO_3 + 3H_2O \qquad (1.1)$$

2.1.1. Results of carbonation products

Carbonated samples with and without sludge and uncarbonated samples were examined. The samples with and without sewage sludge which underwent an accelerated carbonation process only have their displacement band at approximately − 94 ppm, band Q^3. On the other hand, the uncarbonated samples have band Q^1 (see Fig. 1).

2.2. Environmental assessment of carbonated mortars

2.2.1. Results

The carbonation process directly affects the material's properties, and an environmental assessment of this is

Table 2
TOC and sulphates, chlorides and phosphates content in the wastewater sewage sludge

Contaminant	Concentration	Analysis technique
TOC (mg C/l)	807.8 ± 0.0	TOC analyser
Conductivity (μS/cm)	1611	Conductometer
Chlorides (mg/l)	94.47 ± 0.0	Ionic chromatography
Phosphates (mg/l)	35.40 ± 0.001	Ionic chromatography
Sulphates (mg/l)	384.01 ± 0.0	Ionic chromatography

Table 3
Nomenclature and mixes of mortars containing wet sludge from the Manresa Treatment Plant without added fly ash

	Sludge/binder	Water (g)[a]	Sludge (g)	Cement (g)	Sand (g)	Additive (3% weight cement)
(1) CM25A	1:1	62	450	450	900	
(2) CM25A + ad	1:1	62	450	450	900	$CaCl_2$
(3) CM25B	1:1	72	500	500	1000	
(4) CM25B + ad	1:1	72	500	500	1000	$CaCl_2$
(5) CM35A	1.4:1	65	630	450	720	
(6) CM35A + ad	1.4:1	65	630	450	720	$CaCl_2$
(7) CM35B	1:1	34	700	700	600	
(8) CM35B + ad	1:1	34	700	700	600	$CaCl_2$

[a] The amount of water is the water added to the mix without counting the water contained in the sludge. The sludge humidity was 68%.

necessary. This assessment consists in subjecting the mortars to a leaching process after the accelerated carbonation process. The leaching standard used is NEN 7345 [1], which allows the leaching potential to be assessed in matrices that have first undergone a carbonation process with waste stabilised in the long term. The contaminants studied are heavy metals (Ba, Cd, Cr, Cu, Zn, Ni, Pb), anions ($SO_4{}^{-2}$, $PO_4{}^{-3}$ and Cl^-) and the soluble TOC. Tables 5 and 6 and Fig. 2 show the results.

2.2.2. Discussion of leaching carbonated mortars

The concentrations of the toxic contaminants examined in the leaching process with mortars subjected to accelerated carbonation are compared with the results obtained in the mortars which did not undergo an accelerated carbonation process [7].

2.2.2.1. Heavy metals. The carbonated mortars displayed accumulated leaching of metals under the U_1 limit of NEN-7345 standard [1], and showed no kind of environmental restriction for their use. Nevertheless, the levels of copper, nickel and zinc detected are slightly higher in most of the dosages of carbonated mortars than in uncarbonated mortars (Table 5). In certain dosages, there is even a slight presence of manganese. On the other hand, there is a large reduction in barium in carbonated mortars.

Carbonation gives rise to an increase in the concentration of nickel, copper and zinc in the leachates for three reasons: (a) slight increase in the solubility of the metal compounds through the reduction of the pH in the stabilisation system, (b) the decomposing of the ettringite hydrate that had zinc incorporated in its crystalline structure and (c) the polymerisation of the C–S–H, releasing metal cations that were linked to the Si–O groups [8].

The amount of barium element leaching is much lower in the carbonated system, due to its lower insolubilisation through the formation of $BaCO_3$ and $BaSO_4$, with lower solubilities than the barium hydroxide. The $BaCO_3$ is formed by the carbonation process and the $BaSO_4$ through the decomposition of the ettringite. Carbonation decomposes the ettringite to form calcium carbonate, alumina gel and gypsum [9] (see Eq. (1.2)). The gypsum is soluble, releasing sulphates into the leachate.

2.2.2.2. Sulphates, chlorides and phosphates. There is an increase in both chlorides and sulphates in all the dosages of carbonated mortars. The accumulative leaching of chlorides, even at higher concentrations, but is under U_1. On the other hand, the sulphates, depending on the dosage, are either under the U_1 limit or between U_1 and U_2 (see Table 6), which according to the standard would not involve any environmental restriction for their use, but they would require treatment when their useful life ends. The leaching of sulphates in all the mortars subjected to the accelerated carbonation test is greater than in the noncarbonated mortars, whose leaching was limited to a surface washing. The retention of the sulphates was caused by the formation of ettringite in the hydration of Portland cement. In the carbonation process, the ettringite undergoes a decomposition process [9] (Eq. (1.2)). In this, ettringite decomposition

Table 4
Nomenclature and mixes of mortars containing wet sludge from the Manresa Treatment Plant with added fly ash

	Sludge/binder	Water (g)[a]	Sludge (g)	Cement (g)	Sand (g)	Fly ash (g)
(9) CM25L5CV	1:1	90	500	475	1000	25
(10) CM25L10CV	1:1	90	500	450	1000	50
(11) CM25L15CV	1:1	90	500	425	1000	75
(12) CM25L25CV	1:1	90	500	375	1000	125
(13) CM35L5CV	1:1	90	700	665	600	35
(14) CM35L10CV	1:1	90	700	630	600	70
(15) CM35L15CV	1:1	90	700	595	600	105
(16) CM35L25CV	1:1	90	700	525	600	175

[a] The amount of water is the water added to the mix without counting the water contained in the sludge. The sludge humidity was 68%.

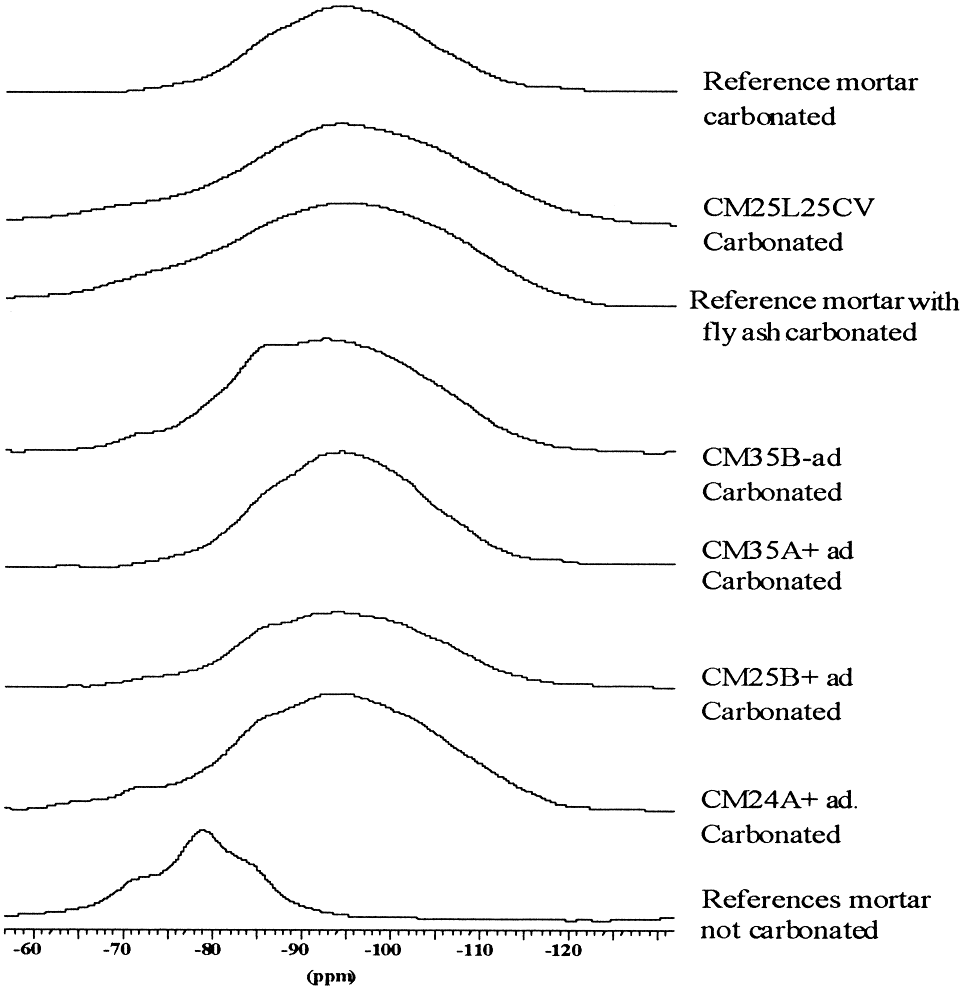

Fig. 1. Spectra of ^{29}Si RNM-MAS. There are carbonated samples with sludge, reference carbonated samples without sludge and reference uncarbonated samples without sludge.

Table 5
Heavy metals concentration in mg/m^2 (Cd, Mn, Cu, Ni, Pb, Cr, Zn and Ba) in uncarbonated and carbonated mortars

	Cd	Cu	Mn	Ni	Pb	Cr	Zn	Ba
Mixed	Uncarbonated/carbonated							
CM25A	<0.19/<0.29	11.07/16.13	<0.19/<0.29	12.97/23.48	<1.93/<2.91	<0.40/<0.58	3.01/10.71	72.51/0.75
CM25A + ad	<0.19/<0.29	9.63/10.58	<0.19/<0.29	9.64/6.10	<1.95/<2.89	<0.40/<0.58	3.16/5.86	77.30/1.80
CM25B	<0.20/<0.28	12.37/11.01	<0.20/<0.28	12.50/10.24	<2/<2.83	<0.40/<0.56	1.71/6.31	89.12/<0.28
CM25B + ad	<0.20/<0.29	11.43/11.61	<0.20/<0.29	12.47/76.85	<2.02/<2.94	<0.40/<0.58	11.12/2.3	71.52/2.22
CM35A	<0.20/<0.23	20.32/24.4	<0.20/0.73	22.85/17.14	<2.03/<2.28	<0.41/<0.45	2.68/3.41	195.03/1.28
CM35A + ad	<0.20/<0.23	22.94/19.38	<0.20/1.96	15.87/12.71	<2/<2.25	<0.40 7<0.45	<0.40/4.11	119.54/1.54
CM35B	<0.18/<0.27	10.34/11.78	<0.18/<0.27	9.92/9.96	<1.87/<2.69	<0.37/<0.54	14.03/4	84.46/0.63
CM35B + ad	<0.20/<0.25	11.05/12.8	<0.20/<0.25	10.04/11.19	<2.02/<2.56	<0.40/<0.51	25.44/3.76	68.80/2.80
25L5CV	<0.20/<0.3	14.47/15.51	<0.20/<0.31	8.45/16.86	<2.01/<3.10	<0.40/<0.62	<0.40/2.86	121.12/0.87
25L10CV	<0.20/<0.29	15.08/18	<0.20/0.63	11.97/18.75	<1.97/<2.91	<0.40/<0.58	<0.40/5.58	94.34/0.91
25L15CV	<0.20/<0.29	12.7/18.39	<0.20/<0.29	7/15.66	<2/<2.94	<0.52/<0.59	<0.40/6.77	54.09/0.82
25L25CV	<0.20/<0.29	14.25/22.91	<0.20/0.42	9.36/18.6	<2/<2.91	0.47/<0.58	4/6.85	77.50/0.84
35L5CV	<0.19/<0.26	17.8/17.10	<0.19/<0.26	9.20/10.24	<1.97/<2.60	<0.40/3.96	<0.40/1.31	137.10/3.59
35L10CV	<0.21/<0.25	17.61/16.65	<0.21/<0.26	10.91/20.83	<2.1/<2.50	<0.42/<0.50	0.8/3.5	126.16/0.90
35L15CV	<0.20/<0.25	15.05/12.45	<0.20/<0.25	7.11/12.45	<2/<2.50	<0.4/<0.51	0.67/2.04	78.77/1.46
35L25CV	<0.19/<0.26	19.86/10.77	<0.19/<0.26	13.47/15.11	<1.94/<2.66	<0.38/<0.53	5/3.72	155.69/0.67
U_1	1	50	–	50	100	150	200	600

And the limit U_1 of NTLT (NEN 7345).

process gypsum is formed, which has greater solubility. The ettringite has $Kps \cong 10^{-40}$ at 20°C and the gypsum $Kps \cong 3.8 \times 10^{-5}$.

$$3CaO{\cdot}Al_2O_3 3CaSO_4{\cdot}32H_2O + 3CO_2 \rightarrow 3CaCO_3 + 3\underset{\text{gypsum}}{(CaSO_4{\cdot}2H_2O)} + \underset{\text{alumina gel}}{Al_2O_3{\cdot}H_2O} + (26-X)H_2O \qquad (1.2)$$

Phosphates are also not detected in the leachates of the carbonated mortars, as occurred with the noncarbonated mortars.

A higher concentration of chlorides in the eluates of the leaching process through the decomposition of Friedel's salt, formed in the hydration process of the cement paste of the mortar [10] (see Table 6).

2.2.2.3. Total soluble organic carbon. In the accumulative leaching of all the carbonated dosages, there was a large reduction in the TOC concentration, and thus a greater retention power of the matrices formed after the carbonation process. In carbonated mortars, there is an increase in the sinuousness of the porous system, and therefore a decrease in porosity. The system's sinuousness makes the leaching process more difficult. This effect is positive on the organic leachates, which are less affected by the polymerisation of the C–S–H, the reduction in the pH of the mortar system and the decomposition of the ettringite in which $CaCO_3$ and gypsum are formed. The amount of leached TOC is consequently less in all the cases (Fig. 2).

The leaching liquids obtained from these carbonated mortars display a reduction in the pH from 12 to 8. The pH value of 8 slightly favours the solubility of metal species.

Table 6
Accumulative leaching of phosphates, chlorides and sulphates (mg/m^2) in uncarbonated and carbonated mortars

	Chloride	Phosphates	Sulphates
	Uncarbonated/carbonated		
CM25A	14.22/1852	< 38.66/< 58.30	890.93/39,719.70
CM25A + add	25499.70/19,796.22	< 39.02/< 57.75	858.6/19,852.53
CM25B	761.13/1292.77	< 40.20/< 56.70	695.82/9221.10
CM25B + add	29655.8/15,214.54	< 40.50/< 58.81	1472.6/22,923.7
CM35A	240.60/4175	< 40.62/< 45.67	68.28/48,852.83
CM35A + add	2858.36/17,925.30	< 40/< 45.14	1229.86/37,494.96
CM35B	7.46/1200.77	< 37.5/< 53.89	1073.35/27,810.50
CM35B + add	35658.54/18,053.41	< 40.48/< 51.17	927.4/24,330.94
25L5CV	< 40.20/1608.96	< 40.20/< 62.09	286.86/26,914.16
25L10CV	< 39.36/2786.19	< 39.36/< 58.27	521.56/41,543.70
25L15CV	< 39.72/1593.10	< 39.72/< 58.77	1589.9/27,992.66
25L25CV	< 40.53/2375	< 40.53/< 58.18	734.02/38,748.6
35L5CV	< 39.47/785	< 39.47/< 51.98	< 39.47/11,858.22
35L10CV	< 41.8/2315.40	< 41.8/< 50.11	610.32/32,535
35L15CV	< 40/1709.68	< 40/< 50.57	1203.11/19,530.91
35L25CV	366.29/1619.80	< 38.88/< 53.29	< 38.88/18,893.27
U_1	20,000	–	25,000
U_2	150,000	–	200,000

Both limits U_1 and U_2 of NTLT.

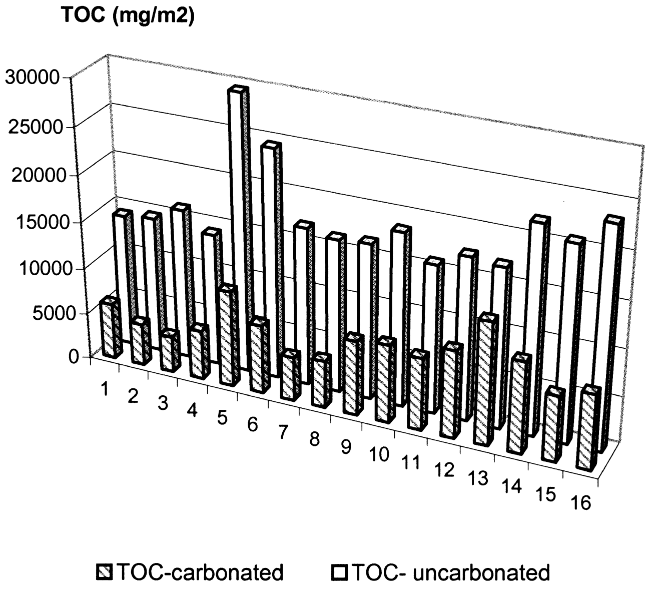

Fig. 2. TOC accumulative leaching in carbonated and uncarbonated mortars.

3. Conclusions

From the results obtained by the magnetic resonance technique (^{29}Si RNM-MAS) and the environmental assessment by the NEN-7345 leaching test [1] of mortars under accelerated carbonation process, the following points are determined.

(1) Hydrates of the cement paste are polymerised in the samples that have undergone an accelerated carbonation process, both in the reference mortars and in the ones including sewage sludge.

(2) The heavy metals concentration do not exceed the U_1 limit of the Dutch standard, meaning that there is no environmental restriction for use in building. Nevertheless, leaching concentration in the carbonated mortars is greater because the ettringite decompose. However, the amount of barium leaching is much lower in the carbonated system, due to its insolubilisation through the formation of $BaCO_3$ and $BaSO_4$.

(3) The concentration of sulphates, depending on the dosage, is below the U_1 limit or between the U_1 and U_2 limits. There is no environmental restriction in either case, and treatment is required when the material's useful life is over only in the last case. Although, the leaching of sulphates in all the mortars subjected to the accelerated carbonation test is greater than in the noncarbonated mortars, because the ettringite undergoes a decomposition process.

(4) Also, the concentration of chlorides in the eluates of the leaching process is higher due to the decomposition of Friedel's salt.

(5) In the accumulative leaching of all the carbonated dosages, there was a large reduction in the TOC concentra-

tion, because there is an increase in the sinuousness of the porous system, and therefore a decrease in porosity.

(6) The developed carbonation process is very aggressive, however, the results obtained in the environmental valuation guarantee the possibility of stabilisation on the part of the cement with the possibility of looking for and investigating applications in the field of engineering.

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