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INFLUENCE OF CHLORIDE IONS AND pH LEVEL ON THE DURABILITY OF HIGH PERFORMANCE CEMENT PASTES (PART II)

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ABSTRACT

The resistance to chemical attack of low water/binder ratio pastes containing silica fume (W/B = 0,25 and 0,38) was studied by soaking small paste disks in three different pH-controlled solutions, with or without sodium chloride, for periods of up to three years. The three solutions in which the paste disks were soaked were the following: 3% NaCl (by mass) at a pH level of 8,5, 0% NaCl at 8,5, and 0% NaCl at 4,5. After three years of exposure, the results confirm that the pH level of the aggressive solution is the most important factor controlling the durability of cement pastes subjected to chemical attack. The total porosity and the depth of decalcification were found to increase with a reduction of the pH level. The results further show that the presence of chloride ions tends to increase the leaching of calcium and the opening of the porosity. The reduction of the water/binder ratio does not influence the degradation processes but affects the kinetics of these processes. Chloroaluminate formation was observed only in the 0,38 mixture and is related to the presence of C_3A. The results obtained after 3 years of exposure confirm those previously obtained after three months of exposure [1].

Introduction

Chloride ions are responsible for many durability problems. A recent OCDE survey [2] indicates that the most important cause of the premature degradation of 800 000 bridges throughout the world is the penetration of chloride ions into concrete structures leading to the corrosion of the reinforcing steel. Chloride ions also contribute significantly to the detrimental action of freezing and thawing cycles, and also participate in the chemical deterioration of concrete structures [3, 4].

Chloride ions penetrate concrete by capillary and diffusion processes. They migrate to the reinforcing steel, break down the oxide passivation film and enhance the corrosion process. In

TABLE 1
Mixture Characteristics

Mix	W/(C+SF)	Type of Cement*	Silica Fume (%)
P25QS	0,25	30	6
P38QS	0,38	30	6

* 30 : ASTM Type III

addition to this, chloride ions can interact with some of the cement paste hydrates. The degradation process in the presence of chloride ions is essentially a decalcification of the hydrates through the formation of (extremely soluble) calcium chloride. The leaching of calcium tends to increase the porosity, and subsequently, the diffusion of chlorides to the reinforcing steel.

The pH level of an aggressive solution also has a very significant influence on the deterioration of concrete. It can alter the microstructure and modify the chemical composition of cement pastes. However, the mechanisms of deterioration are not well understood and the long term durability of concrete to this type of chemical attack is still very difficult to predict. In addition, the presence of aggregates tends to modify the microstructure of cement paste at the interface. From a theoretical point of vue, the higher porosity and the increased portlandite content of the interfacial transition zone (ITZ) should facilitate the ingress of external aggressive agents and increase calcium leaching. However, recent data tend to show that the effect of ITZ on the durability of cement-based materials is limited [5].

In this paper, the results of an investigation carried out to better understand the mechanisms of deterioration of low water/binder ratio cement pastes in contact with corrosive solutions are presented. The test program was designed in order to obtain information on the mobility of chloride ions in cement pastes, to determine the influence of chloride ions as well as that of the pH level of the solution in contact with the cement pastes on the basic characteristics of the microstructure such as porosity, and to find out if new hydrated cement products such as chloroaluminates can be formed. These results are part of a more comprehensive project concerning the mechanisms of penetration of chloride ions into concrete [6].

Test Program

Disks of paste (70 mm in diameter and 4 mm in thickness) were soaked in 3 different pH-controlled solutions (with and without sodium chloride) for a period of up to 3 years. In this part of the research project, only cement pastes were subjected to chemical attack, in order to avoid the influence of the aggregates (particularly that of the interfacial transition zone), and to better understand the mechanisms of deterioration of cement pastes caused by chloride ions. Two water/binder ratios were selected for the tests: 0,25 and 0,38. The same cementitious materials were used for both.

Mercury intrusion porosimetry, X-ray diffraction, microprobe analyses and scanning electron microscopy were the principal techniques used to study the various samples after removal from the solutions. A sufficient number of paste disks were soaked in the aggressive solutions to allow measurements to be made after 1, 3, 12 and 36 months of exposure.

Materials and Mixture Characteristics

A CSA type 30 cement (ASTM type III) with 6% silica fume was used in the preparation of all mixtures. The C_3S content of this cement is 58%, the C_3A content is 8%, and the Blaine fineness is 528 m^2/kg. The silica fume contains more than 90% SiO_2. A naphtalene based superplasticizer was used for the 0,25 water/binder ratio mixture, at a dosage of 2,1% of dry material by mass of cement. The composition of the two mixtures is given in Table 1.

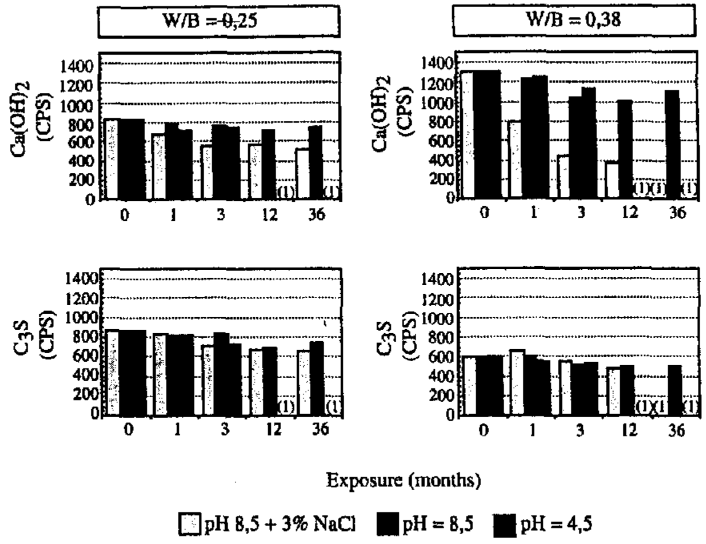
Experimental Procedures

Numerous cylinders (100 mm high and 70 mm in diameter) were cast for each of the two different mixtures. They were demolded after 48 hours, and then immersed in a saturated lime solution for a minimum period of 6 months. After curing, all cylinders were cut into 4 mm thick disks. Except for those required for the initial measurements, the disks were soaked in three 50-litre plastic tanks containing the 3 different aggressive solutions. The solutions were the following: 3% NaCl (by mass) at a pH level of 8,5, 0% NaCl at 8,5, and 0% NaCl at 4,5. Eight disks from each mixture were placed in each tank. The air above the solution in the two tanks containing the solutions at a pH level of 8,5 was flushed by nitrogen to prevent carbonation, and the solutions in the three tanks were constantly stirred. For the solutions at a pH of 4,5 (using carbonic acid), and the solution at a pH of 8,5 with NaCl, the pH levels were kept approximately constant ($\pm$ 0,3) by passing the solution through an ion exchanger resin using an automatic pH-regulation system. For the solution at 8,5, the pH level was adjusted using nitric acid (HNO_3) at a concentration of 0,1N.

After 1, 3, 12 and 36 months of exposure, 2 disks from each mixture were removed from the solutions and tested for mechanical strength using a three-point bending test. During the experiment, only the force (in Newton) required to break the disk was recorded. The broken samples were then dessicated in an environment kept at a pressure of 0,1 Pa for a minimum period of 20 days to prevent any further chemical reactions before the different analyses were performed. In this paper, the measurements made at the end of the curing period ($t = t_0$) define the initial state of the material.

The samples of paste (representing the full thickness of the disk) to be analyzed by the X-ray technique were first ground, and then sieved on a 65 μm sieve. The powders were then compacted and analyzed using a SIEMENS D500 diffractometer at a 40 kV tension and a current of 25 mA. The test results were analyzed qualitatively to determine if new hydration products, such as chloroaluminates, had been formed during the period of exposure to the agressive solutions. Because all the test procedures and test condition were the same for every mixture, the results can be regarded as semi-quantitative and can be used to determine very approximately the degree of calcium leaching, and the degree of hydration of the two cement pastes. These results however are not truly quantitative because the intensity of the peaks is not only a fonction of the quantity of the cristalline phase present in the sample, but is also influenced by the orientation of the crystals in the powdered samples and the degree of compaction of the sample to be analysed.

For the microprobe analyses, the paste disks were broken into small parts to expose the total internal surface (4-mm thick). They were then impregnated with an epoxy resin, polished, and coated with carbon. The microprobe measurements were performed along imaginary lines extending 2000 μm from the external surface in contact with the aggressive solution towards the



(1) no peak left on the X-ray diagram

FIG. 1

Evolution of the C_3S and $Ca(OH)_2$ contents with time. (1) no peak left on the X-ray diagram.

internal part of the disks. At each point of measurement, the concentration of calcium, chlorine, and aluminium was determined.

Mercury intrusion porosimetry tests were made with a porosimeter able to reach pores ranging from 300 µm to 3 nm in diameter. Each test result represents the average value obtained for two small pieces (full thickness) of the same disk. The contact angle considered was 130°. A small number of thermogravimetry tests, scanning electron microscope observations, and determinations of the total chloride concentration (ASTM C1152) were also performed.

Results

X-Ray Diffraction. The X-ray diagrams show that, at the end of the curing period, the 0,38 W/B mixture was more hydrated than the 0,25 W/B mixture. This was observed when comparing the height of the peaks corresponding to some of the anhydrous compounds (C_3S and C_2S) and that of those corresponding to portlandite (calcium hydroxide). However, the degree of hydration (as measured by the loss of water between 150°C and 1000°C) was found to be only 3% lower for the 0,25 mixture.

Figure 1 presents the evolution of the quantity of C_3S and $Ca(OH)_2$ for the two mixtures for each of the three aggressive solutions. The results in all cases show a decrease of the height of the C_3S with time. The reduction of the C_3S content can be partly attributed to hydration. However, it is also highly probable that part of the calcium of that anhydrous compound was leached. The results also show a decrease of the calcium hydroxide content with time even though an increase of $Ca(OH)_2$ should be observed if there was supplementary hydration. The calcium leaching is caused by the chemical attack.

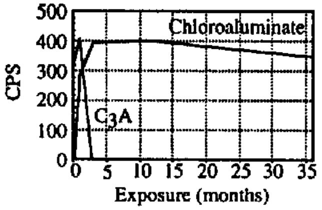


FIG. 2.
Chloroaluminate formation: P38QS mixture, pH 8,5+3% NaCl.

The influence of the pH level on the C_3S and $Ca(OH)_2$ content is clearly visible on Figure 1. There is no more anhydrous compound and $Ca(OH)_2$ left after 1 year of exposure when the paste disks are immersed in a 4,5 pH level solution.

The results presented in Figure 1 also indicate that a reduction of the water/binder ratio contributes to improve the durability of cement pastes to chemical attack. After 36 months of exposure, there is still C_3S and $Ca(OH)_2$ for the 0,25 mixture immersed in a 8,5 pH level solution with chloride ions while there are no more of these compounds for the 0,38 mixture. The $Ca(OH)_2$ content is also influenced by the water/binder ratio. The difference in the height of the peaks between the mixtures immersed in a 8,5 pH level solution with and without chloride ions remains smaller for the 0,25 mixture than for the 0,38 mixture.

The results in Figure 1 further indicate that the presence of sodium chloride has a significant influence on the C_3S and $Ca(OH)_2$ content. For the 0,38 mixture after 36 months of exposure to the sodium chloride solution at a pH of 8,5, there is no anhydrous compound left, whereas the amount of C_3S for the same mixture exposed to the 8,5 pH level solution without chloride ions is still very significant. There is always less portlandite left in the samples when the mixtures are exposed to the chloride solution.

Chloroaluminates were only found in the mixture having a W/B of 0,38. Figure 2 presents the evolution of the intensity of the main chloroaluminate peak and that of the main C_3A peak for this mixture. The results show a rapid increase of the chloroaluminate peak for the first 3 months associated with a decrease of the C_3A peak. It is clear from these results that the formation of chloroaluminate crystals is associated with the presence of C_3A. The presence of chloroaluminates was confirmed by scanning electron microscope observations.

The mixture with a W/B of 0,25 did not show any sign of chloroaluminate formation even though chloride ions were present everywhere in the paste. This can probably be explained by the fact that this mixture is less porous, and that the chloride content was thus not sufficient to promote chloroaluminate formation. This was also observed in a previous research project [7]. Several authors have studied the state of chloride ions in cement pastes. They can be free in the pore solution, adsorbed on the pore walls or chemically bound in products such as chloroaluminates [8,9,10,11]. Midgley and Illston [12] suggest that the governing factors in chloroaluminate formation are the cement mineral composition and the paste physical structure.

Microprobe Analyses. The main results from the microprobe analyses are presented in Figure 3 which shows the calcium concentration after one year for both mixtures and for each of the three solutions. The straight line on each diagram represents approximately the minimum concentration of calcium in the control specimens. The concentrations above this line correspond

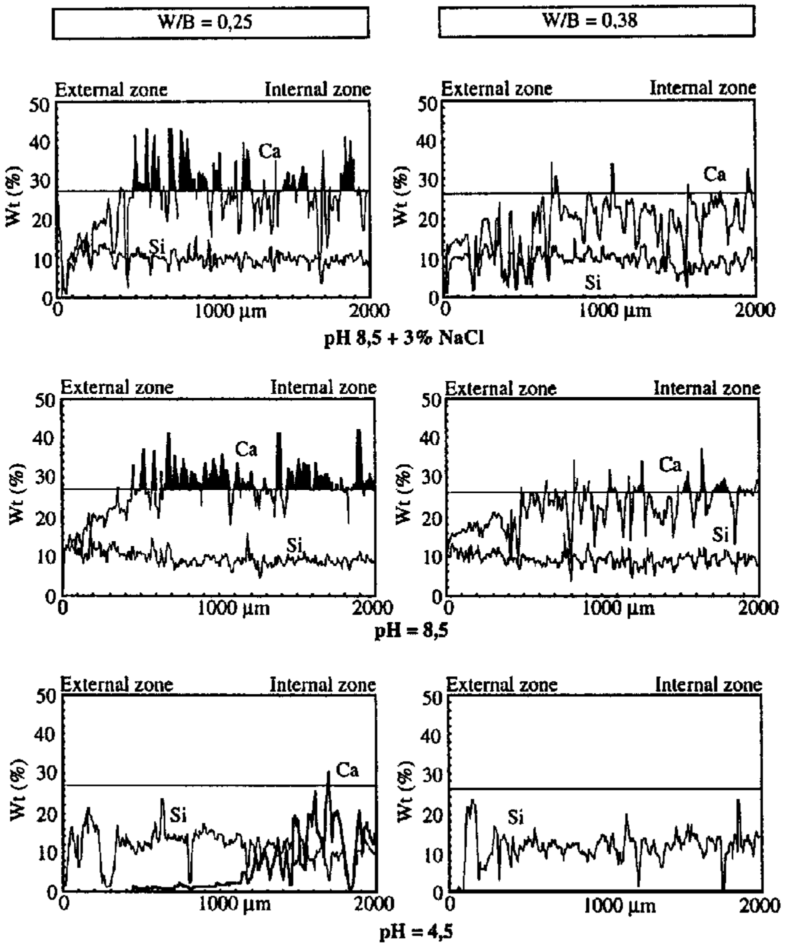


FIG. 3.
Microprobe measurements for mixtures P25QS and P38QS after 1 year of exposure to the different aggressive solutions.

to the calcium held in portlandite crystals or in anhydrous silicates. The concentrations below indicate areas where leaching of the calcium has occurred.

In all control specimens, the calcium and silicium profiles were found to be constant over the full thickness of the disks. After each period of exposure, the calcium content near the external part of the disks (in contact with the aggressive solution) was lower than in the middle of the disks. This leaching phenomenon was observed for both mixtures and all three solutions, and was found to increase with the time of exposure. As can be seen in Figure 3, this decalcified zone is more important for the mixtures soaked in the 4,5 pH level solution. For example, the depth of calcium leaching, after 1 year of exposure, is approximately 500 μm for the 0,25 mixture immersed in the 8,5 pH level solutions, while there is almost no calcium left in the sample immersed in the 4,5 pH level solution. It is interesting to note that the silicium content of each mixture and after each period of exposure to all aggressive solutions remained constant over the full thickness of the disk.

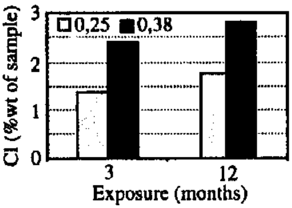


FIG. 4.
Chloride concentration in mixtures P25QS and P38QS.

The results in Figure 3 indicate that the water/binder ratio plays an important role in the chemical degradation process. The 0,25 mixture is always less decalcified than the 0,38 mixture. After 1 year of exposure in a solution maintained at a pH level of 8,5 with chloride ions, the depth of calcium leaching is roughly 500 μm for the 0,25 mixture, while there is almost no portlandite or anhydrous silicates left over the full depth of the sample in the 0,38 mixture.

Chloride ions also seem to have a significant influence on the leaching of calcium. Figure 3 shows that the calcium content is lower in a zone covering approximately the first 500 μm for the 0,25 mixture exposed to a 8,5 pH level solution without chlorides. However, the same mixture in contact with a chloride solution at the same pH level shows evidence of calcium leaching over the full thickness of the sample.

For both specimens in contact with chlorides, the results of the microprobe analyses indicate that the chloride concentration was fairly constant over the full thickness of the disks even after one month of exposure, except in the highly decalcified external zones where there was no chlorides. The value of the chloride concentration can not, however, be determined precisely from such diagrams. The total chloride concentration was therefore determined, using the method prescribed by ASTM C1152-90 (Standard test method for acid-soluble chloride in mortar and concrete). Figure 4 presents the evolution of the chloride concentration for the two mixtures. As can be seen, this concentration increases with time and with the water-binder ratio.

Mercury Intrusion Porosimetry. The results of the mercury porosimetry tests are summarized in Figure 5. For the samples soaked in the 4,5 pH level solution, the total porosity increases very rapidly with the time of exposure (as mentioned in the previous section, the 0,38 mixture was completely decalcified and the 0,25 mixture was also highly deteriorated after 12 months of exposure at this pH level (see Figure 3)). For the samples in the 8,5 pH level solutions, the total porosity generally increases between 0 and 3 months, but it remains fairly constant between 3 and 36 months.

The results in Figure 5 confirm that the presence of chloride ions accelerate the deterioration processes. After 3 years of exposure in the 8,5 pH level solution with chlorides, the increase in total porosity is 45% for the 0,25 mixture and 50% for the 0,38 mixture, while it is 0% and 8% for the 0,25 and 0,38 mixtures respectively in a similar pH level solution without chlorides.

To facilitate the analysis of the results, and to better understand the evolution of the pore structure, the total porosity was divided into four classes of pore sizes. These classes are based on data obtained by Revertégat et al. [13] on similar pastes. These four classes are the following:

Class 1: 300 μm–0,9 μm
Class 2: 0,9 μm–60 nm
Class 3: 60 nm–9 nm
Class 4: 9 nm–3 nm

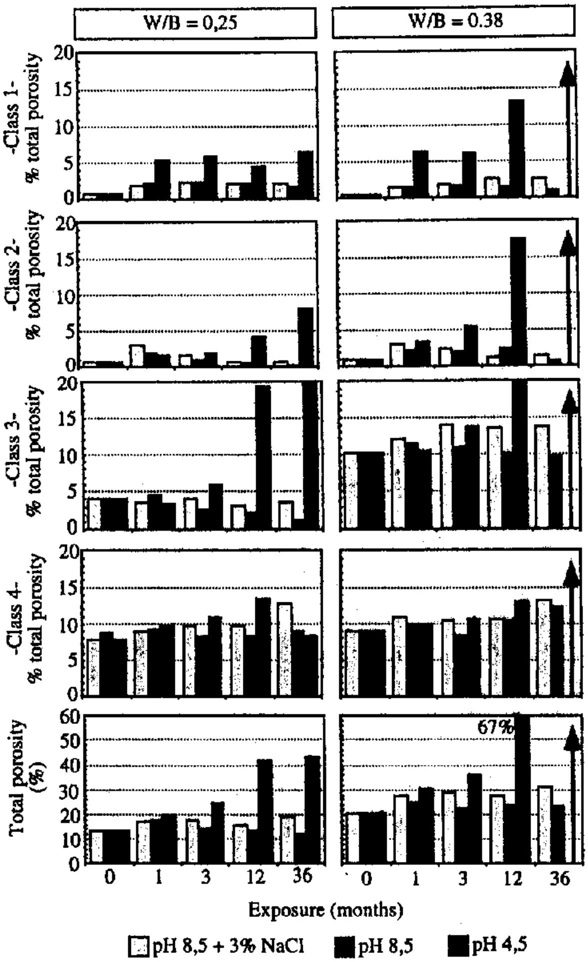


FIG. 5.
Porosity measurements for mixtures P25QS and P38QS exposed to the three different aggressive solutions.

An increase of the class 4 pore volume with a corresponding decrease of class 3 is normally representative of a hydration mechanism. The results in Figure 5 show, in most cases (except for the mixtures immersed in a 4,5 pH level solution), an increase of the class 4 pore volume which indicates that the hydration process has continued during the period of exposure to the aggressive solutions. These results are in agreement with those obtained with the X-ray diffraction technique. However, this increase of class 4 porosity is not generally associated with a decrease of class 3 porosity. This can probably be explained by the leaching caused by the chemical attack. The new hydrates formed can not fill the entire porosity left by the calcium leaching.

The paste disks are probably subjected to two opposite phenomena: hydration continues mainly in the internal part of the disks, while there is calcium leaching mostly near the external part. Since there is an increase in total porosity with the time of exposure, it can be concluded that the increase in porosity due to the leaching of calcium is more important than the decrease

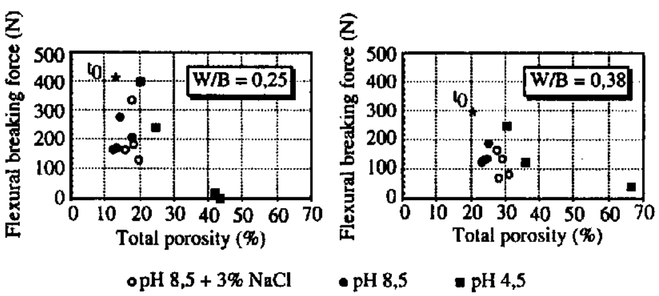


FIG. 6.
Relationship between the total porosity and the flexural breaking force.

due to hydration. This is probably true for the mixtures immersed in a 8,5 pH level solution with or without chloride ions. At a pH of 4,5, however, the rapid increase of every class of porosity and the decrease of the C_3S content of the paste disks is certainly caused by the intensity of the chemical attack.

The pore size distribution of the 0,25 mixture after 36 months of exposure in a 4,5 pH level solution and that of the 0,38 mixture after 12 months represents the microstructure of pastes in which there is no calcium left.

Flexural Breaking Force Results. Figure 6 presents the evolution of the mechanical strength of the disks as a function of the total porosity. As can be seen on this figure, an increase of the total porosity generally leads to a decrease of the mechanical properties. This effect seems more evident for the 0,38 mixtures. It can also be seen that the degredation processes can lead to a very significant loss of strength without a very high increase in porosity. The dominant influence of the pH level is clearly visible on the figure.

Discussion

The degradation of cement pastes subjected to the type of aggressive solutions used in this study is mainly due to the leaching of calcium. With time this phenomenon moves forward into the pastes, and eventually leaves behind a residual skeleton of decalcified hardened cement paste with little mechanical strength. This can be explained by the fact that cement paste hydrates are unstable at pH levels lower than about 13. The paste disks were more deteriorated when immersed in the 4,5 pH level solution than in the 8,5 pH level solutions. This confirms the results obtained at pH levels of 13 and 11,5 [7, 13]. However, the pH level is not the only variable influencing the solubility of the hydrates. The dissolution of the hydrates appears to be dependent also upon the nature of the ions present in the solution. The reduction of the pH level of the external solution increases the chemical activity gradient between the external solution and the pore solution. This gradient is also influenced by the various ions present. The difference between the pore solution and the external solution causes the movement of ions both out of the paste and into the paste. These movements change the chemical activity of the pore solution and lead to the dissolution of hydrates.

For several hydrates, it is possible to determine a range of pH levels in which it is highly probable to find them [14], even though the pH level does not completely determine the activity

TABLE 2
Equilibrium Constants for Various Reactions at 25°C [17]

Species	log K_{sp}
Portlandite	-5,19
Monosulfate	-29,25 ± 0,5
Ettringite	-43,94 ± 0,36

of the solution. Portlandite is the first component to be dissolved when the pH level becomes lower than 13 [14]. Ettringite and monosulphoaluminates are less soluble than $Ca(OH)_2$. Their solubility increases for pH levels lower than 10,7 and 11,6 respectively [15]. The solubility of the C-S-H was noticed at a pH level of approximately 11,5 [13]. The calcium silicate hydrates are thus less soluble than $Ca(OH)_2$. They can be decalcified when the composition of the pore solution is not controlled anymore by the equilibrium with $Ca(OH)_2$, which can only occur when there is no $Ca(OH)_2$ available. The final product may be a silica gel [16]. The anhydrous compounds (which are present in larger amounts in high performance mixtures) also contribute to the calcium content of the pore solution. However, the solubility of these phases is not well-known. Solubility constants for some hydrates are given in Table 2.

The test results show that the presence of chloride ions tends to amplify the phenomenon of calcium leaching and increase the porosity. The microprobe profiles reveal that there is more calcium leaching in the cement pastes when the disks are soaked in a chloride solution (see the results in Figure 3 for the samples soaked in the 8,5 pH level solutions). These results are in accordance with those obtained by Gégout et al. [18]. The presence of chloride ions modify the composition and the ionic force of the pore solution. The penetration of chloride ions into cement paste is associated with a counter-diffusion of hydroxide ions in order to maintain the electroneutrality of the solution. This increases the solubility of portlandite.

The rate at which the paste disks can be decalcified depends not only on the solubility of the hydrates but also on the diffusivity of calcium. The chemical reaction between the pore solution (which is modified by the external solution) and the hydrates is probably extremely rapid compared to the diffusion of calcium [19]. The diffusion process are dependent not only on the activity gradient between the pore solution and the external solution, but also upon the microstructure of the paste. A reduction of the water/binder ratio generally leads to a lower total porosity and a finer pore size distribution. According to Sellevold and Justness [], the use of silica fume also contributes to the refinement of the pore structure. This reduces the diffusivity of the paste and thus slows down the degradation processes. This is confirmed by the test results.

Conclusion

The results of the test described in this paper confirm that the pH level of the aggressive solution is the most important factor controlling the durability of normal and high performance cement pastes subjected to chemical attack. The total porosity was found to increase with the decrease of the pH level. The calcium content (and the mechanical strength) were significantly reduced at a pH level of 4,5, due to the leaching phenomenon. After only 1 year of exposure there was almost no calcium left in the two mixtures immersed in a 4,5 pH level solution.

The water/binder ratio does not appear to affect the deterioration processes due to chemical attack, but only to influence the kinetics of these processes. The degradation of the samples (as measured by calcium leaching, increase in porosity and loss of mechanical strength) was found to be smaller for the high performance mixture. This is considered to be due mainly to the lower diffusivity of the high performence mixture (having a water-binder ratio of 0,25) which slows down the movement of ions.

The influence of chloride ions was clearly put in evidence in this series of tests. The leaching of calcium was amplified when the samples were immersed in the 8,5 pH level solution with chloride ions instead of in the 8,5 pH level solution without chloride ions. The total porosity was also found to increase. However, the influence of chlorides remains smaller than that of the pH level. The formation of chloroaluminate crystals was only observed in the 0,38 mixture.

Acknowledgments

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