Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 759–767

CEMENT AND CONCRETE RESEARCH

Influence of spent catalyst used for catalytic cracking in a fluidized bed on sulphate corrosion of cement mortars: I. Na_2SO_4 medium

Maria Bukowska[a,*], Barbara Pacewska[b], Iwona Wilińska[b]

[a]Institute of Civil Engineering, Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology at Płock, 09-400 Płock, ul. Łukasiewicza 17, Poland
[b]Institute of Chemistry, Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology at Płock, 09-400 Płock, ul. Łukasiewicza 17, Poland

Received 17 January 2002; accepted 4 August 2003

Abstract

The aim of the work was to determine the effect of spent catalytic cracking in a fluidized bed (FBCC), catalyst used for as a partial substitute for cement or sand, and of sodium sulphate solutions of concentration 16,000 or 52,000 mg SO_4^{2-}/dm^3 on the mechanism of sulphate corrosion and on expansion of mortars compacted according to prENV 196-10, as well as on mechanical strength of mortars compacted according to the Polish Standard PN-EN 196-1. The observations indicate that the sulphate corrosion of the mortars proceeds via at least two different mechanisms depending on the concentration of sodium sulphate solution and on the concentration and form of pozzolanic additive used. The extent of corrosion damage depends mainly on the concentration of the aggressive solution and on the degree of compaction of the mortar. No unequivocal correlation was found between the expansion of mortars compacted according to prENV 196-10 and the mechanical strength of mortars compacted according to PN-EN 196-1. The greatest expansion was observed in mortars, which did not exhibit the lowest compressive strength. Therefore, it is questionable to use the measure of elongation, particularly in poorly compacted mortar samples, as the sole standard method for determining resistance to sulphate corrosion in sodium sulphate media.

Keywords: Waste catalyst; Sulphate attack; Pozzolan

1. Introduction

Spent catalyst used for catalytic cracking in a fluidized bed (FBCC) is a material of relatively constant chemical composition, characterized by the presence of pozzolanic components, high specific surface (>100 m^2/g), and varying particle size (depending on its dwell time period in the process of catalytic cracking) [1–5]. In former researches, we have shown [3] that FBCC reacts with $Ca(OH)_2$ released in the process of cement hydration and densifies the structure of the cement paste. It has also been found that the pozzolanic properties of FBCC are a function of its grain size: the smaller the grain size, the higher the pozzolanic activity. In former work [2], finely ground FBCC, used as a substitute of a part of cement, was found to accelerate the binding of cement in the early stage of hydration. For strength enhancement, it is more effective to use FBCC as a partial substitute for sand and not as a partial substitute for cement since in the former case there is less limitation of the pozzolanic reaction. In another paper, it has been shown [4] that an increase in strength of mortars dosed with the spent catalyst used in greater amounts than that used in our experiments [3] may be achieved only with an optimal amount of FBCC used over a particular range of water to cement ratio. When FBCC is applied as a substitute for the finest aggregate fraction in an amount equal to 20% of the weight of cement, with simultaneous addition of plasticizers and superplasticizers, standard, high-, or very high-strength concretes can be obtained providing that the concrete mixtures have been properly designed and prepared and that good moist curing takes place during the first few days of hardening [6]. Thus, FBCC may serve as a valuable pozzolanic additive for cement mortars and concretes exposed to the action of nonaggressive media.

Generally, used pozzolanic additives in cementitious systems increases their corrosion resistance owing to the

---

* Corresponding author. Fax: +48-24-262-4226.
E-mail address: bukowska@pw.plock.pl (M. Bukowska).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2003.08.007

decrease in $Ca(OH)_2$ content, pore refinement, and increase of water tightness, thus impeding the penetration of aggressive media. This has been confirmed for chloride ingress in the case of concrete and cement mortars containing FBCC as a substitute for a part of the sand (concrete) or a part of the cement (mortar), which was exposed to saturated brine medium. FBCC reduced the penetration of chlorides and also reduced the negative effect of brine on mechanical strength [7]. However, the situation might be different in sulphate media.

Generally, the action of sodium sulphate leads to formation of gypsum [8]:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH \quad (1)$$

that can then react with calcium aluminate hydrates to form ettringite or calcium monosulfoaluminate. Addition of FBCC, which can contain more than 40% Al_2O_3, is associated with the formation of calcium aluminate hydrates in the course of the pozzolanic reaction [9,10]; thus, it can have a negative effect on the resistance to sulphate aggression. However, if the concentration of sulphate increases in excess of 3000 mg SO_4^{2-}/dm^3, ettringite is transformed to gypsum [11,12]. It might be expected therefore that in cases of very high concentration of SO_4^{2-} and if the cement material does not contain sufficiently large amounts Al_2O_3 necessary to form complex salts, considerable amounts of gypsum should be observed in the corrosion products. It should be pointed out that under conditions of high concentration of Na_2SO_4, a deficiency of $Ca(OH)_2$ remaining in equilibrium with the C-S-H phase and decrease of pH of the pore fluid may result in decomposition of C-S-H and its decalcification [13]. In the opinion of some authors [14], the lower resistance of cement materials containing pozzolana additives to the aggressive action of sulphate environment is due to the reduced contents of $Ca(OH)_2$ since calcium hydroxide supplies Ca^{2+} ions necessary for formation of gypsum to prevent the decomposition of the C-S-H phase. In cases where the pozzolana additive is used as a substitute of a part of cement, there is a twofold reduction of $Ca(OH)_2$ content in the cement material: from a decrease of cement and as a result of the pozzolanic reaction. Since in order for gypsum to be stable the equilibrium in the system CaO-Al_2O_3-SO_3-H_2O requires relatively high concentrations of both Ca^{2+} and SO_4^{2-} ions, the presence of gypsum may be expected in cases where the content of Ca^{2+} ions is sufficiently high [14]. It may occur, however, that in some parts of the surface of a cement material, the concentration of Ca^{2+} ions will not be high enough to form a stable gypsum phase despite a high concentration of the SO_4^{2-} ions. Such a situation may arise in cement mortars subjected to the action of highly concentrated solutions of sodium sulphate.

Sodium sulphate media can also give rise to flaking of the hard concrete surface in consequence of alternating transformations of anhydrous sodium sulphate (thenardite) into sodium sulphate decahydrate (mirabilite) and vice versa: mirabilite to thenardite. These transformations associated with changes in specific volume are favored by frequent cyclic wetting and drying of the concrete surface [15]. It is assumed that the formation of gypsum and ettringite is accompanied by 1.2- and 2.5-fold increase, respectively, of specific volume, while the crystallization of $Na_2SO_4 \cdot 10H_2O$ results in four- or fivefold increase of the specific volume [16].

The corrosion transformations occurring in cement materials under the action of sulphates are zonal in nature, i.e., the chemical composition, structure, and properties depend on the depth from the material surface. Also, the edges and the corners are exposed to stronger attack than are planar surfaces [13,14]. Depending on the corrosiveness of the sulphate medium, the surface of the corroded material can contain corrosion products such as gypsum, ettringite, and calcite [12]. Maximum amounts of gypsum can be found at a certain distance from the material surface, where they are responsible for bursting of the material, often observed, e.g., in Na_2SO_4 media. At greater depths, in the uncorroded core of the material, the original C-S-H phase may be present along with high contents of portlandite phase [12–14]. The distribution of $Ca(OH)_2$ concentration is sometimes used for determining the thickness of neutralized zone in the material [17].

Studies of the sulphate corrosion and of the resistance of cement materials to sulphate corrosion have been carried out using many different techniques. Besides the abovementioned studies on the corrosion mechanism, physical structure of the corroded materials, and physicochemical properties, many investigations have been carried out on their physical properties: the mechanical strength [16,18–20] and linear expansion [10,21]. At present, there is no standard direct method for determining the resistance of cement materials to the action of sulphates. An attempt has been made by the European Standard Committee, which set out the draft standard prENV 196-10 concerned with the determination of cement resistance to sulphates [21].

The aim of the current work was to study the effect of FBCC additive, used as a substitute for a part of either cement or sand, on the sulphate corrosion of cement mortars in sodium sulphate media of very high aggressive activity. Research has also been undertaken to establish if the method based on measurement of elongation set out in the Standard prENV 196-10 may be used for the evaluation of the strength of cement materials exposed to the action of sulphate media.

2. Experimental

2.1. Materials and sample preparation

The materials used in the experiments were cement CEM I 32,5R and FBCC characterized in Table 1, quartz sand, superplasticizer, and $Na_2SO_4 \cdot 10H_2O$. FBCC in amounts up

Table 1
Chemical composition and particle size of cement and FBCC

Parameter	CEM I 32,5R	FBCC
Chemical composition, %		
CaO	64.1	not specified
SiO_2	21.8	55.0
Al_2O_3	4.6	40.3
Fe_2O_3	2.2	0.52
SO_3	3.2	not specified
Average grain diameter, μm	not specified	76
Specific surface, m^2/g		127

to 20% with respect to cement was used as a substitute for either a part of the cement or a part of the sand. In the former case, the mortars were prepared in the following proportions: water/(cement + FBCC) = 0.5 and sand/(cement + FBCC) = 3. In the latter case, a superplasticizer was used and the proportions were as follows: water/cement = 0.5 and (sand + FBCC)/cement = 3. The recipes of the mortars are given in Table 2 and were identical with those used in a former paper [3].

Two kinds of samples were prepared:

◆ for mechanical strength tests—prismatic specimens dimensions 40 × 40 × 160 mm, strongly compacted according to Polish Standard PN-EN 196-1 [22] in two layers using 60 shocks per layer,

◆ for elongation tests—prismatic specimens dimensions 20 × 20 × 160 mm, with two stainless steel inserts cast into the ends, lightly compacted according to prENV 196-10 [21] with 10 shocks.

After a 24-h setting, the specimens were taken out of the moulds and immersed in tap water for 27 days. Following this time the samples were immersed for 3 months in: distilled water, Na_2SO_4 solution of concentration 16 000 mg SO_4^{2-}/dm^3 (samples NS 16), or Na_2SO_4 solution of concentration 52 000 mg SO_4^{2-}/dm^3 (samples NS 52). The aggressive solutions were changed every 2 weeks, and distilled water was added to replenish the evaporation losses. In order to determine the effect of long-term action of the corrosive media on the cement materials, some of the specimens were left for 10 months in the medium of NS 16 and some, for comparison purposes, in water; in this case, after 3 months storage, the aggressive solution was changed once a month, and water was refilled to eliminate the evaporation losses.

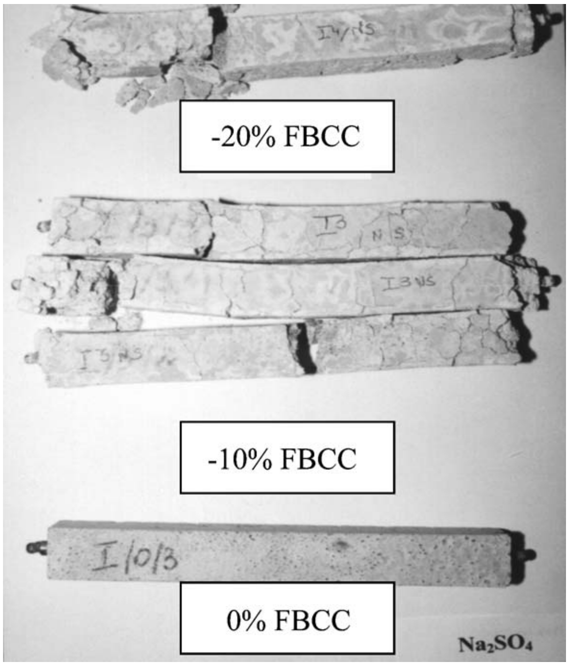

Fig. 1. Samples of lightly compacted mortars containing FBCC additive used as a substitute for a part of cement (− 10% and − 20%) stored for 3 months in NS 52; 0%—mortar with no additive.

2.2. Evaluation methods

The appearance of the samples was evaluated visually both when immersed (samples for strength tests and for elongation measurement) and after drying (samples for elongation measurement). Color photographs of corrosion damage were subjected to electronic processing and presented in various shades of grayness.

The thickness of the zone of reduced alkalinity of cement mortars was determined by sprinkling alcoholic solution of phenophthalein on a fresh fracture surface. Color photographs were again taken in various gray shades.

The change in mass was determined in triplicate for strongly compacted samples (conforming to the standard PN-EN 196-1), saturated with water or with corrosive solutions after surface drying with respect to 28-day-old mortars.

The porosity of the samples was determined by means of mercury porosimetry with the use of an AUTOPORE porosimeter for samples of mass 3–5 g taken from the surface of the strongly compacted mortars preliminarily evacuated under high vacuum at room temperature.

Table 2
Compositions of mortars containing FBCC added in place of a part of cement and in place of a part of sand [3]

Added FBCC	Content of FBCC, %	Cement, g	FBCC, g	Sand, g	Water, cm^3	Chemical admixtures, cm^3
Replaces a part of cement	0	450	0	1350	225	not added
	10	409.1	40.9			
	20	375	75			
Replaces a part of sand	0	450	0	1350	225	2.30
	10		45	1305		4.14
	20		90	1260		5.99

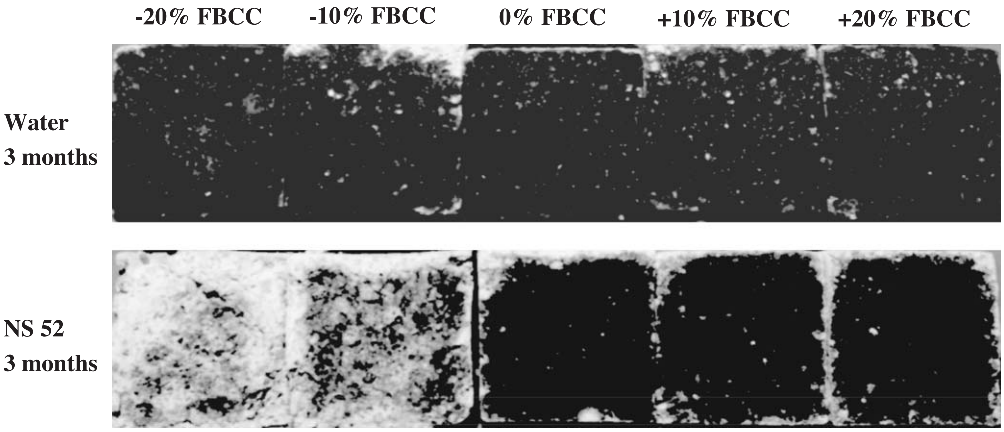

Fig. 2. Fractures of lightly compacted mortars containing FBCC as substitute for a part of cement (− 20, − 10%) or a part of sand (+ 10, + 20%) stored for 3 months in water or for 3 months in NS 52 stained with phenolphthalein; 0%—mortar with no additive.

The phase composition of the surface layer of the lightly compacted mortars was determined by powder X-ray diffraction method using an HZG-4C diffractometer and Cu Kα radiation.

The elongation of mortar samples was determined with reference to 28-day-old samples using a Graf–Kauffmann apparatus for lightly compacted samples, with stainless steel inserts at the ends, saturated with water or with sodium sulphate solution.

The compressive strength of the mortars was determined according to recommendations of Polish Standard PN-EN 196-1 [22]. The measurements were performed on surface dry samples. Average compressive strength was calculated from all the measurements taken after statistical treatment of the results.

3. Results and discussion

3.1. Visual evaluation of damage to the mortars

Visual observations were carried out for mortar samples designed for determination of mechanical strength, subjected to strong compaction, and for the samples designed for determination of elongation, subjected to lighter compaction. The observations were performed for samples after 3 months of exposure to solutions NS 16, NS 52, and water, as well as for the samples designed for the determination of elongation after 10 months of exposure to either water or the solution NS 16.

In the case of the strongly compacted mortar samples, visible symptoms of degradation were observed only in the mortar prepared with the addition of 20% FBCC used as a substitute for a part of the cement that had been kept for 3 months in solution NS 52. The edges and the corners of the samples were damaged.

In the case of the lightly compacted mortars, the symptoms of corrosion damage were more apparent than for the strongly compacted samples and occurred also in the NS 52 medium if FBCC was used as a substitute for 10 or 20 wt.% of the cement (Fig. 1). In contrast, samples of the mortars containing FBCC used as a substitute for a part of the sand showed no evidence of any disintegration. No negative changes were observed in the 4- and 11-month samples stored in water or in a less aggressive sulphate solution, irrespective of the content of FBCC.

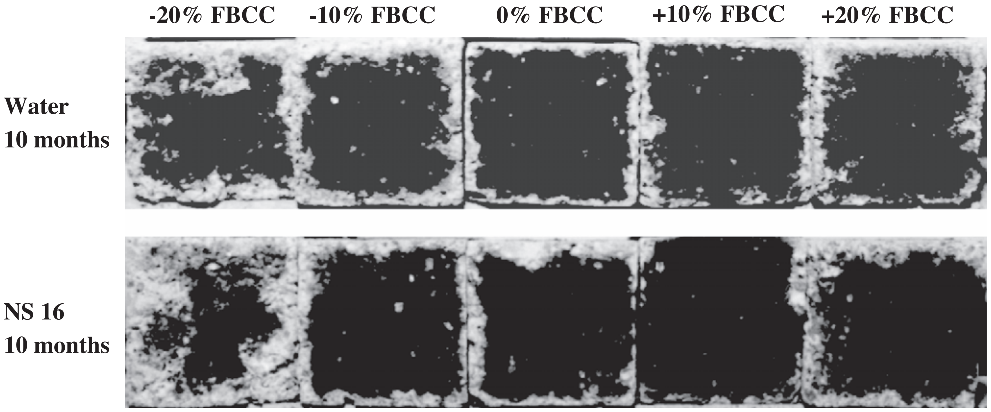

Fig. 3. Fractures of lightly compacted mortars containing FBCC as substitute for a part of cement (− 20, − 10%) or a part of sand (+ 10, + 20%) stored for 10 months in water or for 10 months in NS 16 stained with phenolphthalein; 0%—mortar with no additive.

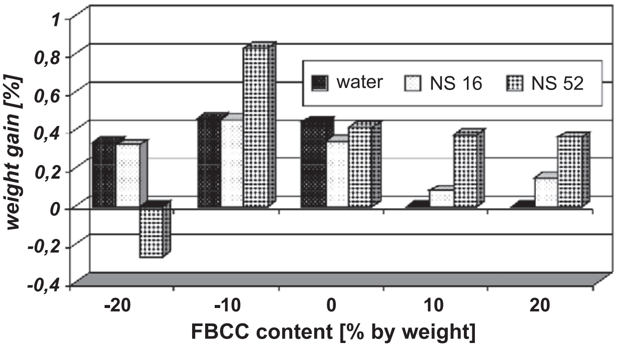

Fig. 4. Effect of FBCC addition on change in mass of strongly compacted mortars exposed for 3 months to water, NS 16, and NS 52 media as compared with 28-day-old mortars.

An analysis of the results of visual observation shows that the addition of FBCC to cement mortars may reduce resistance to the aggressive action of sodium sulphate solution. The extent of corrosion damage did not depend, within the time of the study, on duration of exposure, but it depended on the concentration of the aggressive medium. The harmful effect of FBCC appears at very high sulphate ion concentrations (52 000 mg/dm^3). The effect is stronger in cases where FBCC is used as a substitute for a part of the cement and where light compaction is applied. Cracking of the mortar sample surface shown in Fig. 1 suggests that the probable mechanism of destruction in NS 52 solution is associated with the accumulation of expansive corrosion products at some depth from the sample surface, especially at the corners and edges. Gollop and Taylor [13,14] formerly noted this phenomenon. The kind of corrosion damage may point to the possible occurrence of cyclic processes of hydration and dehydration of readily soluble sodium sulphate, i.e., the transformation of thenardite to mirabilite and vice versa [15].

3.2. Visual evaluation of decrease of alkalinity of the mortars

Figs. 2 and 3 show, as examples, some photographs of the fracture surfaces of lightly compacted mortars after 3 months of exposure to water and to NS 52 solution and after 10 months of exposure to either water or NS 16 solution.

An analysis of the results of observation shows that the decrease of alkalinity down to below pH 8 in the surface layer or in the core of less compacted mortars occurs as early as 3 months on exposure to the NS 52 solution and 10 months on exposure to water or NS 16 solution. It is to be expected, however, that the causes of the alkalinity decrease are different in either case. In the mortars containing 10% or 20% additions of FBCC as a substitute for a part of cement kept in the NS 52 solution, the process consists probably in exhaustion of $Ca(OH)_2$ accompanied by decomposition of the C-S-H phase. Expansive corrosion products are formed at a certain depth, where the concentration of Ca^{2+} is sufficiently high. The fact is evidenced by the lack of phenolphthalein color in the core of the mortar samples and by the surface destruction connected with scaling. At longer contact with water, the diffusion of $Ca(OH)_2$ from the surface layer of the mortar increases and the medium becomes a saturated solution of $Ca(OH)_2$. In the less concentrated solution of sodium sulphate, the diffusion is accompanied by reaction of sulphate with $Ca(OH)_2$, but the corrosion products formed do not result in visible material destruction.

The higher reduction in alkalinity of mortars containing 10% or 20% additions of FBCC used as cement substitute may arise from many reasons including decrease of cement content, $Ca(OH)_2$ consumption in the pozzolanic reaction, exhaustion of $Ca(OH)_2$ in reaction with Na_2SO_4, decomposition of the C-S-H phase as a result of violation of equilibrium in the system $Ca(OH)_2$–C-S-H phase, as well as deposition of roughly neutral corrosion products in the pores of the uncolored part of the mortar or at the boundary between the colored and uncolored parts of the mortar sample.

The smaller decrease of alkalinity in the core of less compacted mortars containing FBCC additive as a substitute for a part of sand and the existence of a distinct boundary between the surface layer and the core may be accounted for by the accumulation of corrosion products, which isolate the core of the mortar and inhibit the elution

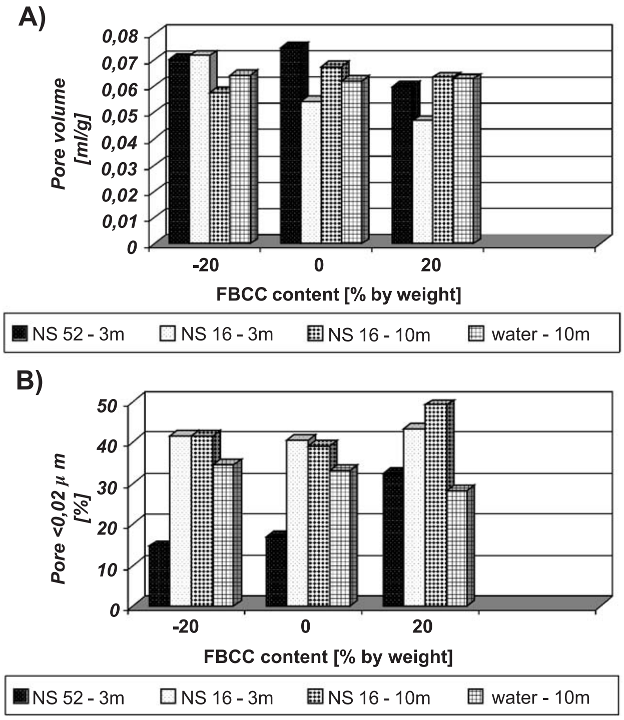

Fig. 5. Effect of FBCC addition on structural parameters of surface layer of strongly compacted mortars stored for 3 months in NS 52 medium and for 3 or 10 months in NS 16 medium or for 10 months in water. (A) Total pore volume, (B) content of pores of diameter below 0.02 µm.

of $Ca(OH)_2$ and the decomposition of the C-S-H phase in the core.

It should be noted that the processes described above are less intensive in the mortars strongly compacted owing to the limited diffusion of aggressive media and water. Nevertheless, the exposure of such mortars to any aggressive media can result in substantial changes of porosity in the surface layers.

3.3. Mass change and microstructure of cement mortars

The effect of FBCC content on the change in mass of strongly compacted mortars after 3 months of storage in water and in the corrosive solutions, as compared with the 28-day-old mortars, is shown in Fig. 4. The effect of FBCC content, kind of aggressive media, and time of exposure of these mortars on selected parameters of microstructure of the surface layers are given in Fig. 5A and B.

An analysis of the results of the studies on porosity of the surface layer of mortars and on mass change of these mortars leads to the following proposed conclusions:

– in mortars containing FBCC additive used as a substitute for a part of cement, stored in the strongly aggressive sulphate medium (NS 52), the main corrosion process consists in decomposition of the C-S-H phase due to the

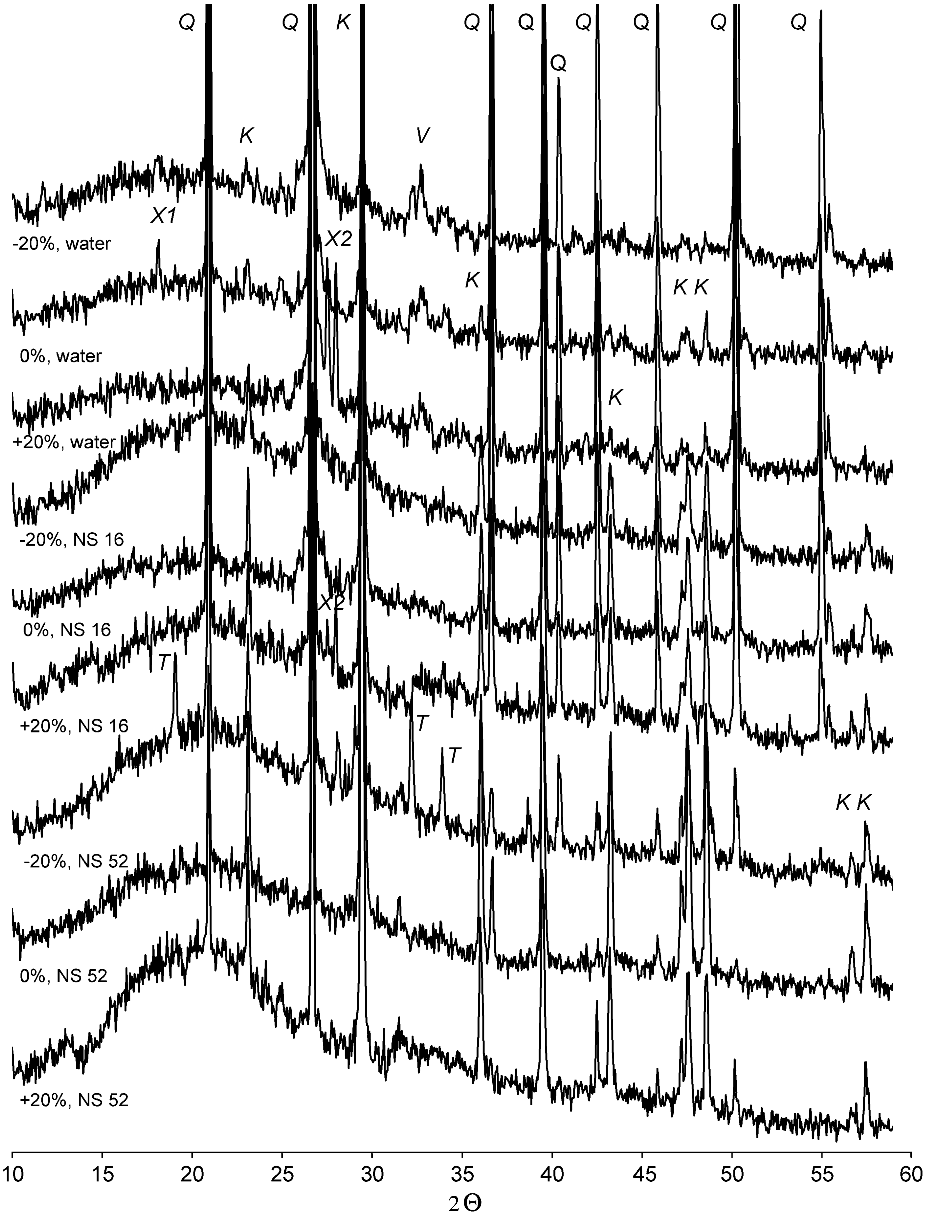

Fig. 6. Comparison of the X-ray diffraction patterns of lightly compacted mortars containing 20% FBCC as substitute for a part of cement (− 20%), part of sand (+ 20%), and mortars with no FBCC (0%) stored for 3 months in NS 52, for 10 months in water, or in NS 16. Denotation of phases: Q—quartz; K—calcite; T—thenardite; V—vaterite; X1—unidentified phase, $d = 4928$ Å; X2—unidentified phases, $d = 3246$ Å and 3192 Å.

leaching action of Na_2SO_4 (very low content of pores of diameter < 0.02 μm). In mortars containing FBCC used as a substitute for a part of sand, the principal process consists in deposition of corrosion products that tighten the structure of the mortars. This may be accounted for by the total pore volume, comparable with that of mortars stored for 10 months in water, and the higher content of pores of diameter < 0.02 μm,

- in the less concentrated sulphate medium (NS 16) there is no decomposition of the C-S-H phase. Instead, the corrosion products are deposited in the pores, as evidenced by the high content of fine pores throughout the whole range of the FBCC concentration. It is also confirmed by the fact that the content of fine pores is higher in the (NS 16) mortars in which the FBCC was used as a substitute of a part of sand than in the mortars stored for 10 months in water. However, the increase of the total pore volume with increasing time of the action of the NS 16 medium for the FBCC (0) and the FBCC (+20) may also be accounted for by the possible formation of microfractures in these mortars,
- the mechanism of sulphate corrosion, within the time range studied, is very sensitive to the concentration of Na_2SO_4 solution. Comparing the effects of a 3-month exposure to NS 52 with a 10-month exposure to NS 16 in terms of changes in the pore structure, it is apparent that a shorter time of exposure to NS 52 has a greater destructive effect on the cement material than a much longer time of exposure to sulphate solution of much lower concentration,
- the generally high increase in mass of the mortars stored in the NS 52 medium results from the increase of porosity due to the leaching effect of the solution and partly due to the diffusion of the external much higher concentration solution inwards into the mortar (the high concentration difference between external and pore solution forces the diffusion). The small increase in mass of the mortars stored in the NS 16 medium is due to isolation of the structure by the corrosion products. The loss in mass of the mortar containing 20% of FBCC stored in the solution NS 52 is due to chipping of corners and edges of the samples (Fig. 4).

To summarize, one may state that from the viewpoint of structure of cement mortars exposed to the action of strongly aggressive Na_2SO_4 solutions, a greater advantage may be gained if FBCC additive is used as a substitute for a part of the sand.

3.4. Phase composition of surface layers of the mortars

The results of X-ray diffraction studies of samples taken from the surface of weak compacted mortars are shown in Fig. 6. X-ray diffraction patterns of all the mortars exhibit reflections due to quartz and calcite; the patterns of the mortars stored in water also contained reflections of vaterite. The intensity of the quartz peaks is not related to the contents of FBCC in the mortars, but reflections due to calcite obtained from mortar exposed to the action of corrosive solutions were more intense than those from samples stored in water. X-ray diffraction patterns of mortar containing 20% FBCC used as a substitute for a part of cement exposed for 3 months to the action of the NS 52 medium contained also reflections of thenardite formed from the dehydration of sodium sulphate decahydrate used in the preparation of the aggressive sodium sulphate solution. The diffraction patterns have revealed also a number of peaks due to unidentified solid phases. Interplanar distances *d* of some the most intense peaks have been given (see the legend for Fig. 6).

The presence of the quartz peaks is probably from the quartz sand. The absence of reflections due to gypsum and ettringite along with the presence of calcite in the diffraction patterns of certain mortars may be explained in the same way as in the case of concrete samples partly buried in ground saturated with sodium sulphate solution [16]: instability of ettringite in low pH media and in the presence of CO_2 favors the reaction of $Ca(OH)_2$ with atmospheric CO_2 as compared with reactions leading to formation of ettringite and gypsum.

The presence of X-ray diffraction reflections due to thenardite only in the mortar that contains a 20% addition of FBCC as a substitute of a part of cement and is kept in the NS 52 solution may be a result of diffusion of the aggressive component of the medium into the mortar containing relatively many pores responsible for the diffusion and subsequent crystallization of thenardite after the removal of the mortar from the aggressive solution. The thenardite–mirabilite transformation described in Ref. [15] is rather improbable for two reasons: no mirabilite was found in the mortar, and the mortar was completely immersed in the solution during the experiment (the crystallization in the system thenardite/mirabilite requires a high concentration of sodium sulphate, and it might only occur at a partial immersion of the mortar in a strongly concentrated solution of the salt).

The studies did not provide unequivocal information concerning the effect of the Al_2O_3 present in FBCC on the mechanism of sulphate corrosion of the mortars. The

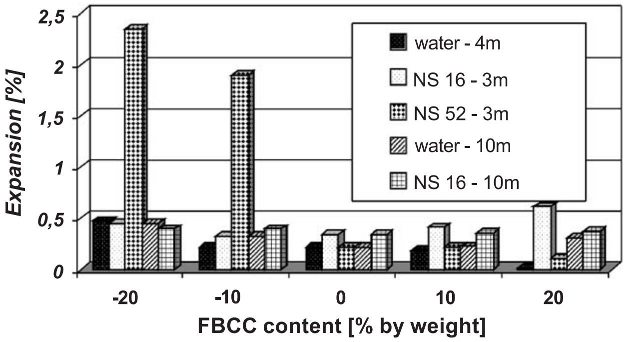

Fig. 7. Effect of FBCC addition on expansion of lightly compacted mortars stored for 3 or 10 months in water, for 3 months in NS 16 or in NS 52, and for 10 months in NS 16.

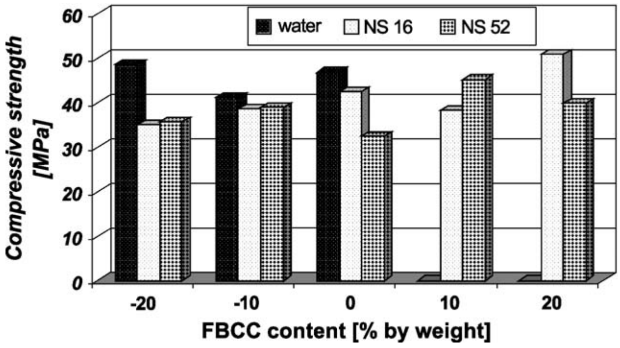

Fig. 8. Effect of FBCC addition on compressive strength of strongly compacted mortars stored for 3 months in water, in NS 16, or in NS 52.

role of Al_2O_3 and the possible formation of ettringite, which finally is transformed into gypsum, are not apparent, as there is no gypsum observed in the diffraction patterns.

3.5. Expansion of the mortars

The results of the elongation studies of the lightly compacted mortars in relation to FBCC contents, concentration of sulphate, and time of exposure are shown in Fig. 7.

The highest expansion was found in samples of the mortars in which the pore structure in the surface layer has undergone degradation caused by decomposition of the C-S-H phase and in which thenardite was present. Small expansion values observed in the other mortars stored in the various media show that the processes of deposition of hydration products and of the corrosion products proceed in the material without resulting substantial changes in dimensions. One may not exclude, however, the possibility that these processes are a source of internal stress and weakening of the material.

3.6. Compressive strength of the mortars

The compressive strength and its scatter depend on the content of FBCC added, on its role in the mortar, and on the medium to which the mortars are exposed (cf. Figs. 8 and 9).

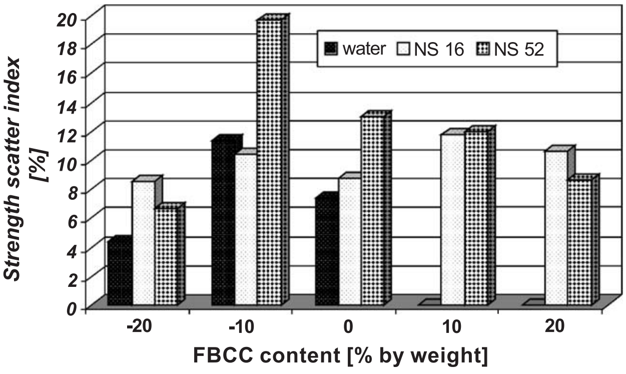

Fig. 9. Effect of FBCC addition on compressive strength scatter index (v) of strongly compacted mortars stored for 3 months in water, in NS 16, or in NS 52 media ($v = 100 \times$ S.D./mean strength).

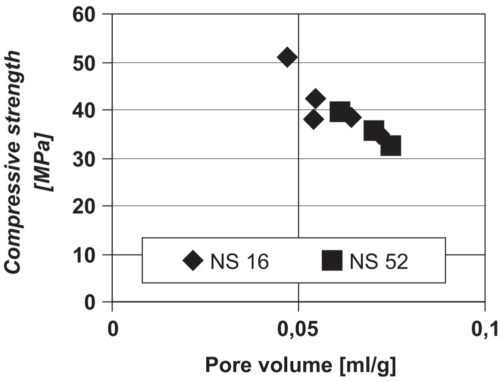

Fig. 10. Effect of total pore volume in surface layer of strongly compacted mortars following a 3-month exposure to NS 16 or NS 52 media on compressive strength.

NS 16 as medium. Addition of FBCC to the mortars as a substitute for up to 20% of cement or up to 10% of sand results in a decrease of strength of the mortar, as compared with the mortars containing no additive. Only an addition of 20% FBCC as a substitute of a part of the sand gives an increase of mechanical strength and a decrease of the scatter. An increase of compressive strength and the smallest scatter of the results of measurements were observed only in the mortar where 20% addition of FBCC was used to replace a part of the sand (Figs. 8 and 9). The FBCC-containing mortars are characterized by a lower strength and a higher scatter of results as compared with the mortars exposed to water.

NS 52 as medium. Addition of up to 20% FBCC as a substitute for a part of cement and a part of sand results in an increase of compressive strength, as compared with a mortar containing no additive (Fig. 8). However, the scatter of results of compressive strength measurements of samples stored in this medium is very high (Fig. 9). The mortars dosed with FBCC exhibit lower compressive strength and higher scatter of results of strength measurements as compared with the mortars exposed to water. On the other hand, their strength is similar or slightly lower than that of mortars exposed to sulphate solutions of lower concentration (NS 16).

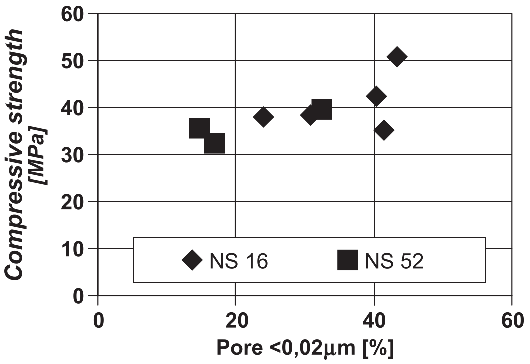

Fig. 11. Effect of content of pores of diameter below 0.02 µm in surface layer of strongly compacted mortars following a 3-month exposure to NS 16 or NS 52 media on compressive strength.

Some references deal with relationships between the compressive strength and the microstructure parameters of cement materials: total pore volume and amount of fine pores that inhibit the propagation of cracking [8,23]. In our experiments, the existence of such relationships is confirmed by the data in Figs. 10 and 11, although the scatter of results is much greater in Fig. 11 than in Fig. 10. A possible explanation of this fact may lie in the depositing of corrosion products in the pores. Such deposits can initially strengthen the material or can subsequently generate stresses and microcracks in the mortar. The lack of correlation between the results of compressive strength measurements and damage due to sulphate corrosion (microcracks) is also pointed out by other authors [16], who recommend in such cases to determine the elastic and dynamic modulus, which appear to be more sensitive to evaluate the progress of corrosion in the cement material.

4. Summary and final conclusions

1. The studies performed have shown that at least two mechanisms of chemical corrosion may occur in Portland cement mortars in which FBCC is used to substitute a part of cement or a part of sand exposed to the action of highly aggressive sulphate solutions: leaching of cement stone and deposition of corrosion products in the pores. The actual mechanism depends on the concentration of the aggressive solution, the amount of FBCC added, and the role it plays in the mortar.
2. The extent of corrosion damage depends mostly on the concentration of sulphate solution and degree of compacting of the mortar. The duration of exposure is of lesser significance. The edges and the corners of the mortar samples are the parts most exposed to the contact with aggressive ions, and hence the most susceptible to destruction.
3. No unequivocal correlation was found between the expansion of mortars compacted according to prENV 196-10 and the mechanical strength of mortars compacted according to PN-EN 196-1. The greatest expansion was observed in mortars, which did not exhibit the lowest compressive strength. Therefore, it is questionable to use the measure of elongation, particularly in poorly compacted mortar samples, as the sole standard method for determining the resistance to sulphate corrosion in sodium sulphate solutions.

References

[1] N. Su, H.-Y. Fang, Z.-H. Chen, F.-S. Liu, Reuse of waste catalysts from petrochemical industries for cement substitution, Cem. Concr. Res. 30 (2000) 1773–1783.

[2] J. Paya, J. Monzo, M.V. Borrachero, Fluid catalytic cracking catalyst residue (FC3R): an excellent mineral by-product for improving early-strength development of cement mixtures, Cem. Concr. Res. 29 (1999) 1773–1779.

[3] B. Pacewska, M. Bukowska, I. Wilińska, M. Swat, Modification of the properties of concrete by a new pozzolan—a waste catalyst from the catalytic process in a fluidized bed, Cem. Concr. Res. 32 (2002) 145–152.

[4] N. Su, Z.-H. Chen, H.-Y. Fang, Reuse of spent catalyst as fine aggregate in cement mortar, Cem. Concr. Compos. 23 (2001) 111–118.

[5] J. Paya, J. Monzo, M.V. Borrachero, Physical, chemical and mechanical properties of fluid catalytic cracking catalyst residue (FC3R) blended cements, Cem. Concr. Res. 31 (2001) 57–61.

[6] M. Swat, J. Kubissa, W. Kubissa, Spent catalyst as highly effective additive for concrete, Inż. Bud. 4 (1997) 180–181.

[7] M. Bukowska, B. Pacewska, I. Wilińska, M. Swat, Effect of saturated brine medium on the properties of Portland cement concretes and mortars dosed with zeolite aluminosilicate, XII Konferencja Naukowo Techniczna KONTRA'2000, Warszawa-Zakopane, maj, 2000, pp. 357–42.

[8] W. Kurdowski, The Chemistry of Cement, PWN, Warszawa, 1991.

[9] B. Pacewska, I. Wilińska, M. Bukowska, Hydration of cement slurry in the presence of spent cracking catalyst, J. Therm. Anal. Calorim. 60 (2000) 71–78.

[10] J.M. Khatib, S. Wild, Sulphate resistance of metakaolin mortar, Cem. Concr. Res. 28 (1998) 83–92.

[11] L. Czarnecki, J. Mierzwa, Sulphate corrosion of concrete—an intensity of aggressive environment influence, XI Konferencja Naukowo Techniczna KONTRA'98, Warszawa-Zakopane, maj, 1998, pp. 71–78.

[12] M. Gruener, Corrosion and Corrosion—Protection of Concrete, Arkady, Warszawa, 1983.

[13] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack: III. Sulfate-resisting Portland cement: reactions with sodium and magnesium sulfate solutions, Cem. Concr. Res. 25 (1995) 1581–1590.

[14] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack: IV. Reactions of a slag cement paste with sodium and magnesium sulfate solutions, Cem. Concr. Res. 26 (1996) 1013–1028.

[15] J. Bensted, The chemistry of efflorescence, Cement, Wapno, Beton (4) (2001) 133–142.

[16] E.F. Irassar, A. Di Maio, O.R. Batic, Sulfate attack on concrete with mineral admixtures, Cem. Concr. Res. 26 (1996) 113–123.

[17] F. Rendell, R. Jauberthie, The deterioration of mortar in sulphate environments, Constr. Build. Mater. 13 (1999) 321–327.

[18] F. Akoz, F. Turker, S. Koral, N. Yuzer, Effects of raised temperature of sulfate solutions on the sulfate resistance of mortars with and without silica fume, Cem. Concr. Res. 29 (1999) 537–544.

[19] S. Miletić, M. Ilić, J. Ranogajec, M. Marinović-Neducin, M. Djurić, Portland ash cement degradation in ammonium-sulfate solution, Cem. Concr. Res. 28 (1998) 713–725.

[20] F. Turker, F. Akoz, S. Koral, N. Yuzer, Effects of magnesium sulfate concentration on the sulfate resistance of mortars with and without silica fume, Cem. Concr. Res. 27 (1997) 205–214.

[21] A. Garbacik, S. Chłądzyński, Standardisation aspects of determination of the cement resistance to sulphate attack, XI Konferencja Naukowo Techniczna KONTRA'98, Warszawa-Zakopane, maj, 1998, pp. 107 –115.

[22] PN-EN 196-1, Methods of testing cement: Part 1. Determination of strength (1994).

[23] M. O'Farrel, S. Wild, B.B. Sabir, Pore size distribution and compressive strength of waste clay brick mortar, Cem. Concr. Compos. 23 (2001) 81–91.