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CORROSION RESISTANCE OF CEMENT MORTARS CONTAINING SPENT CATALYST OF FLUIDIZED BED CRACKING (FBCC) AS AN ADDITIVE

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Abstract

The chemical corrosion and the mechanical strength were studied in cement mortars containing an additive of FBCC under conditions of long-term action of sodium sulphate solution or saturated brine. The observations have shown that saturated brine is a more aggressive agent, since it leaches $Ca(OH)_2$ and contributes to the decomposition of the C–S–H phase thus worsening the compressive strength as compared with that of mortars kept in water. The addition of 20% FBCC inhibits the leaching process and counteracts the decrease of compressive strength in mortars kept in brine. On the other hand, sodium sulphate solution changes favourably the mortar microstructure, increases of the content of small pores and improves both the compressive and the flexural strengths, as compared with those of a mortar kept in water.

Keywords: chemical corrosion, pozzolana, spent catalyst

Introduction

The spent catalyst of catalytic cracking in fluidized bed (FBCC) is a zeolitic material with aluminosilicate structure. Owing to the high content of oxides (more than 90% of SiO_2+Al_2O_3+Fe_2O_3) and high degree of dispersion it can act as a pozzolana microfiller in cement [1–7]. Like in the naturally occurring pozzolana, which is a crystalline zeolite, the action of the spent catalyst consists probably in its dissolving in the cement slurry. The process of $Ca(OH)_2$ binding from the liquid phase proceeds very rapidly and the pozzolana is transformed into an alumino–silica gel [2]. The activity of FBCC depends mainly on its particle diameter and is practically independent of its specific surface [1]. If FBCC is added in excessive amounts to the cement system, its conversion is not complete and the coarsest particles remain in the form of spherical

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inclusions in the material [2]. If the pozzolanic activity of the FBCC added and the amount introduced to the cement material are sufficiently high, the extra amount of the secondary C–S–H phase and of the hydrated aluminate phases produced in the pozzolanic reaction densifies the structure of the cement material [2, 3]. It should also increase the resistance to chemical corrosion in any medium as well as the mechanical strength after a long-term storage in aggressive media.

Essentially, the action of sodium sulphate solutions on cement mortars containing FBCC consists in its reaction with $Ca(OH)_2$ remaining after the reaction with pozzolana. The reaction proceeds according to the following scheme to give gypsum as the main product:

$$Ca(OH)_2+Na_2SO_4+2H_2O\rightarrow CaSO_4\cdot 2H_2O+2NaOH$$

The gypsum formed can then react with aluminium-containing salts to form ettringite and calcium monosulfoaluminate. The addition of FBCC rich in aluminium compounds may then influence unfavourably the resistance to corrosion in sulphate media. At a high concentration of SO_4^{2-} ions and when pH of the liquid in the pores of the mortar falls down to 11.5, ettringite can undergo conversion to gypsum [8]. As for the existence of stable gypsum phase the equilibrium in the system $CaO–Al_2O_3–SO_3–H_2O$ requires relatively high concentrations of Ca^{2+} and SO_4^{2-} ions, hence gypsum cannot be formed as only in places where the concentration of Ca^{2+} is sufficiently high, i.e. in the deep layers of the material [9]. Besides, the reactions of formation of gypsum and ettringite are accompanied by the reaction of $Ca(OH)_2$ with atmospheric CO_2 to form $CaCO_3$. In the opinion of Rendel and Jauberthie [10] this reaction even has a priority to the reactions of formation of gypsum and ettringite. For this reason the analyses of cement material may sometimes not reveal the presence of ettringite, or even of gypsum, and just calcite may be present instead.

The extent and intensity of corrosion effects due to the presence of chloride media depend on their kind and concentration. In the opinion of Gruener [11] pure NaCl is harmless for concrete, but its solutions can affect the material and highly concentrated NaCl solutions are even capable of leaching cement stone. Of course, such situations are likely to occur in saturated brine media.

The aim of the present study was to determine, how the long-term action of sodium sulphate solution or saturated brine affects the chemical corrosion and the mechanical strength of cement mortars containing an addition of FBCC, used as a substitute of a part of the cement.

Experimental

The materials used in the experimental works were: Portland cement class CEM I 32.5R, FBCC with the content of oxide components $SiO_2+Al_2O_3+Fe_2O_3$ exceeding 90%, mean particle size 21 μm, and specific surface exceeding 100 $m^2 g^{-1}$, and quartz sand conforming to Polish Standards [12].

In the mortars FBCC was used to replace 0, 10 or 20% by mass of cement. The ratio of water/binder was 0.5, and that of sand/binder was 3. The mortar samples dimensions 4×4×16 cm were poured into battery moulds and compacted on a vibrator according to PN-85/B-04500 [13] and PN-EN 196-1 [14]. After 28 days of curing in water a part of the samples was transferred to aggressive media, in which they were then stored for 8 months, and the other part was left to be kept in water. Neither the aggressive media nor water was changed during the exposure, only the part of water lost by evaporation was refilled. All the samples were stored in containers covered with a polyethylene foil. The aggressive media used were:

- sodium sulphate solution of concentration 1250 mg SO_4^{2-} dm^{-3},
- saturated brine (NaCl 225 g dm^{-3} and $MgCl_2{\cdot}6H_2O$ 25 g dm^{-3}).

The samples for the measurements were taken after 8 months of keeping in water or in aggressive media.

The thermogravimetric curves and the infrared spectra of mortars were recorded using powdered samples ground down to particle size below 0.38 mm, from which coarser sand grains were separated. The samples were taken from the surface layer of the mortars exposed to the action of the aggressive media or water and, for the sake of comparison, from the middle of the beams. Besides, for the sake of comparison, similar studies were performed for mortar samples kept for 28 days in water and for individual components used for preparing the mortars: cement, FBCC, and sand. The thermal studies were carried out on 150 mg samples by means of a Derivatograph C (Hungary) instrument in the temperature range 20–1000°C in air atmosphere. The IR spectra were recorded by means of Specord 75 IR (Carl Zeiss, Germany) [12].

The phase composition of the surface layers of the mortars was determined by X-ray diffraction measurements in an HZG-4C instrument. CuK_α radiation was employed.

The change in mass of the mortars was determined, in triplicate, for samples saturated with water or with corrosive solutions, after surface drying, with respect to 28-day old mortars.

The microstructure of the mortars was determined by the method of Hg porosimetry using an Autopore instrument and several gram samples taken from the surface layer. Prior to the measurement the samples were dried under high vacuum at room temperature.

The content of calcium ions in the solutions, in which the mortars were kept for 8 months, was determined by the versenate method [15]. The results were calculated per kg of the mortar mass.

The mechanical strength of the surface dried saturated mortars was measured in conformity with the Polish Standard PN-EN 196-1 [14], using at least 3 specimens in flexural strength tests and not less than 6 specimens in compressive strength tests. In both types of the tests mean values ($\overline{R}$) and confidence interval (ΔR) were determined at the confidence level of 0.95.

Discussion of results

Some results of the thermal studies have been shown in Fig. 1. The TG curves were used for evaluating the amount of calcium hydroxide in the mortars from the mass sample loss at about 500°C, corresponding to the decomposition of $Ca(OH)_2$ (Fig. 2).

The thermogravimetric curves of the cement mortars stored in water confirm the loss of $Ca(OH)_2$ due to the decrease of the cement content in the system, as well as due to the pozzolanic reaction with FBCC. This fact is evidenced by the decrease of the peak of $Ca(OH)_2$ decomposition with increasing content of FBCC (compare the DTG and DTA curves in Fig. 1, Ia). Similar phenomena were observed during the examination of other pozzolanic materials [18].

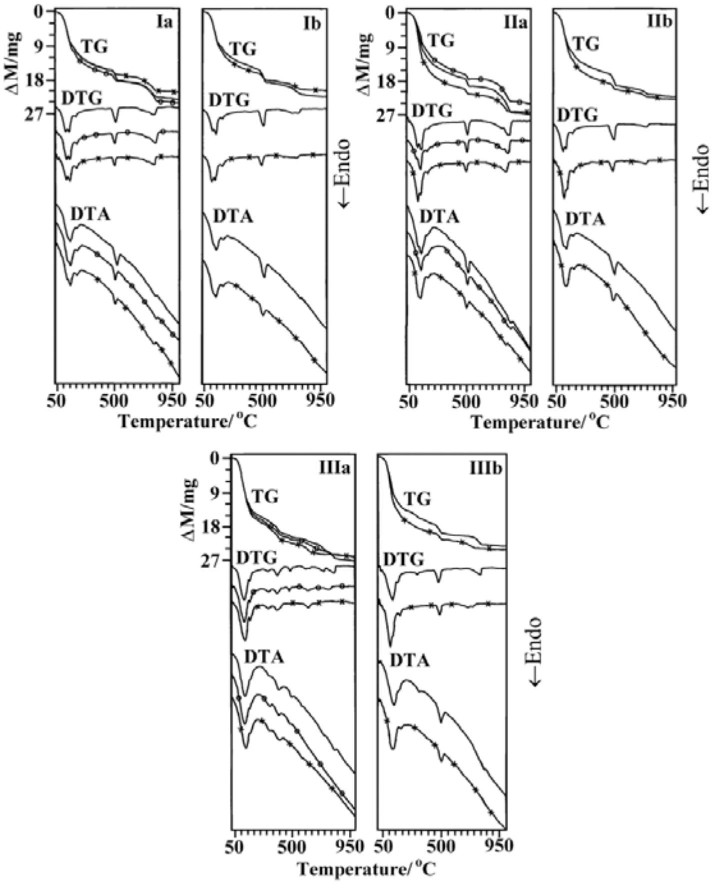

Fig. 1 Comparison of TG, DTG and DTA curves of a – surface layers and of b – the interior of cement mortars kept for 8 months in water (I), sodium sulphate solution (II) or brine (III) after 28 days of curing in water. ----- 0% FBCC, o o o 10% FBCC, ∗ ∗ ∗ 20% FBCC

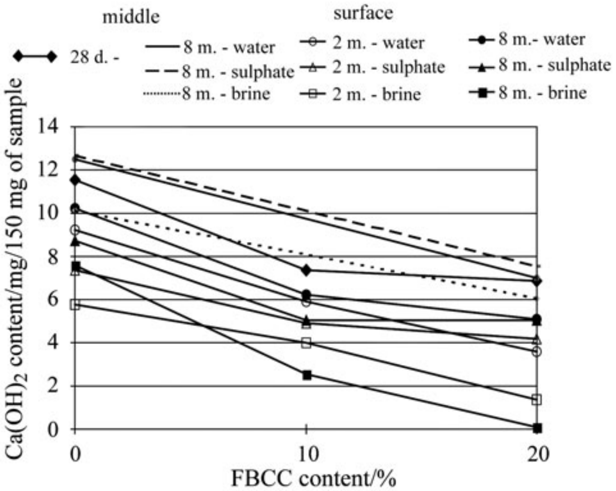

Fig. 2 Comparison of $Ca(OH)_2$ contents in cement mortars cured for 28 days in water and then kept for 2 months [12] or for 8 months in water, sodium sulphate solution, or brine

On the other hand, the endothermic effect observed at about 200°C, suggests the presence of aluminate phases that may have been produced in the pozzolanic reaction and may have a bearing on the intensity of the sulphate corrosion. The presence of the peaks observed at temperatures above 700°C may be accounted for the presence of carbonates in the surface layer. The higher endothermic effect on the DTA curve at a temperature about 500°C, observed in the core sample, as compared with that from the surface layer (Fig. 1, Ia and Ib) shows, that the 8-month action of water results in a decrease of $Ca(OH)_2$ from the surface layer of the mortars due to the formation of carbonates and the leaching processes.

The TG curves of the surface layer of samples, hydrated up to 8 months in sulphate medium, are similar to those of the mortars kept in water. Some differences are observed, however, in mass losses in individual stages of the decomposition at 170°C and above 700°C (Fig. 1, IIa, IIb). At temperatures below 170°C the increase in the sample mass loss, particularly for the mortar with 20% addition of FBCC, may be probably due to the action of sulphate ions on the paste components in cement mortars and formation of gypsum and ettringite. The considerable effect of mortar mass loss at temperatures above 700°C is probably due to the decomposition of calcium carbonate, which is formed along with other products of the sulphate corrosion.

The TG curves of mortars kept for 8 months in saturated brine medium differed widely from the curves obtained for analogous samples kept in the other media. The first difference to be mentioned is the absence of two distinct effects of mass loss at temperatures below 170°C, which has been replaced by a single broad effect with a maximum 150°C. It may be accounted for the superposition of the effects due to the decomposition of cement hydration products and of calcium and magnesium chloride hydrates. A small intensity of the effect due to the decomposition of $Ca(OH)_2$ is also seen on the curves. The decrease of this effect may be due to the leaching of $Ca(OH)_2$ from the surface layer or of its exhausting in formation of Friedel salt. The occurrence of additional peaks on the DTA curves at temperatures 325 about 400, and about 650°C may be due to thermal decomposition of the formerly formed Friedel salt [16] and other corrosion products (Fig. 1, IIIa). It is also interesting to note the presence of an endothermic effect at about 325°C on the DTA curve of the core sample of the mortar containing no additive, connected with the thermal decomposition of chlorine compounds. This fact shows that the depth of chloride penetration in this mortar is greater than that observed in the mortar containing a 20% addition of FBCC. The presence of a double peak above 700°C, observed in the mortars containing no FBCC, may probably be explained by the presence of $MgCO_3$ along with $CaCO_3$. On the other hand, the practical absence of this peak in the mortars containing 20% of FBCC may be accounted for the absence of these two salts.

An analysis of the differences in the contents of $Ca(OH)_2$ in the surface layers of the mortars after 8-month contact in any of the media tested and, for the sake of comparison, in the core (Fig. 2) shows the strong leaching properties of the brine and much weaker leaching activity of the other media. Comparing the contents of $Ca(OH)_2$ in the mortars kept for only 2 months in the same media shows that brine is the main medium responsible for the $Ca(OH)_2$ exhaustion during the next 6 months of the exposure.

The results of the thermogravimetric studies have confirmed the statement that saturated brine is the strongest aggressive medium responsible for the leaching of $Ca(OH)_2$ and formation of complexes of the Friedel salt type. Sodium sulphate solutions give only a small loss of $Ca(OH)_2$ from the surface of the mortars owing to the reaction of gypsum formation. Also the leaching action of water on $Ca(OH)_2$ is not of importance. The natural curing and corrosion processes are accompanied by the carbonation reaction.

Some examples of infrared spectra of cement mortars containing a 20% addition of FBCC and of control samples are shown in Fig. 3. An analysis of the shape of the IR spectra reveals practically only the differences in intensity of the band in excess of 3650 cm^{-1} which are due to the different $Ca(OH)_2$ contents in the systems. In the case of the mortars exposed to the action of brine the occurrence of an additional band was observed at 3700 cm^{-1}, as characteristic for the presence of hydrated chlorides. No clear bands owing to gypsum were observed in the mortars kept in the sulphate solutions, probably owing to the small contents of gypsum in the samples or masking of its bands by the broad absorption band of SiO_2 present in the sand.

Figure 4 shows some examples of X-ray diffraction patterns of mortars kept in water or in aggressive media. The crystalline phases occurring in the mortars include calcium silicates, $CaCO_3$, $Ca(OH)_2$, calcium carbonate aluminates, and NaCl. It is worth mentioning that no gypsum or ettringite was found in both mortars kept in aqueous solutions of Na_2SO_4, but crystalline NaCl is present in the sample exposed to brine and $CaCO_3$ occurs in all the samples studied.

An analysis of the X-ray diffraction patterns shows that the presence of gypsum and ettringite, detected by thermal analysis, has not been confirmed. The reasons may lay in the insufficiently formed crystalline structure or too small amount of the miner-

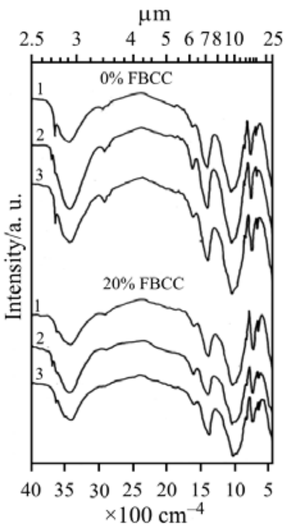

Fig. 3 Comparison of IR spectra of the surface layers of cement mortar containing 20% additions of FBCC and control mortar kept, after 28-day curing in water, for 8 months in 1 – water, 2 – brine 3 – sodium sulphate solution

als present and, in the case of gypsum, also another location of this mineral [9]. The presence of NaCl in the mortars kept in the brine medium allows to suppose that in this case a physical corrosion due to the crystallisation of this salt at certain deeper layers of the cement material can occur. This fact has already been confirmed in our former studies of the concrete containing no FBCC, where an 8-month contact with brine resulted in scaling of the surface layer [16]. The phenomenon did not occur in a concrete containing a 20% addition of FBCC. The presence of $CaCO_3$ in all the mortars studied enables to assume that a part of the loss of $Ca(OH)_2$, supposed to be due to the leaching process, may result from the reaction with atmospheric CO_2.

Table 1 Average mass increase of mortars kept for 8 months in water and in aggressive media in relation to the mass after 28 days of curing. The content of calcium ions determined in the solutions after the removal of mortar samples

FBCC content/mass%	Environment	Mass gain/%	Ca^{2+} content/g kg^{-1}
0	water	0.84	0.012
	sulphate	0.58	0.011
	brine	2.03	2.35
10	water	0.81	0.007
	sulphate	0.86	–
	brine	1.20	0.77
20	water	0.49	0.019
	sulphate	0.50	0.023
	brine	1.17	1.12

Table 2 Microstructure parameters of surface layers of CEM I mortars containing 20% addition of FBCC and of control mortars, kept for 8 months in various media after 28 days of curing in water

FBBC content/ mass%	Medium	Pore volume/ mL g^{-1}	Specific surface/ m^2 g^{-1}	Average pore diameter/ μm	Content of pores <0.02 μm/ %
0	water	0.0627	13.197	0.0190	27.7
	sulphate	0.0601	14.243	0.0169	32.7
	brine	0.0656	9.126	0.0288	21.1
20	water	0.0733	19.505	0.0150	47.7
	sulphate	0.0753	19.880	0.0151	47.5
	brine	0.0684	13.695	0.0200	30.9

The increase in the mass of mortars saturated with water or with aggressive solutions, as well as the results of leaching calcium ions by all the media tested have been collected in Table 1, and the microstructure parameters of the mortars both containing a 20% addition of FBCC and those containing no additive are shown in Table 2. It seemed reasonable to admit that the content of the pores of diameter below 0.02 μm may be a measure of the quantity of small pores, connected indirectly with the content of the C–S–H phase, which might have been formed in the pozzolanic reaction and then partially destroyed in contact with aggressive media. The assumed pore size relates to the lower limit of the capillary pores. It may easily be determined by the Hg porosimetry and thus it may be used for monitoring the changes in the mortar structure. This range of the pore diameter was formerly used for monitoring the corrosion changes due to the action of sulphates [17].

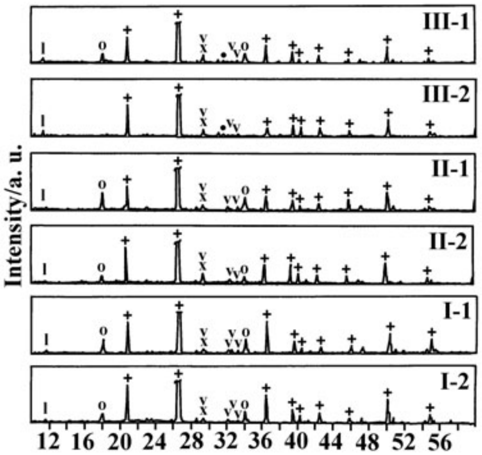

Fig. 4 Comparison of X-ray diffraction patterns of cement mortars kept for 8 months I – in water, II – in sulphate solution and III – in brine. 1 – 0% FBCC, 2 – 20% FBCC. Phase symbols: v – calcium silicates, × – $CaCO_3$, | - calcium carbonate aluminates, o – $Ca(OH)_2$, ● – NaCl, + – SiO_2

An analysis of the included data shows that the microstructure of the mortars, the mass increase related to that of the 28-day old mortars, and the extent of the leaching processes depend largely on the medium applied and on the use of the FBCC additive.

Water medium

An addition of 20% FBCC increases the total pore volume of the mortars with simultaneous increase of the specific surface; as a result the content of fine pores of diameter below 0.02 μm increases by about 20%. This is also confirmed by the mass increase, which is smaller than that observed for the mortars containing no additive. The small concentration of calcium ions shows that the leaching processes are of lesser significance in mortars kept in water (Table 1).

Sulphate solution medium

Owing to the action of sodium sulphate solution the mortars are generally more watertight, as compared with those stored in water. The effect is either due to the decrease of total pore volume (in mortars containing no additive) or due to increase of the content of fine pores (mortars containing 20% FBCC). The compacting action of sodium sulphate is also confirmed by the trend observed in the mass changes. The leaching processes observed in sulphate solutions are similar to those observed in water (Table 1).

Brine medium

As a result of the action of saturated brine the watertightness of the mortars decreases with respect to that of the mortars stored in water. The process is just contrary to that observed in the sulphate medium; the action of the brine results either in an increase of the total pore volume or in a strong decrease of the content of fine pores. However, owing to the presence of 20% FBCC, the content of fine pores is still rather high and is comparable with that in the mortars containing no additive, while stored in water. The considerable decrease of watertightness of the mortars stored in brine and the favourable effect of the presence of FBCC are also confirmed by the mass increase of the mortars, which also confirm the intensive leaching of $Ca(OH)_2$ and the high concentration of Ca^{2+} ions in the brine (Table 1).

A complex analysis of the obtained data shows that an addition of an active pozzolana as represented by the zeolitic FBCC of mean particle size 21 μm results in a natural increase of the specific surface and an increase of fine pores formed due to the deposition of an additional amount of secondary C–S–H phase and hydrated calcium aluminates inside the coarser pores, despite of the cement loss in the mortars. It is possible to state that the loss of cement is largely compensated by the presence of FBCC. The compensation is not complete, however, since the average compressive strength $\overline{R}_c$ remains lower than that in the mortars containing no additive (Table 4). The increase of the mean flexural and compressive strengths of the 9-month old mortars kept in water, as compared to those of the 28-day old mortars, is easy to understand, since the cement hydration processes in these mortars are continued with simultaneous formation of $Ca(OH)_2$, and exhaustion of it in production of a secondary C–S–H phase. The smaller increase in strength of the 20% FBCC mortar, as compared with the control, during the 8-month contact with water, confirms the role of FBCC in the formation of its early strength, as described formerly [5].

Table 3 Flexural strength ($\overline{R}_f \pm \Delta R$) of CEM I mortars containing various amounts of FBCC after 28 days of curing in water and 8 months of contact with different aggressive media

FBCC/mass%	28 days in water	8 months in		
		water	sulphate	brine
0	6.52±1.01	8.87±0.23	8.70±0.78	6.90±0.56
10	6.96±1.52	8.61±0.53	10.3±0.43	10.6±0.50
20	6.93±0.70	8.88±0.47	9.97±0.50	10.2±0.91

The microstructure of the mortars changes under the action of the aggressive media. In sulphate solution of moderately high concentration the microstructure becomes more tight and, in consequence, both the flexural and the compressive strengths of the mortar increase as compared with those observed in the water medium (Tables 3 and 4). If a mortar contains an extra amount of $Ca(OH)_2$, as is the case in the mortar containing no FBCC, an exposure to the action of sulphates generally leads to a decrease of the pore volume and a strong increase of fine capillary pores formed as a consequence of accumulation of corrosion products inside the coarse pores. Much smaller changes in the structure of the material are observed in the case of a smaller availability of $Ca(OH)_2$ (the mortar containing 20% of FBCC).

Table 4 Compressive strength ($\overline{R}_c \pm \Delta R$) of CEM I mortars containing various amounts of FBCC after 28 days of curing in water and 8 months of contact with different aggressive media

FBCC content/mass%	28 days in water	8 months in		
		water	sulphate	brine
0	39.3±1.25	53.7±2.7	55.5±2.1	30.6±2.9
10	30.1±4.98	50.9±4.6	53.3±2.3	24.4±2.6
20	38.4±3.43	47.6±2.4	54.3±2.8	41.7±2.4

In the brine medium the structure of the mortar becomes less tight and thus its compressive strength decreases, with only a small increase of the flexural strength (Tables 3 and 4). The different trends in the changes of these strengths may be accounted for the different mechanisms of the destructive processes in the materials relative to the other media. The brine contributes to the leaching of calcium hydroxide, associated with decomposition of the C–S–H phase, as evidenced by a considerable decrease of the content of fine pores of diameter below 0.02 μm and simultaneous increase of porosity in the mortar containing no FBCC. The very unfavourable changes in the microstructure of the mortars are so drastic that the compressive strength of the 9-month mortars falls down to that of the 28-day old samples. In the mortar containing a 20% addition of FBCC, where the strength does not decrease so much as that of the mortar containing no additive, the process of decomposition of the C–S–H phase can proceed in parallel with deposition of the corrosion products inside the pores and thus it can contribute to the decrease of the total pore volume. In the medium of brine reveals the favourable effect of a 20% addition of FBCC, which gives a 48% increase of $\overline{R}_f$ and a 36% increase of $\overline{R}_c$, as compared with a mortar containing no additive kept under identical conditions.

Conclusions

- Thermogravimetric, IR spectroscopy, X-ray diffraction, and Hg porosimetry studies of cement mortars containing 20% addition of FBCC, kept for 9 months in water, confirm the pozzolanic properties of that additive, but also the occurrence of carbonation process accompanied by leaching.
- A long-term storage of the mortars, containing FBCC, in aqueous solutions containing 1250 mg SO_4^{2-} dm^{-3} confirms the occurrence of corrosion processes. A small decrease of $Ca(OH)_2$ in the sulphate medium is mainly due to its reaction with SO_4^{2-} ions and CO_2, the leaching being of lesser importance. The microstructure of the mortars becomes more watertight.
- A long-term storage of the mortars, containing FBCC, in saturated brine, also points to the occurrence of corrosion processes. A large decrease of the $Ca(OH)_2$ content is mainly due to leaching processes accompanied by the decomposition of the C–S–H phase and, to a lesser degree, formation of complex compounds of the type of Friedel salts and formation of $CaCO_3$ in the reaction with CO_2. These unfavourable processes are inhibited by addition of 20% by mass of FBCC.
- The changes in microstructure of the mortars subjected to the action of moderately concentrated sulphate media or of saturated brine are reflected mainly in the change of compressive strength. The sulphate medium gives a slight increase of strength of the mortars, whereas the action of brine reduces considerably the compressive strength. A 20% addition of FBCC has a favourable effect on compressive strength in the aggressive media.

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