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Effect of pig slurry on two cement mortars: Changes in strength, porosity and crystalline phases

E. Sánchez [a,*], A. Moragues [b], J. Massana [c], A. Guerrero [d], J. Fernandez [b]

[a] Polytechnic University of Madrid, Department of Applied Science and Technology, Ciudad Universitaria s/n, 28040 Madrid, Spain
[b] Polytechnic University of Madrid, Department of Civil Engineering, Construction, Spain
[c] Polytechnic University of Madrid, Department of Construction and Rural Roads, Spain
[d] Institute of Construction Science Eduardo Torroja (CSIC), Spain

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ABSTRACT

The present article addresses the variations observed in porosity and flexural and compressive strength in two types of cement mortar when submerged in pig slurry. The tests were conducted in a 100 m^3 experimental lagoon. The mortars were exposed to three types of environments for 36 months: two submerged in the test lagoon, at two different depths, and one outside it. Bending and compression measurements were taken after 3, 12, 24, 36 and 48 months. In addition, 3, 24, 36 and 48 month specimens were tested for total porosity and pore-size distribution. Changes in the mineralogical characteristics of the mortars after 24, 36 and 48 months were also recorded. The strength studies showed that the load capacity attained by the two cements was similar after 48 months, the use of more expensive 42.5 sulphate-resistant cement is not justified. The XRD results showed no evidence in any of the cements of precipitation originating in the ions in the aggressive medium.

1. Introduction

Pig slurry is an agricultural by-product used chiefly to fertilize cultivated fields. As the demand for fertilizer depends on crop cycles, however, the slurry must be stored over long periods of time. In Spain, the lagoons of different depths generally used for such storage are made of brick covered with plain or reinforced concrete. These lagoons are not watertight due to the occurrence of cracks or leaks, with the concomitant risk of environmental damage in the form of the pollution of underground or runoff water [1]. In farm enclosures slurry is also in contact with other precast concrete structural members, such as continuous or patterned flooring. The degradation of these structures may entail substantial economic loss, in patterned flooring especially, where deterioration-induced collapse can cause severe injury to the animals [2,3].

Slurry composition depends on many factors, including animal physiology, type of feed, facility typology and management and so forth. The pig slurry used in the tests was the result of diluting manure with the runoff from pen hosing. Its complex chemical composition, with organic and inorganic compounds, varied over time. The three main groups of organic components were: organic acids (acetic, propionic and isovaleric), nitrogenous compounds (primarily ammonia-based) and a number of hydrosulphide compounds deriving from urea denaturation. The result is a compound with a pH ranging from 7 to 8. The Spanish structural concrete code, EHE [4], regards substances with a pH of over 6.5 to be non-aggressive from the standpoint of acid damage. Nonetheless, research has shown that concrete and mortar in contact with such slurries deteriorate systematically, with a decline in their load capacity [5]. Clearly then, degradation is the outcome of the synergies between various factors. Some researchers have attempted to reproduce this sort of concrete degradation in the laboratory [6], by testing different types of cements after exposure to specific organic salts with varying pH values or analyzing the mechanism involved in cement matrix alterations caused by a combination of acids [7].

The use of sulphate-resistant Portland cement and pozzolanic cements with silica fume or fly ash additions is standard practice in concrete farm buildings in a number of countries [3]. In Spain, the cements most commonly used in rural environments are type I Portland and Portland with additions, particularly fly ash. The use of the former is based on its availability and suitability for works of all kinds. The latter is used due to its lower cost, and the added advantage that replacing part of the Portland cement with fly ash improves mortar and concrete durability by enhancing resistance to chemical agents and reducing permeability [8–10].

This paper reports on research conducted to ascertain the impact of pig slurry on mortars made with different types of cement. The values found for flexural and compressive strength, total porosity and

* Corresponding author. Tel.: +34 91 336 3702; fax: +34 91 3363727.
E-mail address: elvira.sanchez.espinosa@upm.es (E. Sánchez).

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pore-size distribution at different test times are given, along with the changes in the mineralogical characteristics of the mortars.

2. Materials and methods

2.1. Cements

The study was conducted with two types of cement: a sulphate-resistant Portland cement, CEM I SR 42.5 N, and cement blended with fly ash and limestone filler, CEM II/B-M (V-L) 32.5 N. The exact fly ash content is confidential. However, the ranges 21–35% of fly ash content is specified by Spanish standards UNE-EN 197-1:2000. The chemical and mineralogical compositions of the two cements are given in Table 1.

Three prismatic specimens (40×40×160 cm) with a water/cement ratio of 0.5 and a sand/cement ratio of 3/1 were prepared for each cement type, environment and exposure time. The specimens were made to European standard EN 196-1:194 requirements. They were de-moulded 24 h later and cured in water for 28 days at 22 °C. Zero time tests were conducted on three samples of each mortar type, while the others were placed in the respective aggressive environments.

2.2. Aggressive medium

The aggressive medium used was pig slurry from a farm storage lagoon at Etreros in the Spanish province of Segovia.

The farm is located in central Spain, where the mean summertime relative humidity is 48% and the mean temperature is 20 °C. The values for the rest of the year are 75% and 9 °C, respectively. The area has a mean of 56 days of frost per year.

The slurry composition is variable. It depends on many factors than change over time. Therefore, the slurry was sampled and analyzed after 3, 6, 12, 18, 24 and 36 months. The minimum, maximum and mean values are shown in Table 2.

The highest content values were found for ammonia nitrogen, sulphides, chlorides and acetic and propionic acids. The maximum value of ammonia nitrogen present (0.25%), taking NH_4^+ separately, was sufficiently high to classify the slurry as a highly aggressive medium or substance, according to Spanish structural concrete code EHE [4]. The maximum chloride content, the origin of which is the cleaning water used to hose down the facility, generated salinity similar to the values observed in seawater (1472 mg/l in aerobic, and 780 mg/l in anaerobic environments). Moreover, the acetic acid content was high enough to cause acid attack. Another potentially aggressive agent was the pH, which at values ranging from 7.21 to 8.13 was much lower than the mortar pore solution pH (12.7) [11]. Inasmuch as this pH gradient may lead to the dissolution of the much more basic portlandite, slurry can be regarded to be an aggressive substance.

Table 1
Chemical and mineralogical composition of the cements used.

	CEM I SR 42.5N	CEM II/B-M (V-L) 32.5N
Ca O	64.4	51.36
% CO free	2.1	–
SiO_2	19.1	24.8
Al_2O_3	3.9	9.19
Fe_2O_3	4.7	3.25
MgO	1.3	2.14
K_2O	0.7	1.41
SO_3	3.1	2.58
Cl	–	0.0006
Na_2O	0.2	–
Loss on ignition	2.6	1.75

Table 2
Slurry composition: minimum, maximum and average values.

		Aerobic environment			Anaerobic environment		
		Min.	Aver.	Max.	Min.	Aver.	Max.
pH		7.30	7.67	8.10	7.21	7.52	8.13
Conductivity (mS)		5.05	8.81	13.25	5.62	8.78	13.95
Redox potential (mV)		−304.00	−158.80	−71.00	−340.00	−172.21	−62.00
Total solids (mg/l)		4.07	5.67	7.19	4.34	24.43	80.81
Volatile solids (mg/l)		2.04	2.05	3.98	2.38	18.77	60.40
Total nitrogen (%)		0.06	0.19	0.28	0.06	0.22	0.38
Ammoniac nitrogen (%)		0.05	0.10	0.12	0.05	0.13	0.25
Sulphurs (mg/l)		5.36	81.24	115.00	4.80	90.32	162.87
Bicarbonates (mg/l)		3.38	5.85	10.55	3.37	7.13	11.66
Anions	Sulphurs (mg/l)	0.00	7.35	12.79	0.00	23.55	177.95
	Chlorides (mg/l)	61.00	462.42	1427.00	209.00	445.83	780.00
Acids	Acetic (mg/l)	32.55	153.79	286.70	7.86	89.13	192.00
	Propionic (mg/l)	0.00	48.96	124.60	0.00	27.85	93.890
	Isovaleric (mg/l)	0.00	2.13	3.50	0.00	0.56	1.20

2.3. Experimental procedures

The tests were conducted in an experimental lagoon located near the farm's own storage lagoon. Its two basins measured 4×8 m with depths of 1 m and 3 m, inter-connected by a canal to facilitate the filling process. A detailed sketch of the experimental facility is given in E. Sánchez et al. [12].

The specimens were placed on the bottom of the basins, where conditions were aerobic at a depth of 1 m and anaerobic at a depth of 3 m. These conditions reproduced the environments prevailing on pig farms (lagoons from 1 to 1.5 m deep and tanks or deep lagoons of 2 to 4 m deep). Control specimens were placed in the open air alongside the canal connecting the two basins. Consequently, three aggressive environments were studied:

- A natural environment (I) with full oxygen and carbon dioxide availability, as specimens are completely unsheltered.
- An aerobic environment (II) in slurry 1 m deep, with medium to low oxygen content and aerobic fermentation.
- An anaerobic environment (III) with specimens submerged in 3 m deep slurry, with zero oxygen and anaerobic fermentation.

Three specimens were withdrawn from each environment after 3, 12 and 24 months, and two after 36 and 48 months, washed and submerged in water for 48 h. Compressive and flexural strength tests were subsequently conducted to European standard EN196-1:1994 at INTEMAC's (Instituto Técnico de Materiales y Construcciones) central laboratory.

The variance analysis of the data was carried out by the ANOVA process of StatGraphics v.5 (2000). For the data analysis the model included the dependent variables “flexural” and “compression”. For the analysis of data relating to each dependent variable the factors “cement”, “time” and “environment” and their interaction were included. The method used to discriminate among the means is Fisher's least significant difference (LSD) procedure ($p<0.05$).

Mortar microstructure was characterized after 24, 36 and 48 months of exposure to the aggressive medium.

X-ray diffraction analysis was conducted by the Spanish National Research Council's Materials Science Institute on powder prepared by crushing samples after thorough drying at 40 °C. A Cu Kα cathode was used and the exposure time was 1 min.

Mercury intrusion porosity (MIP) trials were run on a Micromeritics Autopore IV 9500 porosimeter that operates at pressures of up to 33,000 psi (228 MPa) and covers pore diameters of from 175 to 0.006 µm. Each 3 g specimen was dried for 48 h at a temperature of 22 ± 2 °C and a relative humidity of 50%. The samples were taken from one of the exposed sides of the specimen and tested after reaching a constant weight, to an accuracy of 0.01 g. Sample weight was stabilized in an oven at 40 °C.

3. Results and discussion

3.1. Mechanical strength

The ANOVA process was run on the strength values entailed that, for both compressive and flexural strength, verifying the normal distribution fitting of the residual values, finding the difference, for each data item in a given group, between that value and the mean value for the group. The analysis showed that there were no systematic errors attributable to measurements or specimen manufacture.

In Tables 3 and 4 the results of the ANOVA process are shown. *Count* represents the number of measurements for each factor; *Mean and Standard error* are the mean value and the standard deviation of the values of the measurements and finally, *Lower limit* and *Upper limit* are the minimal and maximal values of those measurements respectively.

3.1.1. Flexural strength

Figs. 1 and 2 show the flexural strength for the mortars made with cements CEM I and CEM II in the three environments. Table 3 shows Least Squares Means for flexural strength.

As shown in Table 3 there are significant differences between the main effects and their interactions.

The average flexural strength values for the Cement effect are 9.39 MPa for CEM I and 10.67 MPa for CEM II. Over time there is a slight increase in strength for the submerged environments. This behaviour is probable related to the hydration of the cement. It must be taken into account that there are two hydration processes: only cement hydration for CEM I and cement hydration and pozzolanic reaction of fly ash for CEM II. The average value for CEM I is 9.74 MPa and 11.47 MPa for CEM II in submerged environments. These results can be explained for the presence of fly ash in CEM II, in accordance with the findings reported by other authors [10,12–14].

For the CEM II, the flexural strength values are similar at all stages. There are no significant differences in submerged environment (seen Fig. 2). However, CEM I shows a random behaviour (seen Fig. 1). There are no significant differences between aerobic and anaerobic environment for both cements.

The samples from the submerged environments showed similar or significantly greater values than the natural environment for both cements types.

In the case of the natural environment, the mortars with cement CEM I show a slight decrease in their flexural strength (about 10%), while the mortars with cement type II show a substantial decrease of about 40%.

One possible explanation for the behaviour in the natural environment could be the natural freezing–thawing cycles suffered by these specimens, due to the fact that the weather exposure in that area was extreme, with frosts for almost 56 days a year.

From these results it can be concluded that for aerobic and anaerobic environments, and for both types of cement, the behaviour is the same, with a slight increase over time. For the natural environment, a decrease in the flexural strength over time was observed for both cement types, with a more pronounced decrease in the case of cement CEM II.

3.1.2. Compressive strength

Figs. 3 and 4 show the results for the compressive strength of the mortars made with cements CEM I and CEM II, in all three environments. Table 3 shows Least Squares Means for compression strength.

As shown in Table 3 there are significant differences between the main effects and their interactions.

The average compression strength values for the cement effect are 65.18 MPa for the CEM I and 63.71 MPa for the CEM II. Over time there are significant increases up to 24 months' exposition, which slows and stabilizes until the end of the test period.

Table 3
Least squares means for flexural.

Level	Count	Mean	Std. error	Lower limit	Upper limit
Grand mean	96	10.0334			
Cement					
CEM I	48	9.39^{a}	0.0704	9.25	9.53
CEM II	48	10.68^{b}	0.0704	10.53	10.82
SEM	0.0704				
Time					
0	18	$9.95^{a,\ b}$	0.1129	9.73	10.18
3	18	10.22^{a}	0.1129	10.0	10.45
12	18	9.85^{b}	0.1129	9.62	10.08
24	18	10.84^{c}	0.1129	10.61	11.06
36	12	9.73^{b}	0.1383	9.46	10.01
48	12	9.60^{b}	0.1383	9.32	9.88
SEM	0.1193				
Environment					
Aerobic	32	10.63^{a}	0.0862	10.45	10.80
Anaerobic	32	10.58^{a}	0.0862	10.41	10.77
Natural	32	8.89^{b}	0.0862	8.72	9.06
SEM	0.0863				
Cement by time					
CEM I—0	9	8.97^{a}	0.1597	8.65	9.29
CEM I—3	9	9.43^{a}	0.1597	9.11	9.75
CEM I—12	9	9.26^{a}	0.1597	8.94	9.58
CEM I—24	9	10.57^{b}	0.1597	10.25	10.89
CEM I—36	6	8.88^{a}	0.1956	8.49	9.27
CEM I—48	6	9.24^{a}	0.1956	8.85	9.63
CEM II—0	9	10.94^{b}	0.1597	10.62	11.26
CEM II—3	9	11.02^{b}	0.1597	10.70	11.34
CEM II—12	9	10.44^{b}	0.1597	10.12	10.76
CEM II—24	9	11.11^{c}	0.1597	10.79	11.43
CEM II—36	6	10.58^{b}	0.1956	10.19	10.97
CEM II—48	6	$9.96^{a,b}$	0.1956	9.57	10.35
SEM	0.1687				
Cement by environment					
CEM I—aerobic	16	9.68^{a}	0.1219	9.43	9.92
CEM I—anaerobic	16	9.80^{a}	0.1219	9.56	10.04
CEM I—natural	16	8.70^{b}	0.1219	8.45	8.94
CEM II—aerobic	16	11.58^{c}	0.1219	11.33	11.82
CEM II—anaerobic	16	11.37^{c}	0.1219	11.12	11.61
CEM II—natural	16	9.09^{d}	0.1219	8.84	9.32
SEM	0.1220				
Time by environment					
0—aerobic	6	9.96a	0.1956	9.56	10.35
0—anaerobic	6	9.96^{a}	0.1956	9.56	10.35
0—natural	6	9.96^{a}	0.1956	9.56	10.35
3—aerobic	6	10.59^{b}	0.1956	10.19	10.98
3—anaerobic	6	10.16^{a}	0.1956	9.76	10.55
3—natural	6	9.93^{a}	0.1956	9.53	10.32
12—aerobic	6	10.09^{a}	0.1956	9.70	10.48
12—anaerobic	6	10.55^{a}	0.1956	10.15	10.94
12—natural	6	9.91^{c}	0.1956	8.52	9.30
24—aerobic	6	11.46^{d}	0.1956	11.07	11.85
24—anaerobic	6	11.67^{d}	0.1956	11.28	12.06
24—natural	6	9.39^{a}	0.1956	9.0	9.78
36—aerobic	4	10.89^{b}	0.2396	10.41	11.37
36—anaerobic	4	10.17^{a}	0.2396	9.69	10.65
36—natural	4	8.13^{e}	0.2396	7.66	8.61
48—aerobic	4	10.78^{b}	0.2396	10.30	11.26
48—anaerobic	4	11.01^{b}	0.2396	10.53	11.49
48—natural	4	7.01	0.2396	6.54	7.49
SEM	0.2066				

a, b, c, d, e, f for each factor or combination of factors with different superindices differ significantly. SEM is the standard error of the mean.

CEM II submerged in pig slurry followed a pattern typical of Portland cement with fly ash additions, i.e., a steady increase about of 30% in the first 24 months [12–15]. The falling off observed, (about 6%) in the compressive strength values until the end of the test period may be due to the start of the process of degradation. The increase in the compressive strength values for CEM I is approximately 16% up to the

Table 4
Least squares means for compression.

Level	Count	Mean	Std. error	Lower limit	Upper limit
Grand mean	96	64.45			
Cement					
CEM I	48	65.12^{a}	0.2568	64.66	65.69
CEM II	48	63.71^{b}	0.2568	63.20	64.23
SEM	0.2568				
Time					
0	18	58.72^{a}	0.4119	57.89	59.54
3	18	62.05^{b}	0.4119	61.23	62.87
12	18	64.25^{c}	0.4119	63.43	65.08
24	18	69.07^{d}	0.4119	68.24	69.89
36	12	66.70^{e}	0.5044	65.69	67.70
48	12	65.90^{e}	0.5044	64.89	66.91
SEM	0.4350				
Environment					
Aerobic	32	65.54^{a}	0.3146	65.91	67.17
Anaerobic	32	65.52^{a}	0.3146	64.89	66.15
Natural	32	61.28^{b}	0.3146	60.65	61.91
SEM	0.3146				
Cement by time					
CEM I—0	9	64.62^{a}	0.5825	63.45	65.78
CEM I—3	9	64.14^{a}	0.5825	62.97	65.30
CEM I—12	9	62.30^{b}	0.5825	61.13	63.46
CEM I—24	9	69.55^{c}	0.5825	68.39	70.72
CEM I—36	6	66.38$^{a, d}$	0.7134	64.95	67.80
CEM I—48	6	64.09^{a}	0.7134	62.66	65.51
CEM II—0	9	52.82^{e}	0.5825	51.65	53.98
CEM II—3	9	59.96^{f}	0.5825	58.79	61.12
CEM II—12	9	66.21$^{a, d}$	0.5825	65.04	67.37
CEM II—24	9	68.58^{c}	0.5825	67.41	69.74
CEM II—36	6	67.01^{d}	0.7134	65.59	68.44
CEM II—48	6	67.70^{d}	0.7134	66.28	69.13
SEM	0.6152				
Cement by environment					
CEM I—aerobic	16	68.59^{a}	0.4449	67.70	69.48
CEM I—anaerobic	16	65.76^{b}	0.4449	64.87	66.65
CEM I—natural	16	61.19^{c}	0.4449	60.30	62.08
CEM II—aerobic	16	64.49^{b}	0.4449	63.60	65.38
CEM II—anaerobic	16	65.28^{b}	0.4449	64.39	66.17
CEM II—natural	16	61.38^{c}	0.4449	60.49	62.27
SEM	0.4449				
Time by environment					
0—aerobic	6	58.72^{a}	0.7134	57.29	60.15
0—anaerobic	6	58.52^{a}	0.7134	57.29	60.15
0—natural	6	58.72^{a}	0.7134	57.29	60.15
3—aerobic	6	63.52^{b}	0.7134	62.09	64.25
3—anaerobic	6	62.29$^{b, c}$	0.7134	60.86	63.71
3—natural	6	60.34^{c}	0.7134	58.91	61.77
12—aerobic	6	66.64^{d}	0.7134	65.22	68.07
12—anaerobic	6	65.63$^{d, b}$	0.7134	64.21	67.06
12—natural	6	60.48^{c}	0.7134	59.05	61.91
24—aerobic	6	73.64^{e}	0.7134	72.21	75.07
24—anaerobic	6	70.29^{f}	0.7134	68.86	71.71
24—natural	6	63.27^{b}	0.7134	61.84	64.70
36—aerobic	4	69.39^{f}	0.8737	67.64	71.14
36—anaerobic	4	66.12^{d}	0.8737	64.37	67.86
36—natural	4	64.58$^{d, b}$	0.8737	62.83	66.32
48—aerobic	4	67.32$^{d, f}$	0.8737	65.57	69.07
48—anaerobic	4	70.07^{f}	0.8737	68.33	71.82
48—natural	4	60.29^{c}	0.8737	58.54	62.04
SEM	0.7535				

a, b, c, d, e, f for each factor or combination of factors with different superindices differ significantly. SEM is the standard error of the mean.

24-month point, reducing around 5% until the end of the test period. The reactions of the cement types over time show that after 48 months of exposure the compressive strength values are greater for the CEM II than the CEM I. The pozzolanic activity of fly ash could have increased as a result of the high concentration of salts in the slurry [16] and therefore its high ionic strength [11].

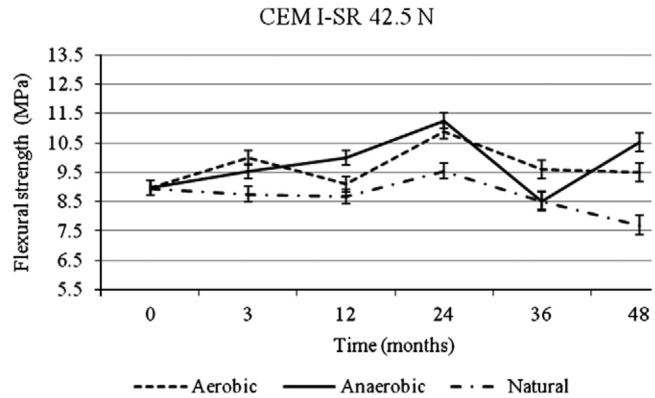

Fig. 1. Mean values of flexural strength for the CEM I in the three environments.

In the natural environment there were no significant differences between the cements studied. The natural environment was significantly different to the submerged environments.

The increase in strength observed in the submerged environments can be explained by an increase in the level of hydration. No significant differences were recorded in cement CEM II performance in the two submerged environments, a finding that concurred with earlier results obtained by E. Sánchez et al. [12]. However, there are differences between the three environments for the CEM I cement. This fact can be explained by the composition of the cement types. The fly ash content in the type II cement reduces porosity and increases chemical resistance [9,20]. The increased porosity and the presence of portlandite in the type I cement cause increased vulnerability to acid attack. Also the presence of different oxygen levels in the aerobic and anaerobic environments affect the redox reactions between the species present in the slurry. This would explain the attacks being different, leading to significant variations over prolonged periods of exposure. It can be concluded that the compressive strength behaviour is similar for both types of cement, with increases up to 24 months and decreases to the end of the test period. The values reached by 48 months of exposure are greater in the CEM II type, even though this has a lower resistance class. There are significant differences between the natural and submerged environments for both cement types. The compressive strength values in the natural environment are the same for both cements.

3.2. Porosity tests

Fig. 5 shows the total porosity for the two cements studied at different test ages and in different environments. Porosity was seen to decline in all cases after 24 months of exposure, except for the CEM II in the natural environment which showed similar porosity levels to

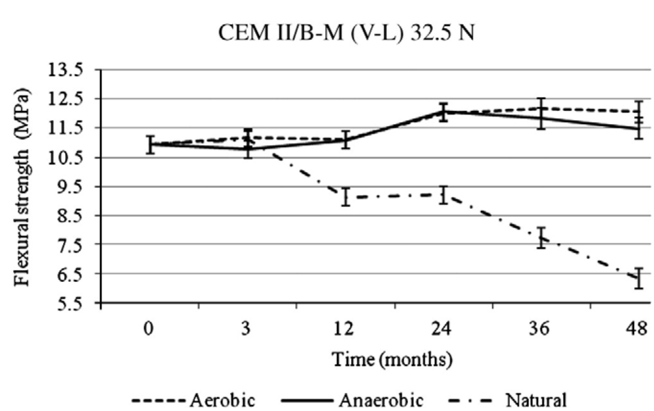

Fig. 2. Mean values of flexural strength for the CEM II in the three environments.

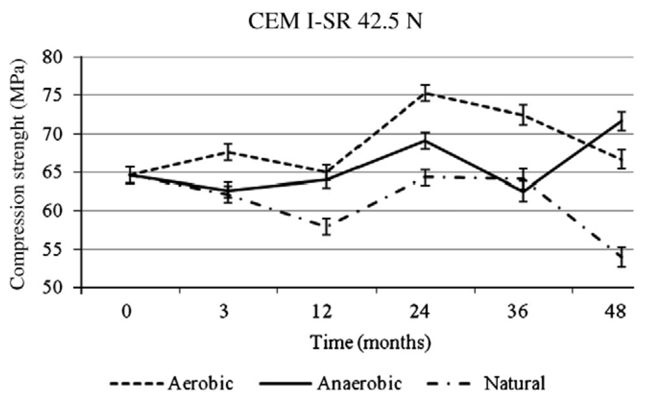

Fig. 3. Mean values of compressive strength for the CEM I in the three environments.

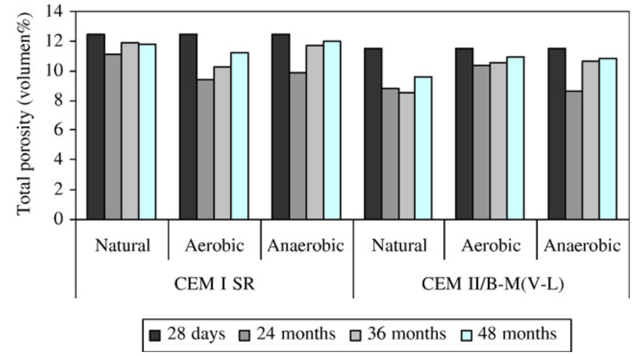

Fig. 5. Total porosity by mercury intrusion porosimetry expressed in volume percentage.

those obtained at 36 months of exposure. The greatest decline, at around 30%, was recorded for cement CEM I in the aerobic environment and CEM II in the anaerobic environment. After 36 months, porosity generally tended upward. Initial porosity was not attained in any of the cases.

Total porosity and compressive strength values in specimens exposed to slurry attack are inversely related, which is in line with findings reported by other authors. Pandey et al. [15] obtained that the strength was decreased with the increase in porosity on samples of ordinary Portland cement mortars made with mineral additives such as fly ash. O'Farell et al. [16] show similar results when clay brick deriving was used to partially replace cement in standard mortars. They asserted than the increase in relative strength corresponds to increasing pore refinement and decreasing threshold radius of mortar. These works agreed with other authors [17,18].

Figs. 6 and 7 show pore-size distribution for cements CEM I and CEM II, respectively, after 28 days of curing and 3, 24, 36 and 48 months in a natural environment. Figs. 8 and 9 show pore-size distribution for cements CEM I and CEM II, respectively, after 28 days of curing and 3, 24, 36 and 48 months in an aerobic environment.

Both cement types show significantly different pore-size distributions. The CEM II type clearly shows less porosity and greater change over time. This fact is due to its fly ash content, the influence of which is not appreciable until after the 90 days of hydration [19].

The effect of the medium on the two cement types is markedly different with respect to the pore-size distribution. In the natural environment both types show an initial reduction in porosity up to the 24-month point. This can be associated with the increase in the level of hydration and the appearance of precipitates due to atmospheric agents. In the submerged environments, the reduction in porosity is much more notable in the CEM I, maintaining a similar average pore size. For the CEM II a clear reduction was noted both in porosity and pore size, which continued to generate significant variations in the time periods studied. It is worth noting that the precipitation in the early stages did not occur at the same point with the type II cement. The lower level of porosity and lower level of free Portlandite may prove this fact.

In summary, the predominant phenomenon in outside (open air) environments over long time periods is lixivation with increasing pore size. In submerged environments the predominant phenomena is precipitation with a reduction in total porosity and also pore size in CEM II. That decline was consistent with the presence of fly ash in its composition [20,21], no other mechanism appears to be involved [8].

3.3. X-ray diffraction analysis

The X-ray diffraction patterns for cements CEM I and CEM II after exposure to the aerobic environment at 24, 36 and 48 months are shown in Fig. 10.

The main crystalline phases present in CEM I after 24 months were: calcite ($CaCO_3$)(JCPDS 5-586), silica (SiO_2)(JCPDS 86-2237) from the aggregate in the mortar, ettringite ($C_6AS_3.H_{32}$) (JCPDS 41-1451), di- and tri-calcium silicates and portlandite ($Ca(OH)_2$) (JCPDS 44-1481). The intensity of the portlandite ($Ca(OH)_2$) and ettringite peaks was seen to decline over the period of hydration (48 months), while no other signals were emitted that would suggest the presence of new crystalline phases. These findings would explain the increase in the microstructural porosity of the material and would concur with the results shown in Fig. 5, as well as with the decline in mortar strength at that age. Moreover, the fact, also reported by other authors [6,7], that no new crystalline phases appeared, corroborates the absence of precipitating salts with molecules containing the ions present in the aggressive medium.

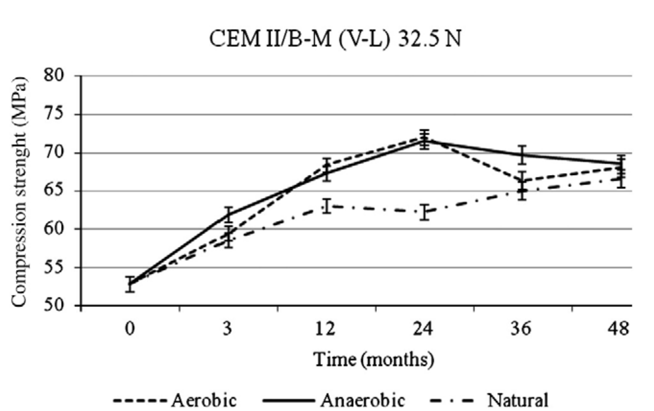

Fig. 4. Mean values of compressive strength for the CEM II in the three environments.

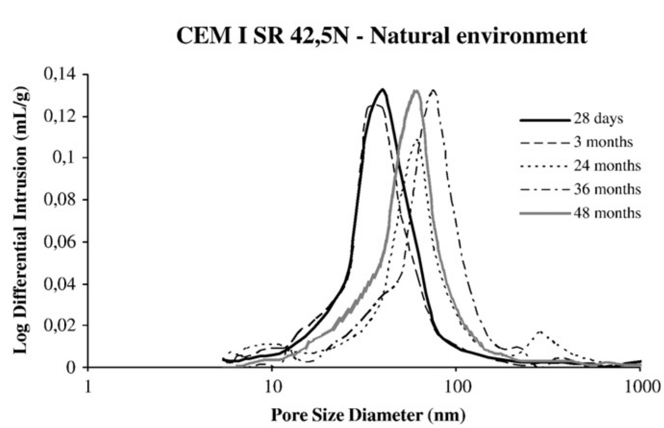

Fig. 6. Pore-size distribution for the CEM I cement in the natural environment.

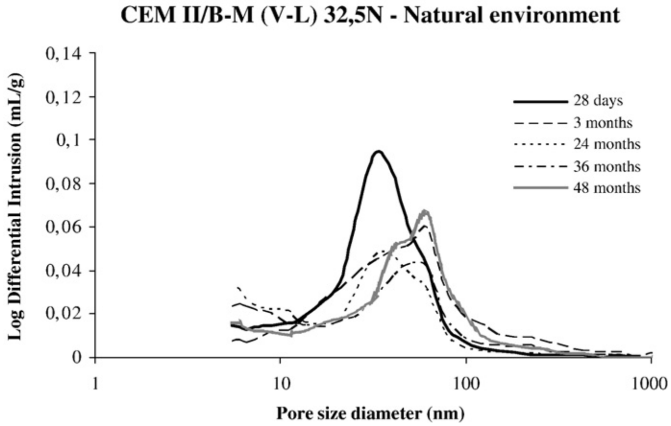

Fig. 7. Pore-size distribution for the CEM II cement in the natural environment.

After 24 months, the crystalline phases observed in CEM II included gypsum ($CaSO_4.2H_2O$), calcite ($CaCO_3$), silica (SiO_2) from the aggregate in the mortar, di- and tri-calcium silicates, as well, although in smaller proportions than found in CEM I, as ettringite ($C_6AS_3.H_{32}$) and portlandite ($Ca(OH)_2$). After 36 months, the ettringite reflections began to decrease and the portlandite levels dropped substantially; at 48 months the reflections of the both crystalline phases decreased significantly. No new crystalline phases originating from the ions in the aggressive medium were detected after 48 months.

While these results are similar to the findings for CEM I, since the decline in portlandite intensity was smaller, the variations in total porosity and pore-size distribution were greater in this cement after 24, 36 and 48 months. In both cements, at 48 months, it is difficult to separate the sand from the cement paste, this indicates a good adherence of the cement and the sand, which could be indicative of a compact microstructure that leads to good mechanical behaviour and durability of the materials under the conditions studied, see Figs. 5 and 9. These data are consistent with the lower availability of free portlandite, consumed in the fly ash pozzolanic reaction.

Gypsum ($CaSO_4.2H_2O$) may appear on the outer part of the specimens in environments containing sulphide ions that can potentially be oxidized to sulphates [22,23]. Gypsum accumulating on the surface of the mortar may form a protective seal that retards the rate of degradation.

Other authors [24–26] have also reported the appearance of ettringite on the surface of the mortar in aqueous solutions with a pH of around 8. In other studies, carry out for the authors [27], conducted with mortar specimens made with CEM III/B 32.5 N/SR and subjected to accelerated ageing in media with pH = 8 (ammonium/ammonia buffer), ettringite formations, such as in Fig. 11, were found in the pores also only a few days after the attack. Fig. 11 depicts several forms

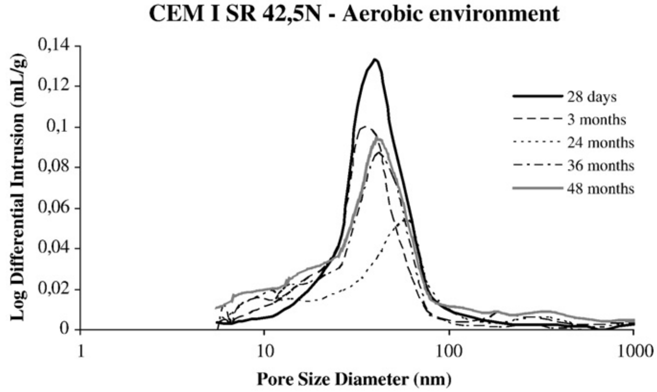

Fig. 8. Pore-size distribution for the CEM I cement in the aerobic environment.

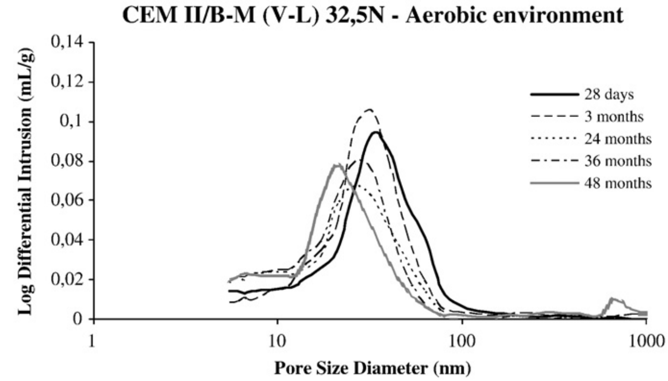

Fig. 9. Pore-size distribution for the CEM II cement in the aerobic environment.

of ettringite (A) as well as pores occupied by this mineral (B). Portlandite had been previously observed to dissolve in those specimens. A possible explanation for this development may be the increase in the concentration of free calcium associated with the decline in the pH in the pores. This increase may in turn prompt the precipitation of sulphate salts, not observed at higher pH values.

These two processes may explain the changes in porosity following the slurry attack. Since the same pH is found in the medium, portlandite dissolves and the calcium spreads outward.

The increase in the calcium ion concentration in the aqueous phase of the outer pores may determine secondary ettringite precipitation, reducing porosity in the earlier stages (up to 24 months).

As the attack continues (from 24 to 48 months), portlandite continues to dissolve and ettringite re-dissolves, with the consequential increase in porosity.

4. Conclusions

The following conclusions may be drawn from the above findings:

- Since the 36 month load capacity of the cements studied was similar, the use of a higher strength, sulphate-resistant cement is not justified. Lower strength class cement with fly ash additions performed equally well, at a lower price.
- In submerged environments, the two cements exhibited greater strength at the various ages. In such media, the decline recorded after 36 months was never smaller than the variation observed in the natural environment.
- According to the XRD results, after 36 months of exposure, the ettringite disappeared entirely in the CEM II type cement, and the portlandite levels dropped substantially in both cement types,

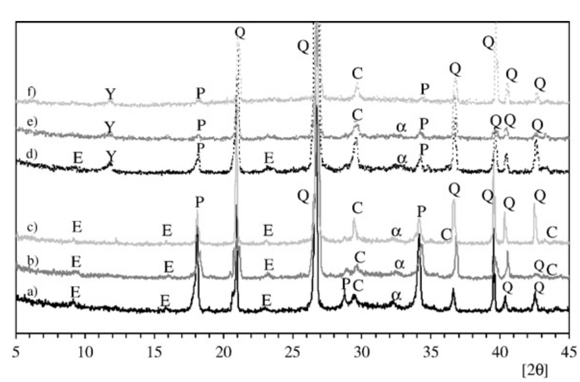

Fig. 10. X-ray diffraction patterns for two cements exposed to an aerobic medium during different months: a) CEM I—24 m; b) CEM I—36 m; c) CEM I—48 m; d) CEM II—24 m; e) CEM II—36 m and f) CEM II—48 m: E $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$; C $CaCO_3$; Q SiO_2; α α′-Ca_2SiO_4; P $Ca(OH)_2$; Y $CaSO_4\cdot 2H_2O$.

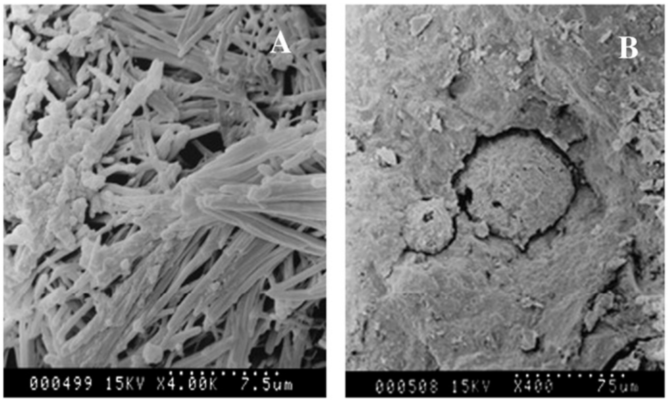

Fig. 11. Ettringite formations in aged mortar exposed to a medium with pH = 8 (ammonium/ammonia buffer).

while no new crystalline phases originating in the ions in the aggressive medium were detected.

- The increase in the mean pore size observed in the natural environment did not lead to lower strength in the test period. The changes in pore-size distribution and mean pore-size values were scantily significant in submerged environments.
- Although up to the 24-month point porosity declined in submerged environments, after that stage and up to 48 months, this parameter increased. This may indicate the onset of mortar degradation. In CEM II, where the changes were less significant, the degradation process could be expected to proceed at a slower pace.
- The slurry used can be regarded as a mildly aggressive compound for cement mortars after 24 months of exposure, in both aerobic and anaerobic conditions.

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