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BEHAVIOUR OF REPAIR LIME MORTARS BY WET DEPOSITION PROCESS

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ABSTRACT

New repair mortars with biocide properties were subjected to acid rain wet/dry cycles in aggressive environment simulation chambers. Those mortars based on lime had a sepiolite addition as a biocide support. The aim of this work was to determine the influence of both the clay and the biocide on mortar behaviour under aggressive solutions. The aggressive solutions used were the following: 1) H_2SO_4 solution, with pH = 4.5; and 2) "acid rain" solution with pH = 3.5. In the first case (H_2SO_4 solution), neither the sepiolite nor the biocide had a significant influence on mortar behaviour, while in the second aggressive medium ("acid rain"), sepiolite plus biocide, a decrease in the reaction between the mortar and the "acid rain" were noted. *© 1998 Elsevier Science Ltd*

Introduction

Building materials exposed to weathering experience various decay processes caused by aggressive agents such as water, wind, "acid rain," etc. In recent years, these processes have been accelerated due to increased pollutant emissions into the environment from industries, domestic heating, cars, etc. In order to understand material responses and allow comparisons of performance, environmental chambers were designed that could simulate aggressive acidic conditions (1).

The importance of lime mortars for use in repair and restoration is well known. Most of the ancient knowledge with respect to workability, preparation characteristics, etc., of this material has been lost with time, and it is necessary to take up again the technical procedures of lime treatment.

The causes of decay of different building materials, including lime mortars, were studied by Furlan (2). He concluded that the vulnerability of lime mortars is due to their low internal

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cohesion and high porosity, factors that provide high water retention capacity, and little resistance to salt crystallisation and frost.

Factors influencing mortar decay processes, in addition of their structure, are considered as follows to be:

1. Physical factors, including wind, temperature changes, freeze-thaw cycles, solubility, crystallisation processes, salt hydration.
2. Chemical factors, involving all processes leading to direct chemical reaction between mortar and aggressive reagents, such as water dissolution processes, reaction between mortar and pollutant gases (CO_2, SO_2, NO_x), etc.
3. Biological factors related to growth of microorganisms in the mortar. These processes create a chemical decay process via microorganism metabolism that produces different organic and inorganic acids and a pH variation in the medium.

In addition, microorganism growth (with roots and hyfas) promote mechanical stresses and mortar decay.

Water plays an important role in many mortars decay processes, acting as a transport medium for aggressive agents, creating favourable conditions for decay.

In previous work (3,4), the properties and characteristics of new repair mortars based on lime and with biocide properties have been described. A clay-type mineral called sepiolite has been added to lime mortar; sepiolite acts as a support of biocide due to its high adsorption/desorption capacity. In this case, the biocide used is pentachlorophenol (C_6Cl_5OH). The aim of this work is to determine the modifications introduced by sepiolite (with or without biocide) to the behaviour of the new mortars subjected to acid solution attack. The tests were carried out in a salt spray cabinet with control of solution composition misting/fogging cycles and dry cycles (1).

The aggressive agent employed within the chambers is in aqueous solution, and thus, the reaction occurs relatively fast, at low pH conditions, according to the following scheme:

$$CaCO_3 = 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O.$$

The mortar binder ($CaCO_3$) will react with acid, forming free calcium ions in aqueous solution.

Experimental

The test were undertaken in mixed salt solution chambers (1). The specimens used were 3.5 cm cubes, prepared with sand/aggregate (relationship 3/1) and water/lime (relationship 0.9).

TABLE 1
Chemical analysis of lime, sand, and sepiolite.

	SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	SO_3	L.I.*	I.R.**
Sand	98.92	0.28	0.18	0.00	0.06	0.00	0.05	0.40
Lime	0.39	0.00	1.10	73.82	0.20	0.00	24.45	0.02
Sepiol.	55.10	19.43	5.91	5.13	1.96	0.00	12.02	0.10

* Loss of ignition at 1000°C
** Insoluble residue in HCl 1:5

TABLE 2
pH of the run-off after exposured in H_2SO_4.

Time (days)	M0	M5	M5*
0	4.5	4.5	4.5
21	7.8	7.6	7.1
50	n.d.	7.0	7.3
65	7.6	n.d.	7.4

n.d., not determined

In the case of the mortar with sepiolite, the water/(lime + sepiolite) ratio was 0.9. The exposure area was 17.5 cm^2 per sample.

The chemical analysis of the lime, sand, and sepiolite used in mortars preparation are given in Table 1.

The amount of biocide (pentachlorophenol) retained in sepiolite was about 1 g/100 g sepiolite. After preparation, the mortars were subjected to carbonation by CO_2 flow in a chamber at a relative humidity of 50% for 28 days. $Ca(OH)_2$ content in the mortar was then analysed (% $Ca(OH)_2 < 0.15$) by ethylene-glycol method (5).

Two specimens of each mortar were exposured in the chamber. The operation of the cabinet involved a wetting and drying cycle, typically 2 h spraying at ambient temperature 292 ± 2 K, followed by drying for 2 h using warm air at 313 ± 2 K. The exposure runs were running continuously for 65 days.

During the spray cycle, the simulated "acid rain" solution entered the chamber as a fine mist, with an average run-off rate of 1 L per cycle and 6 wet cycles and 6 dry cycles daily.

Collecting tubes and vessels were arranged beneath the samples to collect solution running off the surface of the mortars.

The mortar with 0% of sepiolite is called M0, the mortar with 5% of sepiolite is called M5, and the mortar with 5% of sepiolite plus biocide is called M5*. Preparation of sepiolite plus biocide has been specified previously (6).

The acid solutions used in wet cycles were: 1) H_2SO_4 solution of pH = 4.5; and 2) "acid rain" solution with the following composition: H_2SO_4 (98%) 31.85 mg/L; $(NH_4)_2SO_4$ 46.20 mg/L; Na_2SO_4 31.95 mg/L; HNO_3 (70%) 15.75 mg/L; $NaNO_3$ 21.25 mg/L; NaCl 84.83

TABLE 3
Cumulative Ca^{2+} in run-off ($mg\ Ca^{2+}/g$ sample).

	mg Ca^{2+}/g sample		
Time (days)	M0	M5	M5*
21	25.8	17.1	16.6
50	n.d.	34.7	24.9
65	35.3	63.2	37.2

n.d., not determined

TABLE 4
Cumulative concentration of Mg^{2+}.

	mg Mg^{2+}/g sample		
Time (days)	M0	M5	M5*
21	0.1	0.1	0.1
50	n.d.	0.2	0.1
65	0.5	0.6	0.3

n.d., not determined

mg/L; with the pH adjusted to 3.5 with $NaHCO_3$. The concentration of this solution is 10 times that found in Manchester "acid rain," with a pH one unit lower (7).

The following analysis were performed: 1) for the run-off solution, pH was measured, and Ca^{2+} and Mg^{2+} concentrations, were determined by atomic absorption; and 2) retained salts were extracted in water and $SO_4{}^{2-}$ and $NO_3{}^{-}$ analysed by high-pressure liquid chromatography. Those salts retained in 1 g of sample were extracted in 100 cc of deionized water.

Results

Results obtained separately in each of the aggressive solutions are presented.

H_2SO_4 Medium with pH = 4.5

The run-off was collected at 21, 50, and 65 days of exposure, which pH and Ca^{2+} and Mg^{2+} concentrations determined.

Run-off pH. The pH measurement of the run-off solutions are shown in Table 2, revealing after exposured that the run-off solution pH had a value nearest to 7.5, which remained practically constant through the test.

Ca^{2+} and Mg^{2+} concentrations in the run-off. Table 3 shows the cumulative concentrations Ca^{2+} in the run-off. Over 21 days the Ca^{2+} concentration present in the run-off is similar for all three mortars with values between 35–37 mg Ca^{2+}/g sample. However, for the mortar with 5% of sepiolite, the amount of Ca^{2+} in the run-off over the period test is about 63 mg Ca^{2+}/g sample, almost two times higher than for mortar without sepiolite and with sepiolite plus biocide.

TABLE 5
Extracted sulphates in H_2SO_4.

Sample	[$SO_4{}^{2-}$] (mg/g sample)
M0	0.1
M5	1.0
M5*	0.7

TABLE 6
pH in "acid rain" solution.

Time (days)	M0	M5	M5*
0	3.5	3.5	3.5
5	n.d.	7.6	7.6
14	7.3	7.5	7.3
65	5.7	5.1	2.7

n.d., not determined

The cumulative concentration of Mg^{2+} are shown in Table 4. These concentrations are relatively low, not exceeding 0.6 mg Mg^{2+}/g sample after 65 days exposure.

Retained salts. Concentrations of sulphate extracted in water are shown in Table 5, the values being relatively low, less than 0.1 mg SO_4^{2-}/g sample in every cases. Further, the extracted sulphate concentration are not influenced by addition of sepiolite and sepiolite plus biocide.

"Acid Rain" Medium pH = 3.5

For tests undertaken with "acid rain" solution, the run-off was collected at 5, 14, and 65 days, and the pH, Ca^{2+}, and Mg^{2+} concentrations were determined.

Run-off pH. The pH value increased for the initial "acid rain" solution value from 3.5 to close to 7.5 for the early exposures; with longer exposures, the run-off solution decreased particularly for M5* mortar with a final value of 2.7 (Table 6). M5 and M0 mortars had final run-off pH values between 5 and 6.

Ca^{2+} and Mg^{2+} concentration in the run-off. Cumulative calcium concentration in the run-off at 5, 14, and 65 days are given in Table 7, which shows that the calcium concentration increases with exposure time for all the mortars. Ca^{2+} concentration for the mortar with sepiolite plus biocide, increases to a lower degree than the other two mortars without biocide (M0 and M5). At the end of the exposure, Ca^{2+} concentrations present in the run-off for mortar M5* were almost half those for the other two mortars (M0 and M5).

With regard to Mg^{2+} concentrations, for M5 mortar the value in the run-off is 0.1 mg

TABLE 7
Cumulative Ca^{2+} in run-off.

	mg Ca^{2+}/g sample		
Time (days)	M0	M5	M5*
5	n.d.	27.3	15.2
14	18.9	53.0	26.1
65	64.0	81.5	29.0

n.d., not determined

TABLE 8
Cumulative magnesium concentration in the run-off.

	mg Mg^{2+}/g sample		
Time (days)	M0	M5	M5*
5	n.d.	n.d.	0.4
14	0.6	0.0	0.5
65	0.4	0.1	0.6

n.d., not determined

Mg^{2+}/g sample, while for M0 and M5* mortars values close to 0.5 mg Mg^{2+}/g sample are evident throughout the test (Table 8).

As in the former medium, Mg^{2+} concentration is very low in all cases, lower than 1 mg Mg^{2+}/g sample for all mortars.

Retained salts. Extracted anion concentration in the mortars exposed to “acid rain” solution are shown in Table 9. Sulphate levels are below 0.005 ppm for all mortars and remains approximately constant independent of mortar type.

Similarly, low nitrate concentrations below 0.005 ppm are revealed, independent of sepiolite or sepiolite plus biocide addition.

Discussion

The attack of the acid solution on the mortar binder produce Ca^{2+} ions, therefore the amount of this ion inform2 us about the mortar behaviour. If the acid solution attacks the sepiolite, Mg^{2+} ions in the run-off will be detected.

The discussion of the results obtained for both aggressive solutions are described below.

H_2SO_4 Medium with pH = 4.5

The pH of the run-off increases from 4.5 to 7.8 (Table 1), remaining approximately constant throughout the exposure and indicating that reaction [1] between calcium carbonate from mortar and the aggressive solution occurred. This is confirmed because calcium content in the run-off increased, as is shown in Table 2. However, sepiolite presence does not seem to affect the pH of the run-off that is in the values in which $CO_3^{2-}/HCO_3^{-}/H_2CO_3$ equilibrium occurs.

TABLE 9
Extracted anions in “acid rain” medium.

Sample	$[NO_3^-]$ (mg/g sample)	$[SO_4^{2-}]$ (mg/g sample)
M0	0.03	0.01
M5	0.03	0.03
M5*	0.04	0.03

From cumulative Ca^{2+} in run-off, the presence of sepiolite in the mortar increases the reaction between acid solution and lime mortar. However, for mortar with both sepiolite and biocide this reaction is inhibited.

Sepiolite does not modify the porous structure of the mortar, at least, in the porosity accessible to water (4). However, because of its adsorption/desorption properties, it modifies the mortar hydric behaviour (8), retaining more acid solution in each cycle, and, thus, accelerating the $CaCO_3$ dissolution (mortar binder). Also, sepiolite with retained pentachlorophenol inhibits this effect due to zeolitic channels occupation or due to the hydrophobic character of the biocide.

Mg^{2+} levels in the run-off are low (Table 4) and practically independent of sepiolite presence in the mortar, even the run-off of the mortar without sepiolite has similar Mg^{2+} concentrations. Moreover, the sand has 0.17% of Mg^{2+} (about 9 mg Mg^{2+}/g sample) and this could also be reacting with the acid. If all the sepiolite present in the mortar (5%) is attacked, then about 1% Mg^{2+} (almost 10 mg Mg^{2+}/g sample) will be present in the solution. The values in Table 4 suggest that the reaction between sepiolite and acid solution is a slight one.

Retained sulphate analysed in the three mortars is very low, suggesting most of the salts formed (presumably gypsum) were removed in the run-off. Moreover, after exposure the samples were analysed by x-ray diffraction (XRD) and infrared (IR) but no evidence of sulphates was found. Calcium sulphate dihydrate solubility in water is very low (0.24 g/100 cc), but according to the data presented here most of the formed salts were removed into the run-off.

“Acid Rain” Medium pH = 3.5

The pH of the run-off (Table 6), increases initially and later decreases, reaching the pH value of the initial solution (pH = 3.5), indicating that reaction [1] occurs in a decreasing way. Similar results have been obtained by other authors (9–11) for petreum materials such as limestone, marbles, etc., in which an initial increase of pH is observed that then decreases until, at the end of the test, the value is close to the initial one.

In the case of M5 and M0 mortars, the pH decreases (in a lower range than M5*), although Ca^{2+} concentration increases with time (Tables 6 and 7). Mg^{2+} contents in the run-off are low, not greater than 0.6 mg Mg^{2+}/g sample, confirming sepiolite stability on these aggressive environments (Table 8).

At the end of the test, the pH of the run-off in M5* mortar (sepiolite + C_6Cl_5OH) was close to the initial value (as it is seen in Table 6), indicating that reaction was inhibited in this medium. This was confirmed by calcium analysis in the run-off, in which, Ca^{2+} concentration remains constant from 12 until 65 days (Table 7).

In order to understand the influence of pentachlorophenol in this behaviour, another test was carried out.

First, 0.1 g of sepiolite with biocide retained was placed in 50 mL of “acid rain” solution; as well as lime mortar with sepiolite plus biocide. Furthermore, 0.1 g of pentachlorophenol was added to 50 mL of the same “acid rain” solution and used like a blank. In this test, the solution was not spray; therefore, the samples were in contact with the solution.

After 11 and 60 days, the solid was removed by filtration and the filtrate was extracted with diethylether (3 × 10 mL) and ethylacetate (3 × 10 mL). The combined organic extracts were then analysed by thin layer chromatography (TLC) in silica gel.

In the first solution, when the biocide was supported in the sepiolite, after 11 days of exposure in "acid rain" solution no organic compound was extracted. However, when the exposure time was 60 days, a small amount of one organic compound was extracted.

Therefore, after 11 and 60 days the same organic compound was extracted from the filtrate of the "acid rain" solution coming from the lime mortar with sepiolite plus biocide. Moreover, the extracted amount of the organic compound after 60 days was slightly greater than after 11 days.

The study of the combined organic extracts by TLC using different system solvents revealed that the only organic compound present in the solution was unaltered pentachlorophenol.

The pH of the pentachlorophenol in "acid rain" solution is 2.7; therefore if only pentachlorophenol was presence in the solution, the decrease in the pH run-off is due to the presence of this organic compound.

With regards to extracted salts (Table 9), nitrate and sulphate concentrations are very low. Moreover, XRD and IR of the samples after 65 days exposure did not reveal any sulphates or nitrates. According to this data, most of the salts formed are not retained in the mortar.

Conclusions

In both aggressive media, damage is produced mainly via $CaCO_3$ dissolution, in the mortar binder, and not on sepiolite or sepiolite plus biocide. The clay protection effect on pentachlorophenol is maintained over 65 days of mortar exposure in the studied environments.

Most of the salts formed are removed in the run-off and not retained in the mortar.

In the H_2SO_4 medium, reaction is maintained over the test, whereas it becomes retarded at 15 days when "acid rain" is the aggressive solution.

In mortars subjected to H_2SO_4 solution chambers, mortars without sepiolite and with 5% of sepiolite plus biocide exhibited similar behaviour; however, the latter are more resistant to H_2SO_4 solution attack.

Mortars exposed to "acid rain" initially present similar behaviour to mortars exposed to H_2SO_4 solution, but at 15 days, the attack reaction decreases, mainly for the mortar with sepiolite plus biocide.

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