ACIDIC CORROSION OF HYDRATED CEMENT BASED MATERIALS

PART 1. - MECHANISM OF THE PHENOMENON

ALI ALLAHVERDI, FRANTIŠEK ŠKVÁRA

Institute of chemical technology,
Department of glass and ceramics,
Technická 5, 166 28 Prague 6, Czech Republic
E-mail: skvaraf@lvscht.cz

INTRODUCTION

Corrosion of hydrated cement based materials comprises a number of complex processes leading to reduction of engineering properties such as strength, elastic modulus and durability. Such complex processes may happen due to a number of various physical, chemical, and physico-chemical factors and their interactions [1, 2, 3] reflecting peculiarities of both material aspects and external factors (service conditions).

As a general simple description the physico-chemical processes of corrosion of porous hydrated inorganic materials which are relatively heterogeneous and brittle consists of three steps. The first step is convective and diffusional transport of aggressive medium (gas or liquid) through interconnected pores to the corrosion front. In the second step the aggressive substance reacts with the material resulting in the formation of some soluble and/or insoluble products. Deposition of insoluble products in the corroded parts and/or transport of soluble products through corroded layer to the aggressive medium, can be considered as the third step. It is to be noted that the phenomenon is very complicated and mathematical description of which is very difficult due to the followings:

Firstly, accurate characterization of pore system is quite difficult whereas diffusion of ions and rate of permeation of potentially deleterious substances across a porous cementitious matrix are intuitively related to the volume of pores, pore size and shape and pore interconnectivity (open and closed pores). Pore radii in cement pastes span a huge range from a few nanometers to nearly 100 microns (gel and capillary pores). In more complex composite systems such as concrete a pore size distribution of entrained and entrapped air voids is also present [4]. Such a complex and irregular structure in concrete causes the stochastic character of concentration patterns and flows [5].

Secondly in cement mortar and concrete, the reaction of aggressive molecules and/or ions with reactive aggregate and the phenomena taking place at the interface between cement hydrates and aggregate make the problem more complicated.

The most common causes of corrosion of concrete structures include ; salt attack (mostly sulfate and sea water), acid attack including carbonation, alkali-silica reaction, efflorescence, and freezing-thawing (frost damage). There are some another causes which occur in industrial environments. These include; high temperature attack, abrasion (cavitation and erosion), and attack by specific chemical or biological agents.

A quick review of the literature in this field (durability of cement based materials) shows that much effort has been spent by researchers during the past fifty years. For instance, Struble [6] cited 638 references drawn from three conference proceedings and various journal articles only for the year 1987 alone. The related literature has been presented in a number of different information sources. Here in tables 1 and 2 we listed a number of general sources providing information in both electronic (database) and printed forms. It is to be considered that in spite of such a voluminous literature comparison of the results and acquirement of relevant information is usually difficult because of firstly differences in experimental conditions including temperature, concentration and composition, static and dynamic conditions, time period of experiment, etc, and secondly the fact that, in practice, corrosion of concrete is usually due to two or more causes working simultaneously.

The object of this paper is to present a summary of the literature on damage to hydrated cement based materials by the phenomenon of acid attack (both organic and inorganic). This theme of research has attained more importance in the recent decades due to the deteriorating effects of acidic media (e.g. acidic rains, acidic groundwaters, etc). In spite of the importance of the phenomenon there are relatively few publications available in the literature compared to the other common types of corrosion of cement based materials. In addition most of the existing publications also deal with the case of attack by carbonic acid (i.e. carbonation or aggressive effects of CO_2). On the other hand

Table 1. General information sources in electronic form (material problems only).

source	notes
Chemical Abstracts, CD	abstracts available since 1975
Materials Science Citation Index, CD	inorganic, organic materials, process (data since 1991)
http://ep.espacenet.com/ http://www.uspto.gov/patft/	Patent, full text, US, EP, PCT, WO Since 1976
Cross Fire System	Gmelin compendia (inorganic data since 1772) Available only for members of Cross Fire System
http://www.rilem.enscachan.fr/index.html RILEM Web site	Properties of building materials, corrosion Proceedings and reports
http://www.ce.gatech.edu/www-CE/home.html	Virtual library of civil engineering
http://www.abf.cz/	Czech civil engineering database

Table 2. General information sources in printed form (material problems only).

source	notes
Chemical Abstracts	in written form since 1907 to approx. 1995
Proceedings of International Congress on Chemistry of Cement	Paris 1980, Rio de Janeiro 1986, New Delhi 1992, Gothenburg 1998, reviews and papers in section "Durability"
Cement Research Progress	published every year, section "Durability of pastes, mortars and concretes"
Conference proceedings	Published in: Am.Concr.Inst.SP-100 (1987) Am.Concr.Inst.SP-122 (1989) Am.Concr.Inst.SP-126 (1991) Am.Concr.Inst.SP-1145 (1994)
RILEM publications	Proceedings and reports
Material Science in Concrete	Series of Am. Ceram. Soc. I-VII
Journals: Cement Concrete Research Zement-Kalk-Gips Cem.-Hormigón ACI Journal Concr. Intern. Matériaux et Constructions Concrete Science and Engineering	Special papers on corrosion and durability problems
Some basic books (old)	*Korozija betona* by V. M. Moskvin (1952) *Betonkorrosion, Betonschutz* by I. Biczók (1968) *Beton in aggressiven Wässern* by H. Lieschke and K. H. Paschke (1968) *Bauschäden* by G. Mall (1963) *Koroze betonu ve stavební praxi* by O. Dobrý and L. Palek (1988) *Ochrana stavebního díla proti korozi* by F. Vavřín and K. Retzl (1987)

development of new cements or inorganic binders like pore-reduced gypsum-free Portland cement (PRGFPC) [7, 8, 9] and in particular alkali-activated materials (aluminosilicate hydrates) [10, 11, 12, 13, 14, ...] with considerably improved properties including acid resistance necessitates more detailed investigations on their durability in aggressive acidic environments.

To limit the scope of this paper, the civil engineering aspects of the phenomenon including service life, repair and maintenance, protective layers, etc are not considered. We mostly concentrate on the material aspects of the acidic corrosion of hydrated cement based materials and the importance of the phenomenon, the involved mechanisms of deterioration and the rate controlling factors along with a survey of the literature from the year 1980 up to now (mostly the last decade) are discussed. The case of attack by carbonic acid or the phenomenon of carbonation which has been studied in detail is not of our principal interest and is discussed only briefly.

THE IMPORTANCE
OF THE PHENOMENON

Concrete can be subjected to attack by various inorganic and organic acids including sulfuric, nitric, hydrochloric, phosphoric, acetic, lactic and so on. However sulfuric acid can be considered as the most common cause of deterioration of concrete structures, since attack by which can occur in many various ways. Buried concrete structures can be attacked by groundwater. The presence of sulfuric acid in ground--water may be either naturally or due to dumping of chemical wastes from industrial processes.

In natural groundwater only sulfuric acid is likely to be found as a result of oxidation of sulfide minerals such as pyrites and marcasite, a process which is catalyzed by the presence of aerobic bacterium, thiobacillus ferro-oxidans [15]. Higher concentrations of sulfuric acid attack on concrete can occur in industrial environments in the forms of leakage and random spillage varying from a steady long term drip to a sudden and brief dousing [15, 16]. It is to be considered that disposal of colliery waste , ash from coal combustion in older power plants or from refuse incineration, or gasworks waste [17], can give rise to acidic groundwater.

Another important form of sulfuric acid attack which is very common all over the world and especially severe in hot climate occurs in sewage systems and usually is referred to as biogenic sulfuric acid corrosion. The harmful biogenic sulfuric acid is formed as the result of a relatively complex mechanism of both anaerobic and aerobic microorganisms [18, 19]. The deteriorating effect of biogenic sulfuric acid is relatively rapid and finally will lead to the failure of the sewer system. The corresponding repair expenses are unexpectedly very high for example 50 million DM for the sewer network of Hamburg city in the seventies [19].

Acidic rain or mist referred to as acid deposition or precipitation is another aggressive agent for cement concrete structures. The phenomenon which has been known from a long time nowadays has become worrying due to the growing activities in industrial areas particularly over the past decade. Irresponsible industrial emissions of sulfur and nitrogen compounds which later can be converted to sulfuric and nitric acids are encountered as the origin of such acid precipitations with a *pH* level ranging from 5.0 to 3.0 [20].

Chemical degradation of concrete structures exposed to aggressive agricultural chemicals which is often underestimated, is another serious technical and economical problem. Acetic acid along with some more organic acids such as lactic and formic acids , which are usually referred to as feed acids, can be produced in the natural degradation process of organic materials and in particular agricultural products. In animal houses and farms decomposition of meal or agricultural products in the presence of water leads to the formation of lactic and acetic acids resulting in acidic environment with a *pH* possibly lower than 4.5 [21, 22, 23]. In concrete silos, attack by the same acids which are present in silage effluent can result in leakage of the polluting effluent through wall [22].

MECHANISM OF THE PHENOMENON

Ordinary Portland cement (OPC) and its usual derivatives which are highly alkaline with *pH* values normally above 12.5 [24, 25, 26] are easily attacked by acidic solutions. As the *pH* of the solution decreases the equilibrium in the cement matrix is being disturbed, and the hydrated cement compounds are essentially altered by hydrolytic decomposition which leads to the severe degradation of the technical properties of the material. At *pH* values lower than 12.6 portlandite is the first constituent starting dissolution. If *pH* decreases to values lower than stability limits of cement hydrates i.e. calcium silicate, calcium aluminate, and calcium alumino-ferrite hydrates, then the corresponding hydrate loses calcium and decomposes to amorphous hydrogel. The final reaction products of acid attack are the corresponding calcium salt of the acid as well as hydrogels of silicium, aluminum, and ferric oxides [24 - 34]. The solubility of $Al_2O_3 \cdot aq$, and $Fe_2O_3 \cdot aq$ depends on the *pH* value of the acting solution, while $SiO_2 \cdot aq$ is insoluble in acidic solutions except in HF. At pH values less than 3 to 4, it dissolves $Al_2O_3 \cdot aq$ and at values less than 1.5 to 2, it also dissolves $Fe_2O_3 \cdot aq$ [26, 30]. The chemical reactions of OPC with a mono-proton acid of the general formula HA can be written as follows:

1. Direct attack of acid on portlandite:

$$Ca(OH)_2 + 2HA \rightarrow CaA_2 + 2\,H_2O$$
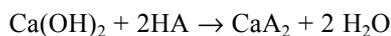
2. Decomposition of hydration products e.g. CSH:

$x\mathrm{CaO} \cdot y\mathrm{SiO}_2 \cdot n\mathrm{H}_2\mathrm{O} + 2x\mathrm{HA} \rightarrow$
$\rightarrow x\mathrm{CaA}_2 + y\mathrm{Si(OH)}_4 + (x + n - 2y)\mathrm{H}_2\mathrm{O}$
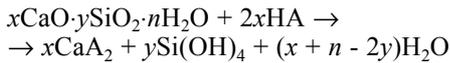
The corresponding reactions for high alumina cement (HAC) are as follows:

1. The first reaction is the aluminate hydrate decomposition by the acid:

$x\mathrm{CaO} \cdot y\mathrm{Al}_2\mathrm{O}_3 \cdot n\mathrm{H}_2\mathrm{O} + 2x\mathrm{HA} \rightarrow$
$\rightarrow x\mathrm{CaA}_2 + 2y\mathrm{Al(OH)}_3 + (x + n - 3y)\mathrm{H}_2\mathrm{O}$
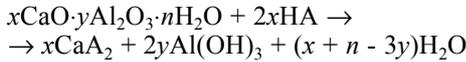
2. The first reaction is followed by attack on the aluminum hydroxide if the *pH* value of the acidic solution is below 4:

$2y\mathrm{Al(OH)}_3' + 6y\mathrm{HA} \rightarrow 2y\mathrm{AlA}_3 + 3y\mathrm{H}_2\mathrm{O}$
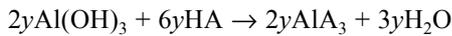
Therefore all the phases present in OPC and HAC react with acidic solutions and dissolution of phases occurs either congruently like portlandite or incongruently such as CSH phase causing residual layers on the exposed surface of material. The severity of the acid attack is significantly dependent on solubility of the calcium salt of acid and stability of the corroded layer.

At the beginning of the acid attack, the corrosion process which is very fast is controlled by diffusion of acid molecules and /or ions through solution to the surface and /or by the chemical processes taking place at the surface itself. As the corrosion process proceeds, the thickness of the corroded layer and hence its protective effect increases and finally the process becomes entirely diffusion controlled [33, 34, 36]. In the cases where the corroded layer is removed continuously without any considerable growth, the corrosion rate that is controlled by the interfacial processes, i.e. transport across the phase boundary or corrosion reactions, is maximum [36].

OTHER MECHANISMS OF DETERIORATION

In most cases, the mechanism of acid attack is not simply the formation of either soluble or insoluble calcium salt, and a corroded layer consisting of amorphous hydrogels. In fact some another physical and/or physico-chemical processes are involved. In the case where the reaction of acid with portlandite results in the formation of an insoluble or less soluble calcium salt, physical attack caused by crystallization of calcium salt may alter the total process of deterioration. The importance of deterioration due to physical attack by salt crystallization itself is discussed in a recently published paper by Yang et al [37]. Physical damage caused by salt crystallization manifest itself in the form of microcracks which finally lead to the mechanical failure, i.e. spalling [38]. The mechanism of attack is intensified particularly when the matrix is under the action of alternative wetting and drying cycles [37]. However if the cement matrix is continuously immersed in the acidic solution, the expansion caused by salt crystallization is less and even in some cases questionable.

It is to be noted that a little of salt crystallization and deposition of corrosion products in the relatively open pore structure of cement based material can make it denser with the corresponding consequences of increases in weight and compressive strength. Such a behavior generally seen within the first few days or weeks of attack and frequently reported by authors [38, 39, 40, 41], is temporarily and upon the continuation of attack the expansion by salt crystallization is high enough to show its deteriorating effects.

Another mechanism by which the total process of deterioration of acid attack may be accelerated is the expansion and crack propagation based on the formation of voluminous compounds such as Friedel′s salt and ettringite [24, 38, 41, 42, 43, 44]. Two of the several hypothesis that have been proposed to explain the mechanism by which ettringite formation causes expansion are based on the crystal growth of ettringite and water adsorption by which respectively [1]. In an experimental work Attigobe and Rizkalla [40] observed that in a 70 days period of exposure to 1 vol.% sulfuric acid solution an air-entrained concrete mixture showed negligible weight loss, comparing to 15% weight loss of a similar concrete mixture without any air entrainment. A similar effect for entrained air in concrete was also reported by Yang *et al* [37] in the process of concrete deterioration due to physical attack by salt crystallization. Such an improvement in chemical resistance of concrete can be explained by the effect of entrained air in relieving internal disintegrating stresses.

Shrinkage of the corroded layer due to leaching of the calcium salt can also accelerate the total process of deterioration. In general when the calcium salt of attacking acid is soluble, volume contraction of the cement matrix in the process of decalcification may result in the formation of cracks. These cracks make the transport of the acid molecules and/or ions and also dissolved constituents to and from the corrosion front easier than transport by diffusion through porous structure of the corroded layer and this means a higher rate of corrosion.

Sulfuric acid attack

In the case of sulfuric acid attack, although the formation of gypsum has been reported frequently, there is no agreement on its consequences. Some authors believe that the relative insolubility of gypsum leads to the formation of a protective layer which slows down the process of deterioration [33, 39, 46, 47], whereas some another authors report expansion and cracking due to the formation of gypsum [41, 48, 49, 50]. In an experimental work, Torii and Kawamura [41] attributed the progressive deterioration process accompanied by the scaling and softening of the matrix to the early decomposition of calcium hydroxide and the subsequent formation of large amount of gypsum. In another

experimental work, Israel *et al* [38] reported that sulfuric acid attack causes extensive formation of gypsum in the regions close to the surfaces, and tends to cause disintegrating mechanical stresses which ultimately lead to spalling and exposure of the fresh surface. They concluded that in the case of sulfuric acid owing to its poor penetration, the chemical changes of the cement matrix are restricted to the regions close to the surfaces, the conclusion made previously by other authors [40, 52, 53].

In an experimental work Reardon [54] simulated the phase changes that occur with the progressive addition of sulfuric acid to a mixture containing C_4AH_{13}, CH, and CSH. He concluded that in the *pH* range of 12.5 to 12 firstly calcium hydroxide and calcium aluminate hydrate dissolve and ettringite is formed. Later with decreasing *pH* in the range 11.6 to 10.6, gypsum is formed. Below *pH* value of 10.6, ettringite is no longer stable and will start decomposing into aluminium hydroxide and gypsum as previously confirmed by Gabrisova *et al* [55]. On the other hand with lowering the *pH* value below 12.5, the CSH phase is also subjected to cycles of dissolution and reprecipitation which continue until it is no longer stable at or below *pH* values of 8.8. Therefore knowing that the *pH* in the corroded layer changes from low values of the acidic solution to the values close to 12.6 in the undamaged cement matrix [24, 25, 26], ettringite is likely to be formed only in a layer adjacent to the undamaged part of the cement matrix having *pH* values in the range 12.5 to 12 as reported by Madrid *et al* [43]. This explains that why the appearance of ettringite in the exposed specimens have been reported occasionally.

The chemical reactions involved in sulfuric acid attack on cement based materials can be given as follows:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$$

$$3\,CaO \cdot 2\,SiO_2 \cdot 3H_2O + H_2SO_4 \rightarrow$$
$$\rightarrow CaSO_4 \cdot 2H_2O + Si(OH)_4$$

$$3\,CaSO_4 + 3\,CaO \cdot Al_2O_3 \cdot 6H_2O + 26\,H_2O \rightarrow$$
$$\rightarrow 3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 32H_2O$$
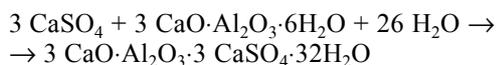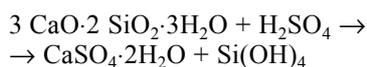
Hydrochloric acid attack

The effect of hydrochloric acid on cement based materials have been studied by some authors [15, 24, 28, 38, 57]. The chemicals formed as the products of reaction between hydrochloric acid and hydrated cement phases are some soluble salts, mostly with calcium, which are subsequently leached out, and some insoluble salts along with amorphous hydrogels which remain in the corroded layer. Chandra [24] hypothesized that besides dissolution, the interaction between hydrogels may also result in the formation of some Fe-Si, Al-Si, Ca-Al-Si complexes which appear to be stable in *pH* range above 3.5. In addition Chandra also mixed pure C_3A synthesized in laboratory with hydrochloric

acid. Indications were received for the formation of Friedel's salt, $C_3A \cdot CaCl_2 \cdot 10H_2O$, by the action of $CaCl_2$, formed due to the reaction of hydrochloric acid with $Ca(OH)_2$, and C_3A phase. He concluded that attack by hydrochloric acid is a physico-chemical process of deterioration. Formation of the expansive Friedel's salt was also reported by some another authors [38, 58, 59, 60]. On the other hand De Ceukelaire [28] did not confirm Chandra's hypothesis concerning a supplementary expansive reaction due to hydrochloric acid attack. Since the voluminous Friedel's salt was not traced in his work, he concluded that the difference in the used acid concentrations could have an influence on the formation of certain reaction products.

Hydrochloric acid attack is a typical acidic corrosion which can be characterized by the formation of layer structure [24, 28, 38, 61]. Chandra [24] studying the influence of 15 vol.% HCl on mortar prisms made with Portland cement (PC) divided the cross section of damaged prisms into three main zones; undamaged zone, hydroxide mixture zone or brown ring, and attacked zone. By hydroxide mixture zone, he referred to a layer formed by undissolved salts seen as a dark brown ring.

Aggressive attack of nitric acid

The corrosion of hardened cement paste by nitric acid was studied in detail by Pavlík [26, 33, 34, 35]. He reported [26] that the corroded layer developed by the action of nitric acid solution with concentrations ranging between 0.025 to 0.5 mol l^{-1} is soft, and porous with visible cracks. He added that the color of such a corroded layer is white with the exception of a relatively thin brown zone adjacent to the uncorroded cement paste. Pavlík [26] analyzed the chemical composition of the two main zones in the corroded layer. The white zone of the corroded layer was almost totally composed of SiO_2, i.e. 96.7 wt.%, while the brown zone contained a markedly increased amount of ferric oxide, i.e. 15.7 wt.% besides a high content of SiO_2, i.e. 79.1 wt.%.

Nitric acid attack is a typical acidic corrosion for shrinkage of the corroded layer due to leaching of highly soluble calcium nitrate. Pavlík and Unčík [34] reported values of approximately 13 % and 7 % of shrinkage per length of the corroded layer for OPC paste with a *w/c* = 0.5 exposed for a period of nearly 300 days to solutions of nitric and acetic acids respectively. Such volume contractions of the corroded layer, especially for the case of nitric acid, can result in the formation of visually observable cracks across the corroded layer. In the presence of these cracks the transport rate of acid and corrosion products to and from the corrosion front increases and this accelerates the process of deterioration.

Acetic acid attack

According to Pavlík [26], attack by acetic acid

resembles the process of corrosion in nitric acid. However the growth of the corroded layer in solutions of acetic acid is relatively slower than that in the same concentrations of nitric acid solution. Attack of acetic acid with concentration of 0.5 mol l^{-1} on hardened PC paste with a *w/c* = 0.4, resulted in the formation of a whitish or light brown corroded layer along with a very thin gray zone in the vicinity of the core. The chemical composition of the corroded layer was different from that observed in nitric acid solution of the same concentration. Pavlík [26] stated that this difference is probably due to the higher pH values of the acetic acid solution, and due to its buffering effect in the corroded layer. At lower concentrations of acetic acid, the color of the corroded layer became darker due to the increasing content of hydrated ferric oxide.

Pavlík [26] further showed that the corrosion of PC paste in low concentrations of both acetic and nitric acid solutions, e.g. 0.025 mol l^{-1}, results in the formation of an additional zone, called as core-layer, which is located behind the corroded layer. This core-layer with light gray color, is relatively hard and grows with time. Chemical compositions of the core-layers developed in both acetic and nitric acid attacks are similar. In both cases an important difference between the chemical compositions of the core-layers and the corresponding unaffected cores of the cement pastes is in the content of CaO. Pavlík [26] concluded that this core-layer originates due to portlandite dissolution in the unaffected part of the cement paste and diffusion of Ca^{2+} and OH^- ions towards the corrosion zone (*pH* = 7) where they meet the acid diffusing from the opposite direction. Pavlík stated that formation of the core layer is noticeable only when the concentration of acid is low because in such a case the rate of diffusion of H^+ ions from the acidic solution is high enough to dissolve portlandite, but not sufficiently high to decalcify the other hydrates.

Corrosion due to carbonic acid attack

When cement based materials are exposed to atmospheric carbon dioxide or carbonic acid i.e. dissolved CO_2 in water, a reaction producing carbonates takes place which is accompanied by shrinkage. The process is simply termed as carbonation. Reaction of cement based materials with atmospheric CO_2 is generally a slow process and is highly dependent on the relative humidity of the environment, temperature, permeability of the material, and concentration of CO_2 [64]. Carbonation of concrete with atmospheric CO_2 occurs at a rapid rate at 50 to 75% relative humidity and is accelerated by open pore structure[64]. The results of carbonation can be beneficial or harmful depending on the extent to which it occurs. Limited carbonation of surface layer of concrete is known to seal the pores by forming calcium carbonate, which may have the effect of reducing the permeability and increasing the strength of the carbonated layer [64]. However continued carbonation may cause a reduction in alkalinity of the cement paste which can be a serious problem not only in depassivation and corrosion of steel bars but also in dissolution of cement hydrates. Grube and Rechenberg [36] described that continued carbonation due to carbonic acid attack causes:

1　The transformation of calcium carbonate into soluble bicarbonate which is removed by leaching into the acidic solution and thus increasing the porosity:

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

$$CaCO_3 + H_2CO_3 \Leftrightarrow Ca(HCO_3)_2$$
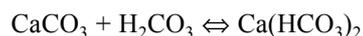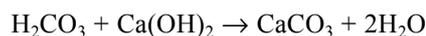
2.　Decomposition of other products of cement hydration, leading to the formation of a gel-like layer consisting of hydrogels of silica, alumina, and ferric oxide.

Carbonic acid attack usually occurs in the case of buried concrete structures exposed to acidic ground-water for a long time. Atmospheric carbon dioxide absorbed by rain enters groundwater as carbonic acid. The rate of attack depends upon the quality of the concrete, the concentration of the aggressive carbon dioxide, and mostly the external exposure conditions. It has been reported in some studies that water containing more than 20 parts per million (ppm) of aggressive CO_2 can result in rapid carbonation of the hydrated cement paste. On the other hand, freely flowing waters with 10 ppm or less of aggressive CO_2 may also result in significant carbonation [64].

Acknowledgement

References

1.　Mehta P.K., Schiessl P., and Raupach M.: Proc. Int. Cong. Chem. Cement, NCCB, New Dehli, India, vol. IB, 571-659, 1992.
2.　Krivenko P. V.: Proc. Int. Conf. Alkaline Cem. & Concr. 2nd, pp. 3-43, Kyiev, Ukraine, 1999.
3.　Mullick A.K., and Chandra S.: Proc. Int. Cong. Chem. Cement, pp. 695-734, NCCB, New Dehli 1992.
4.　Mater. Res. Soc. Symp. Proc., vol. 137, *Pore structure and permeability of cementitious materials*, by Robert L.R. and, Skalny J.P., 1989.
5.　Vyrodov I.P. and, Lekarev V.M.: Proc. Int. Cong. Chem. Cement, pp.256-261, NCCB, New Dehli 1992.
6.　Struble L.: Cem. Res. Progress, Edited by Brown P.W., Am. Ceram. Soc., pp. 157-238, 1989.
7.　Škvára F.: Mater. Res. Soc. Symp. Proc. *370*, 153 (1995).
8.　Škvára F.: Ceramic-Silikáty *40*, 36, (1996).
9.　Škvára F.: Ceramic-Silikáty *38*, 159-162, (1994).
10.　Proc. Int. Conf. Alkaline Cem. & Concr. 1st, Kyiev,

Ukraine, 1997.

11. Proc. Int. Conf. Alkaline Cem. & Concr. 2nd, Kyiv, Ukraine, 1999.

12. Škvára F., Bohuněk J.: Ceramic-Silikáty, *43*, 111 (1999).

13. Rostami H., Silverstrim T.: Proc. Annual Int. Pittsburgh Coal Conf. 13th (2), pp. 1074-1079, 1996.

14. Silverstrim T., Rostami H., Clark B., and Martin J.: Proc. Int. Conf. Cem. Microsc. 19th, pp. 355-373, 1997.

15. Harrison W.H.: Concrete *21*, 18 (1987).

16. Pulm D.R., Hammersly G.P.: Concrete *18*, 8 (1984).

17. Plowman C.: Stud. Environ. Sci. *60*, 917 (1994).

18. Schmidt M., Hormann K., Hofmann F.J., Wagner, E.: Betonwerk Fertigteil Tech. *63*, 64 (1997).

19. Hormann K., Hofmann F.J., Schmidt M.: Proc. Int. Cong. Chem. Cement 10th, Gothenburg, Sweden, 4, 4iv038, 4pp, 1997.

20. Sersale S., Frigione G., Bonavita L.: Cem. Concr. Res. *28*, 19 (1998).

21. De Belie N., Verselder H.J., De Blaere B., Nieuwenburg D.V., Verschoore R.: Cem. Conc. Res. *26*, 1717 (1996).

22. De Belie N., Debruyckere M., Nieuwenburg D.V., De Blaere B.: ACI Mater. J. *94*, 43 (1997).

23. De Belie N., De Coster V., Nieuwenburg D.V.: Mag. Conc. Res. *49*, 337 (1997).

24. Chandra S.: Cem. Conc. Res. *18*, 193 (1988).

25. Revertegat E., Richet C., and Gegout P.: Cem. Conc. Res. *22*, 259 (1992).

26. Pavlík V.: Cem. Conc. Res. *24*, 1495 (1994).

27. Bajza A. : Mater. Res. Soc. Symp. Proc. *137*, 325 (1989).

28. De Ceukelaire L.: Cem. Conc. Res. *22*, 903 (1992).

29. Bajza A., Rouseková I. : Proc. FIP Symp. Budapest, HSSB, pp. 275-280,1992.

30. Bajza A.: Proc. Int. Cong. Chem. Cement 9th, NCCB, New Dehli, India, vol. V, 402-408, 1992.

31. Bajza A., Rouseková I., Unčík S.: Slovak J. Civil Eng. *4*, 26 (1994).

32. Delagrave A., Pigeon M., Revertegat E.: Cem. Conc. Res. *24*, 1433 (1994).

33. Pavlík V.: Cem. Conc. Res. *24*, 551 (1994).

34. Pavlík A., Unčík S.: Cem. Conc. Res. *27*, 1731 (1997).

35. Pavlík A.: Cem. Conc. Res. *26*, 475 (1996).

36. Grube H., Rechenberg W.: Cem. Conc. Res. *19*, 783 (1989).

37. Yang Q., Wu X., and Huang S.: Proc. Int. Cong. Chem. Cement 10th, Gothenburg, Sweden, 4, 4iv032, 5pp, 1997.

38. Israel D., Macphee D.E., Lachowski E.E.: J. Mater. Sci. *32*, 4109 (1997).

39. Mehta P.K.: Cem. Conc. Res. *15*, 969 (1985).

40. Attigobe E.K., and Rizkalla S.H.: ACI Mater. J. *85*, 481 (1988).

41. Torii K., and Kawamura M.: Cem. Conc. Res. *24*, 361 (1994).

42. Ravindrarajah R.S., and Mercer C.M.: *Durability of Build. Mater. and Comp.*, edited by; Nagataki S., Nireki T., and Tomosawa F., 1993 E&FN Spon.

43. Madrid J., Diez J.M., Goni S., Macias A., Proc. Int. Cong. Chem. Cement, Gothenburg, Sweden, 4, 4iv040, 9pp, 1997.

44. Stegemann J.A., Shi C.: Stud. Environ. Sci. *71*, 551 (1997).

45. Marsh B.K., Joshi R.C.: Durability Build. Mater. *4*, 67 (1986).

46. Fattuhi N.I., Hughes B.P.: Cem. Conc. Res. *18*, 545 (1988).

47. Cohen M.D., Mather B.: ACI Mater. J. *28*, 62 (1991).

48. Lawrence D.: Mag. Conc. Res. *42*, 249 (1990).

49. Wang J.G.: Cem. Conc. Res. *24*, 735 (1994).

50. Gollop R.S., Taylor H.F.W.: Cem. Conc. Res. *25*, 1581 (1995).

51. Fattuhi N.I., Hughes B.P.: Cem. Conc. Res. *13*, 655 (1983).

52. Raju P.S.N., Dayaratnam P.: Build. Envir. *19*, 75 (1984).

53. Hendrik L.K., Orbison J.G.: ACI Mater. J. *84*, 110 (1987).

54. Reardon R.J.: Cem. Conc. Res. *20*, 175 (1990).

55. Gabrisova A., Havlica J., Sahu S.: Cem. Conc. Res. *21*, 1023 (1991).

56. Berke, N.S., Durning T., and Hicks M. C.: Proc. Int. Corros. Cong., 12th, 5A, 3242-3259, NACE, Houston, Tex., U.S.A., 1993.

57. Kilinckale F.M.: Cem. Conc. Res. *27*, 1911 (1997).

58. Midgley H.G., Illston J.M.: Cem. Conc. Res. *14*, 546 (1984).

59. Beaudoin J.J., Ramachandran V.S., Feldman R.F.: Cem. Conc. Res. *20*, 259 (1990).

60. Al-amoudi O.S.B., Rasheeduzzafar M., Maslehuddin M., Abduljauwad S.N.: Mag. Concr. Res. *46*, 113 (1994).

61. Moskvin V.M., Rubetskaya T.V., Ljubarskaya G.V.: Beton i Zhelezobeton *10*, 10 (1971).

62. Lea F.M.: Mag. Conc. Res.. *17*, 52, 115 (1965).

63. Bayoux J.P., Letourneux J.P., Marcdargent S., Verschaeve M.: Proc. Int. Symp. on High alumina cement. E. and F.N. Spon, London, U.K., 1990.

64. Committee Report ACI 201.2R: ACI Mater. J. *88*, 544 (1991).

Submitted in English by the authors.