

**Mechanism of Deterioration and Mix
Design of Durable Concrete Structures**

by M. Collepardi*

Synopsis: The mechanisms of concrete deterioration have been recently reviewed by Mehta (1, 2). Only few complementary aspects of this subject have been examined in the present report: *a*) influence of pozzolanic additions on the carbonation process; *b*) effect of chloride-based deicing salts on concrete deterioration; *c*) influence of temperature on the sulfate attack.

The above items have been critically considered with respect to ACI and ENV recommendations for durable concrete.

A mix design case history, in agreement with the American and European standard requirements, has been adopted to diagnose and repair a deteriorated dry dock concrete structure.

Keywords: Carbonation. Chloride attack. Sulfate attack. Durability. Pozzolan additions. Air-entrainment. Mix design.

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INTRODUCTION

Concrete durability is defined as the ability of a material to resist weathering action, chemical attack, or any other process of deterioration. Concrete structures in the field of civil engineering are substantially exposed to very few types of aggressive actions caused by atmospheric environments or natural waters and soils containing chemicals, in particular:

- Carbonation of concrete
- Freezing-thawing
- Penetration of chloride-based salts used as deicers
- Seawater attack
- Sulfate attack

The deterioration mechanism of these aggressive actions have been recently reviewed by Mehta et al. (1, 2), whereas the relevant recommendations for durable concrete structures exposed to these actions have been studied by ACI Committee 201 (3).

The main objective of this paper is to give additional information on some deterioration mechanisms and to try for a critical evaluation of the above ACI recommendations (3) in comparison with those recently emanated from the European Committee for Standardisation (4). An example of mix design for durable concrete on the basis of the American and European standard requirements will also be examined in this paper in the form of a case study.

The present article purposely does not deal with the aggressive actions caused by special chemicals, such as organic and inorganic acids, which may attack concrete structures in industrial processes. These special actions are covered by ACI Committee 515 (5), whereas the relevant concrete deterioration mechanisms have been examined by Biczok (6) and more recently by Mullick and Chandra (7).

CONCRETE DETERIORATION MECHANISMS

Mehta (1) has reviewed critically the most recent available data in comparison with the extensive literature about concrete deterioration published during the past time.

In the present paper only few complementary aspects of the deterioration mechanisms will be examined in relation to some specific requirements recommended for durable concretes, in particular:

- Influence of pozzolans on the carbonation process
- Effect of sodium and calcium chloride on concrete deterioration
- Influence of temperature on the sulfate attack

Influence of pozzolans on concrete carbonation

In general, portland cement concrete provides adequate protection of steel reinforcements against corrosion. The protective action of the concrete is mainly ascribed to its high alkalinity produced by $Ca(OH)_2$ formed by portland cement hydration. However, in porous concrete structures, especially those with relatively small depth of cover, carbon dioxide can easily and quickly penetrate the concrete cover by reacting with $Ca(OH)_2$ and then removing the protective value of the concrete against the steel corrosion.

When pozzolanic additions, such as fly ash or ground blast-furnace slag, are used in the concrete mix there are potentially two effects on the penetration of CO_2 through the cover and its protection against the steel corrosion. These are:

- Reduction of lime content caused by the pozzolanic reaction: this effect is more remarkable where the mineral addition substitutes for part of portland cement rather than used in the concrete mix as independent ingredient without reducing the cement content.
- Transformation of lime into calcium silicate hydrated (*C-S-H*) and reduction of porosity in the cement matrix.

The reduction of lime accelerates the CO_2 penetration whereas the production of *C-S-H* retards the diffusion of carbon dioxide as well as other molecules, such as oxygen and water, which are involved in the corrosion process of embedded steel. Figures 1 and 2 show the influence of fly ash (type F) and slag, respectively, on the penetration of CO_2 through concrete specimens exposed to air after a moist curing of 7 days. In Tables 1 and 2 the compositions of the concrete mixtures of Fig. 1 and 2, respectively, are shown. When fly ash or slag are used without reducing the normal portland cement content, the CO_2 penetration rate is reduced, and this means that the *C-S-H* formation caused by the pozzolanic reaction is more effective than the reduction in the lime content, so that the total effect results in a reduction of the CO_2 penetration. On the other hand, when the mineral additions replace part of portland cement content, the CO_2 penetration rate is accelerated. For instance, the initial penetration rate is 1.3 mm/month in the reference concrete mixture with a cement factor of 300 kg/m^3 and becomes 1.5 mm/month when 50 kg/m^3 of cement is replaced by fly ash (Fig. 1). This effect becomes more significant in leaner concrete mixes and with higher percentages of mineral additions. This means that the reduction in lime content, caused by both pozzolanic reaction and decrease in portland cement content, becomes more effective than the *C-S-H* formation, and the total result is an increase of the CO_2 penetration.

From a practical point of view, when fly ash or slag are needed in lean concrete mixes for other beneficial effects on reinforced concrete structures (e.g. to produce sulfate-resistant concrete), their negative influence on

concrete carbonation and protection of embedded steel against corrosion should be compensated for one of the following methods:

- Mineral additions should be used without reducing the portland cement content.
- Substitution of fly ash and slag for portland cement should be accompanied by a counter-balancing reduction in the *w/c* ratio and/or an increase in the concrete cover depth in order to produce a less porous cement matrix and/or increase the path length of CO_2 from the environmental air to the reinforcement.

Effect of sodium and calcium chloride on concrete deterioration

Sodium and calcium chloride are widely used as deicing salts to remove ice from concrete pavements. It is well known that chloride can diffuse through the concrete cover and induce pitting corrosion of embedded steel. It was also learned that these salts cause or accelerate concrete surface deterioration in the form of scaling, and the mechanism of such damaging effect has been ascribed to physical rather than chemical actions (3). However, Chatterji (8,9) has found that sodium and calcium chloride can also affect concrete durability through chemical actions as well. Sodium chloride can aggravate alkali-silica reaction when potentially reactive aggregates are used (8), whereas calcium chloride can react with the cement paste by producing disruptive stresses (9). Collepardi et al. (10, 11) have found that $CaCl_2$ reacts with $Ca(OH)_2$ produced by portland cement hydration and forms a calcium oxychloride hydrate ($3CaO \cdot CaCl_2 \cdot 15H_2O$) which is responsible for this specific chemical action. They have found that fly ash and especially blast furnace slag or silica fume counter-act the $CaCl_2$ attack by reducing the $Ca(OH)_2$ content in the cement paste (12). Therefore, in concrete structures exposed to freezing-thawing and deicers actions, pozzolanic additions in the form of fly ash, slag, or silica fume should be advantageously used, besides air-entraining agents and water reducers, to improve the chemical protection of the aggregate against the alkali-aggregate reaction caused or aggravated by $NaCl$, and of the cement paste against the oxychloride produced by $CaCl_2$ (13). Moreover, Collepardi et al. (12) have found that even in the absence of pozzolan additions concrete can resist the $CaCl_2$ attack provided that a *minimum* air volume is entrained which corresponds to the *average* value recommended by ACI 201 in severe exposure (frost and deicers actions).

Influence of temperature on the sulfate attack

There are three chemical reactions involved in sulfate attack on concrete:

- Combination of free $Ca(OH)_2$ produced by the hydration of portland cement with sulfate to form gypsum ($CaSO_4 \cdot 2H_2O$).
- Combination of gypsum and calcium aluminate hydrate (*C-A-H*) to form ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$).
- Combination of gypsum and calcium carbonate with *C-S-H* to form thaumasite ($CaCO_3 \cdot CaSiO_3 \cdot CaSO_4 \cdot 15H_2O$).

All these reactions result in an expansion and disruption of concrete, and thaumasite in particular is accompanied by a very severe damaging effect which is able to transform hardened concrete in a pulpy mass (Fig. 3).

Thaumasite formation is favoured by high relative humidities ($> 90\%$) and temperatures as low as 0 to $10^\circ C$ (13). Independently of the thaumasite formation, there are indications that lower temperatures in the range of 0 to $10^\circ C$ favour a more severe attack caused by ettringite (14, 15) and gypsum formation (16).

Cement paste specimens have been kept in a 10% $MgSO_4$ aqueous solution at $5^\circ C$ or $20^\circ C$, and the resistance to sulfate attack has been monitored by determining changes in compressive strength, length, and dynamic modulus of elasticity. Thaumasite formation has been avoided purposely by protecting the specimens from carbonation: in the absence of $CaCO_3$ only ettringite can be formed besides gypsum. The specimens at $5^\circ C$ have been damaged much more severely than those at $20^\circ C$ (Fig. 4), although the XRD patterns (Fig. 5) indicate that approximately the same amount of ettringite is formed. A different morphology (Fig. 6) of ettringite crystals developed at $5^\circ C$ or $20^\circ C$ and could be responsible for the different damaging effect: more colloidal or less crystallized ettringite formed at $5^\circ C$ would adsorb more water and swell to a greater extent in agreement with the Mehta theory (17).

On the other hand, at $5^\circ C$ a much higher amount of gypsum has been found by XRD (Fig. 5). Gypsum is produced in form of large and well-grown crystals on which very fine crystals of ettringite are deposited (Fig. 6A).

It is difficult to conclude whether the more severe damaging effect at $5^\circ C$ is ascribable to either the different morphology of ettringite or the larger amount of gypsum. However, from a practical point of view the above results would indicate that the sulfate attack is much more severe in concrete structures exposed to cold weather. Therefore, a lower *w/c* ratio should be designed for durable concrete devoted to structures exposed to sulfate attack and cold climates in service. It has been found that at hygrothermal conditions favorable for the formation of thaumasite (13, 18), as well as for large amounts of gypsum and/or more colloidal forms of ettringite, a *w/c* ratio lower than 0.40 is required to produce concretes able to resist the sulfate attack. In such a case, a relatively higher dosage of superplasticizer (for example, about 0.8% as dry sulfonated naphthalene polymer by weight of cement) is required to produce a workable concrete mix which is able to resist the sulfate attack.

REQUIREMENTS FOR DURABLE CONCRETE IN NORTH AMERICA AND EUROPE

Requirements for durable concrete in North America are included in the mission of ACI Committee 201 (3), and the standard recommendations will be examined in the present paper as "ACI 201 requirements". More recently, even in Europe there are standard specifications (4) for durable concrete which in the present article will be called "ENV 206 requirements".

Two comprehensive tables have been prepared in the original ENV 206 standardization giving a classification of all the possible environments ("exposure classes") and the corresponding requirements in terms of *w/c* ratio, air entrainment, etc. to attain durable concretes. There are five exposure classes (rated as 1 for the least aggressive environment and 5 for the most aggressive conditions) which include carbonation, freezing-thawing, deicing salts, seawater, and chemical aggressive agents mainly based on sulfate attack. In some cases, exposure sub-classes (2a and 2b; 4a and 4b; 5a, 5b, and 5c) have also been provided to take into account freezing-thawing effects combined with other aggressive agents (2a and 2b, 4a and 4b) or different levels in the concentration of chemical (5a, 5b, and 5c).

On the other hand, the ACI 201 requirements are given in form of tables which are different from those reported by ENV 206: for instance, the seawater attack is included in the table dealing with the sulfate attack. Moreover, many recommendations are given not in the form of specific or comprehensive tables, but in form of general statements or specific sentences: for instance, the reinforced concrete structures exposed to a fluctuating seawater level are not included in the same table as that devoted to marine concrete.

In order to compare the ACI 201 requirements with those given by ENV 206, all the data in form of tables or general statements have been segmented and then re-arranged by the author by trying to find the most similar environmental exposure situations. Tables 3 to 8 summarize the results of this effort. In particular, Table 3 deals with concrete structures exposed to carbonation; Table 4 gives the requirements for frost-resistant concrete; Table 5 indicates the requirements of durable concrete exposed to freezing-thawing and deicing salts; Table 6 deals with durable concrete exposed to seawater; Table 7 indicates the requirements for durable concrete exposed to seawater and frost action; Table 8 deals with sulfate resistant concretes.

Moreover the ENV 206 requirements have been integrated by: a) the specification for the concrete cover depth given by Eurocode No. 2 (19), another European Standardisation more specifically devoted to problems of structure design; b) by the ISO/DP 9690 (20) giving the classification of environmental exposure for chemical aggressive agents, and in particular for the sulfate attack.

Some general comments on the main differences in requirements between ENV 206 and ACI 201 are noted:

1. The air volume required in concrete structures exposed to frost action is in general slightly higher in the ACI 201 requirements than in the corresponding ENV 206 ones. Figure 7 indicates the *minimum* air volume for ENV 206 and the corresponding *average* value (with a tolerance of 1.5%) for ACI 201. The latter provides two different levels of air volume depending on the moderate or severe exposure. In the opinion of the author, ACI 201 and especially ENV 206 appear to be a little "optimistic" for the life in service of concrete structures exposed to frost action and deicing salts (Table 5). Recent experiments (12) have indicated that in the absence of a *minimum* air volume, corresponding to that required as an *average* value by ACI 201 for severe exposure, portland cement concretes exposed to $CaCl_2$ as deicer are seriously damaged independently of the frost action, because of the oxychloride formation examined in the present paper. According to these results, for the *exposure class* 3 in ENV 206, a higher level in the *minimum* air volume (about 2% more) should be a better requirement unless pozzolan additions are used.
2. Even for the *w/c* ratio requirement, ENV 206 appears to be less restrictive than ACI 201; for all the aggressive exposure situations (Table 4 to 8) the maximum *w/c* required by ENV 206 is higher than the corresponding value recommended by ACI 201, except for reinforced concrete structures exposed to carbonation (dry or humid air) for which ACI 201 does not give specific requirements (Table 3). Therefore, it seems that in general a better concrete quality, in terms of *w/c* ratio is required for durable concrete by ACI 201 than by ENV 206.
3. The lower quality of concrete, for both higher *w/c* ratio and lower air volume, is compensated by thicker concrete cover required by ENV 206 - Eurocode No. 2 comparing to ACI 201, except for the special case of roadway decks and adjacent appurtenances where ACI 201 recommends nominal cover of at least 50 mm (Table 5). It is difficult to say whether thicker cover depths, as those required by ENV 206, can compensate for the lower quality concrete in protecting the embedded steel against corrosion. Moreover, it seems that concrete cover as thick as 50 mm (required by Eurocode No. 2 for prestressed concrete in exposure classes 3, 4a, 4b, and 5c) could be a problem for very thin section, as sometimes required particularly in precast prestressed structures.
4. Neither ENV 206 nor ACI 201 specify any particular type of cement or mineral additions for concrete structures exposed to $NaCl$ or $CaCl_2$ as deicing salts (Table 4). There is evidence that concrete with pozzolan or slag cements, or with mineral additions used as independent pozzolanic

ingredients besides portland cement, would perform much better in resisting both the attack of $NaCl$ against reactive aggregate and that of $CaCl_2$ against the $Ca(OH)_2$ of the cement paste, as it has been shown in the present paper.

- 5. There is also evidence that the sulfate attack becomes more severe when the environmental temperature is low ($< 10^\circ C$), and the relative humidity is high ($> 90\%$). These hygrothermal conditions favour the thaumasite formation and may aggravate the sulfate attack related to gypsum and/or ettringite production. A w/c ratio as low as 0.40 would be required (13, 18) to produce durable concrete exposed to cold climates. This value appears to be significantly lower than the maximum w/c ratio (0.45) recommended by ACI 201 and ENV 206 even when the most severe sulfate attack is taken into account (Table 8).
- 6. When the aggressive environmental action is due to carbonation alone, portland cement in general should be preferred to a partial replacement of cement by a pozzolan or slag for durable reinforced concrete structures. Because of the higher content of $Ca(OH)_2$ generated by portland cement hydration, with respect to that present in concrete with pozzolan or slag cement, the embedded steel would be more protected against corrosion. This would be particularly true in lean concrete mixes as it is in the case of relatively high w/c ratios required by ENV 206 (Table 3) or in the absence of any specific requirement (ACI 201). When pozzolan or slag cement should be preferred for other beneficial effects, as for instance in the case taken into account by ACI 201 for concrete exposed to sulfate attack, carbonation is not a problem since the low w/c required (0.40 - 0.50 in Tables 7 and 8) produces a low porosity concrete which is able to reduce the penetration of CO_2 as well as that of oxygen and humidity, and protect the steel reinforcement against corrosion.

MIX DESIGN CRITERIA FOR DURABLE CONCRETE STRUCTURES

In general, the design compressive strength (σ_c) determines the w/c ratio of the concrete through a σ_c versus w/c ratio relation as that shown, for instance, in Fig. 8 for ordinary portland and pozzolan cements available in Italy (type 325).

However, when durable concretes should be produced, the w/c ratio determined by the design compressive strength must be compared with that required by durability criteria, as those summarized in Table 3-8, and therefore the following limiting restriction should be met:

$$\sigma_c \longrightarrow w/c < (w/c)_D$$

where $(w/c)_D$ is the maximum water/cement ratio allowed by durability criteria. If this restriction is not met, the $(w/c)_D$ should determine the compressive strength (σ_{CD}) which obviously will be higher than σ_c designed on the basis of mechanical loading only:

$$(w/c)_D \longrightarrow \sigma_{CD} > \sigma_c$$

In the following section a practical example, in form of a case history, will be examined where the mix design procedure has been used to diagnose the deterioration mechanism and repair the deteriorated concrete structures of a dry dock construction.

Repair of a deteriorated dry dock

The peripheral walls of a dry dock have been seriously damaged by the action of seawater in combination with wetting-drying cycles which determined more than moderate concentrations of chloride and sulfate into the concrete for a depth of about 100 mm in less than 8 years. The local warm weather has favoured the diffusion of chloride and sulfate ions into the concrete. The steel reinforcement has been severely corroded, thus creating a subsequent disruptive stress on the already damaged concrete cover.

On the other hand, the reinforced pavement of the dry-dock exposed to the same aggressive conditions was sound and with negligible penetration of chloride.

The thickness of the concrete cover was 40 mm for the walls as well as for the pavement.

Natural aggregate with maximum size of 30 mm and ordinary portland cement (OPC) were used for both of these structures.

The original compressive strength (on cylindrical specimens) designed for the concrete of the walls (σ_{CW}) and the pavement (σ_{CP}) can explain the different behaviour of the two structures:

$\sigma_{CP} = 45 \text{ MPa}$	(for the concrete of pavement)
$\sigma_{CW} = 20 \text{ MPa}$	(for the concrete of walls)

The reason why the structural civil engineers adopted relatively low design compressive strength for the concrete of the walls was due to the lower mechanical stress considered to be negligible in comparison with the high dynamic loads acting on the top of pavement devoted to dry dock activities in service. However, the "chemical loading" caused by the seawater penetration and its consequent aggressive action on the concrete, as well as on the embedded steel, were completely ignored notwithstanding a disconcerting number of cases have been reported in which expensive works have been required to repair damages caused by steel corrosion promoted by seawater (3).

By using the OPC curve of Fig. 8 the water/cement ratios adopted for the structures (corresponding to the above values of design compressive strength) have been determined.

$$\begin{aligned} \sigma_{CP} = 45 \text{ MPa} &\longrightarrow (w/c)_P = 0.40 && \text{(with OPC)} \\ \sigma_{CW} = 20 \text{ MPa} &\longrightarrow (w/c)_W = 0.70 && \text{(with OPC)} \end{aligned}$$

By examining the ACI 201 requirements for seawater reinforced structures, the maximum water/cement ratio exposed to fluctuating water level (Table 6) for durable concrete the $(w/c)_D$ value should be not higher than 0.45 with a cover of at least 38 mm. Thus, the designed compressive strength, as a matter of fact, has determined a durable concrete for the pavement, but not for the walls:

$$\begin{aligned} \sigma_{CP} = 45 \text{ MPa} &\longrightarrow (w/c)_P = 0.40 < (w/c)_D = 0.45 \\ \sigma_{CW} = 20 \text{ MPa} &\longrightarrow (w/c)_W = 0.70 > (w/c)_D = 0.45 \end{aligned}$$

Even with the less restrictive ENV requirement for the w/c ratio (< 0.55) of structures exposed to seawater (Table 6), the concrete could be durable for the pavement but not for the walls.

For the mix design of the repairing concrete, a $(w/c)_D$ ratio of 0.40 was adopted. This value meets the most restrictive requirement of ACI 201 (Table 6) for the w/c ratio of durable maritime works exposed to fluctuating water level. On the other hand, for the concrete cover a depth of 40 mm was adopted to meet the most restrictive requirement of ENV 206 for reinforced concrete structures exposed to seawater (Table 6).

Because of the relatively small section to be repaired (100 mm) and the special technique adopted (flowing concrete poured between the scarified concrete surface and a formwork) the maximum size of the coarse natural aggregate was limited to 19 mm. With this aggregate the amount of mixing water to produce a self-levelling mix with a slump of 240 mm was limited to 160 kg/m^3 due to the presence of a 40% aqueous solution naphthalene-based superplasticizer (2% by weight of cement). Therefore, a pozzolan cement (ACI 201 in Table 6) content of 400 kg/m^3 was adopted:

$$(w/c)_D = 0.40 \qquad w = 160 \text{ kg/m}^3$$

$$c = (w)/(w/c) = 160/0.40 = 400 \text{ kg/m}^3$$

An entrapped-air volume of 2% has been considered and then the balancing volume of aggregate has been determined for 1 m^3 of concrete:

$$V_a = 1000 - (400/3.10) - 160 - 20 = 690 \text{ L/m}^3$$

where 3.10 is the specific gravity of cement and V_a is the volume of the aggregate in liters per 1 m^3 of concrete. The weight of the aggregate (a) with a specific gravity of 2.69 is then:

$$a = V_a \cdot 2.69 = 1855 \text{ kg/m}^3$$

Therefore, the following composition of the mix has been adopted:

- pozzolan cement: 400 kg/m^3
- mixing water: 160 kg/m^3
- natural aggregate (max. size of 19 mm): 1855 kg/m^3
- superplasticizer: 8 kg/m^3

The compressive strength based on durability criteria (σ_{CD}) for the mix has been determined by the pozzolan cement curve in Fig. 8:

$$(w/c)_D = 0.40 \longrightarrow (\sigma_{CD}) = 36 \text{ MPa} \quad \text{(with pozzolan cement)}$$

Therefore, the following technical parameters have been adopted to check if the above composition requirements have been met:

- Compressive strength (cylinder): 36 MPa
- Slump: 240 mm
- Maximum size of aggregate: 19 mm
- Minimum cover depth: 40 mm

CONCLUSIONS

The durability requirements of ACI Committee 201 have been analyzed and re-arranged in order to compare them with the corresponding durability criteria adopted by the European Standardization (ENV 206).

In general, the ACI recommendations for the mix composition appear to be more adequate for durable concretes than those required by ENV 206: lower w/c ratios and slightly higher volumes of entrained air are required by ACI. On the other hand, the depth of concrete cover for durable reinforced concrete structures is in general higher in ENV requirements than in the corresponding ACI ones.

According to the experience presented in this paper on the deterioration mechanism, both ACI and ENV should be more specific for the cement types or more restrictive for the w/c ratio in the following three aggressive situations:

- for reinforced concrete structures exposed to carbonation, portland cement should be required rather than pozzolan or slag cements in lean mixes ($c < 250 \text{ kg/m}^3$) with relatively high w/c ratio, (> 0.70)
- for concrete structures exposed to chloride deicing salts, pozzolan or slag additions should be required in order to protect more safely concrete against the alkali-aggregate reaction (for NaCl) and the oxychloride attack (for CaCl_2)
- for concrete structures exposed to sulfate attack in cold climates ($< 10^\circ\text{C}$), a w/c ratio lower than the maximum value recommended (0.45) for the most aggressive sulfate attack should be required

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Table 1 - Composition of concrete mixtures of Fig. 1. Maximum size of natural aggregates = 25 mm.

Portland cement (Kg/m ³)	Fly ash (f.a.) (Kg/m ³)	w/c	w/(c + f.a.)
300	-	0.58	-
300	50	0.58	0.50
250	50	0.70	0.58
250	-	0.70	-
250	50	0.70	0.58
200	50	0.88	0.70

Table 2 - Composition of concrete mixtures of Fig. 2. Maximum size natural aggregates = 25 mm.

Portland cement (kg/m ³)	Slag (s) (kg/m ³)	w/c	w/(c + s)
300	-	0.58	-
300	100	0.58	0.44
200	100	0.88	0.58
250	-	0.70	-
250	100	0.70	0.50
150	100	1.17	0.70

Table 3 - Durability requirements for concretes exposed to carbonation and potential corrosion of embedded steel according to ACI 201 and ENV 206 (exposure classes: 1 and 2a)

EXPOSURE CLASS	ENV 206		ENV 206	ACI 201
	1	2a		
ENVIRONMENT	DRY AIR (INTERIOR OF BUILDING)	HUMID AIR OR WATER (EXTERIOR COMPONENTS)		(EXPOSURE TO CARBONATION)
REQUIREMENTS:	---	0.70* 0.60 0.60		No specific requirement but only general recommendation on good quality concrete, proper consolidation and curing, and adequate cover depth.
maximum w/c ratio for: plain concrete reinforced concrete prestressed concrete				
Curing		From 2 to 15 days of moist or membrane curing depending on temperature, R.H., etc.		

* Only to protect concrete from leaching away by the mildly acidic water containing free CO₂.

Table 4 - Durability requirements for concretes exposed to humid environment with frost according to ACI 201 (moderate exposure) and ENV 206 (exposure class : 2b)

EXPOSURE CLASS	ENV 206 2b	ACI 201 (MODERATE EXPOSURE TO FREEZING-THAWING)
REQUIREMENTS: maximum w/c ratio :	- 0.55 (minimum cover of 25 mm for reinforced concrete and 35 mm for prestressed concrete*)	- 0.55 (nominal cover higher than 25mm) - 0.45 (nominal cover less than 25 mm)
Air volume (%) at maximum aggregate size of: - 9.5 mm - 19 mm - 38 mm	5.75** 4.75** 3.75**	6 5 4.5
Curing	From 2 to 15 days of moist or membrane curing depending on temperature, R.H., etc.	Compressive strength > 20.7 MPa before being exposed to freezing

* From Eurocode N° 2 (19)
** Interpolated values from Fig. 7

Table 5 - Durability requirements for concretes exposed to humid environment with frost and to deicers action according to ACI 201 (severe exposure) and ENV 206 (exposure class : 3)

EXPOSURE CLASS	ENV 206 3	ACI 201 (SEVERE EXPOSURE TO FROST AND DEICERS ACTION)
REQUIREMENTS: maximum w/c ratio	- 0.50 (minimum cover of 40 mm for reinforced concrete and 50 mm for prestressed concrete*)	- 0.40 (nominal cover of at least 50 mm for concrete roadway decks and adjacent appurtenances) - 0.45 (nominal cover less than 25 mm for other concrete structures) - 0.50 (for all other concrete structures)
Air volume (%) at maximum aggregate size of: - 9.5 mm - 19 mm - 38 mm	5.75** 4.75** 3.75**	7.5 6 5.5
Curing	From 1 to 15 days of moist or membrane curing depending on temperature, R.H., etc.	Compressive strength > 27.6 MPa before being exposed to freezing

* From Eurocode N° 2 (19)
** Interpolated values from Fig. 7

Table 6 - Durability requirements for concretes exposed to seawater environment without frost according to ACI 201 and ENV 206 (exposure class: 4a)

EXPOSURE CLASS	ENV 206 4a	ACI 201 (SEAWATER EXPOSURE)
REQUIREMENTS: maximum w/c ratio	-0.55 (minimum cover of 40 mm for reinforced concrete and 50 mm for prestressed concrete*)	-0.40 (nominal cover of at least 25 mm for reinforced concrete structures within the range of fluctuating water level or spray) -0.45 (nominal cover of at least 38 mm for reinforced concrete structures within the range of fluctuating water level or spray) -0.50 (for unreinforced concrete or reinforced concrete structures above the sea for a height of 8 m or within a horizontal distance of 100 m)
Type of cement		Type II, IP, IS
Curing	"The length of curing given in Table 2 should be substantially increased"	At least 7 days of uninterrupted moist curing or membrane curing

* From Eurocode N° 2 (19)

Table 7 - Durability requirements for concretes exposed to seawater environment with frost according to ACI 201 and ENV 206 (exposure class: 4b)

EXPOSURE CLASS	ENV 206 4b	ACI 201 (SEAWATER EXPOSURE + FROST ACTION)
REQUIREMENTS: maximum w/c ratio	-0.50 (minimum cover of 40 mm for reinforced concrete and 50 mm for prestressed concrete*)	-0.40 (nominal cover of at least 25 mm for reinforced concrete structures within the range of fluctuating water level or spray) -0.45 (nominal cover of at least 38 mm for reinforced concrete structures within the range of fluctuating water level spray) -0.50 (for unreinforced concrete or reinforced concrete structures above the sea for a height of 8 m or within a horizontal distance of 100 m)
Type of cement		Type II, IP, IS
Air volume (%) at maximum aggregate size of: - 9.5 mm - 19 mm - 38 mm	5.75** 4.75** 3.75**	7.5 6 5.5
Curing	From 1 to 15 days of moist or membrane curing depending on temperature, R.H., etc.	At least 7 days of uninterrupted moist curing or membrane curing

* From Eurocode N° 2 (19)

** Interpolated values from Fig. 7

Table 8 - Durability requirements for concretes exposed to sulfate attack (without frost) according to ACI 201 and ENV 206. Air entrainment (see Table 4) should be provided to concrete exposed to sulfate attack and frost action

EXPOSURE CLASS	ENV 206		ACI 201	
	5a	5b	5c	(SULFATE EXPOSURE)
SULFATE CONTENTS (ppm) of the environment	250-500	500-1000	1000-6000	150-1500 (in water) > 10000 (in water) 1000-2000 (in soil) > 20000 (in soil)
REQUIREMENTS: maximum w/c ratio	0.55	0.50	0.45	0.50 0.45 0.45
Type of cement	sulfate-resistant cement (for sulfate content > 500 ppm in water or > 3000 ppm in soil)			Type II IP IS Type V Type V + Pozzolan
Minimum cover (mm)** for: - reinforced concrete - prestressed concrete	25 35	30 40	40 50	
Curing	*The length of curing given in Table 4 should be substantially increased"			At least 7 days of uninterrupted moist curing or membrane curing
Surface protection	Additional protection by coatings is recommended when sulfate content is more than 6000 ppm			

* According to ISO/DP 9690 Classification (20)
** From Eurocode N° 2 (19)

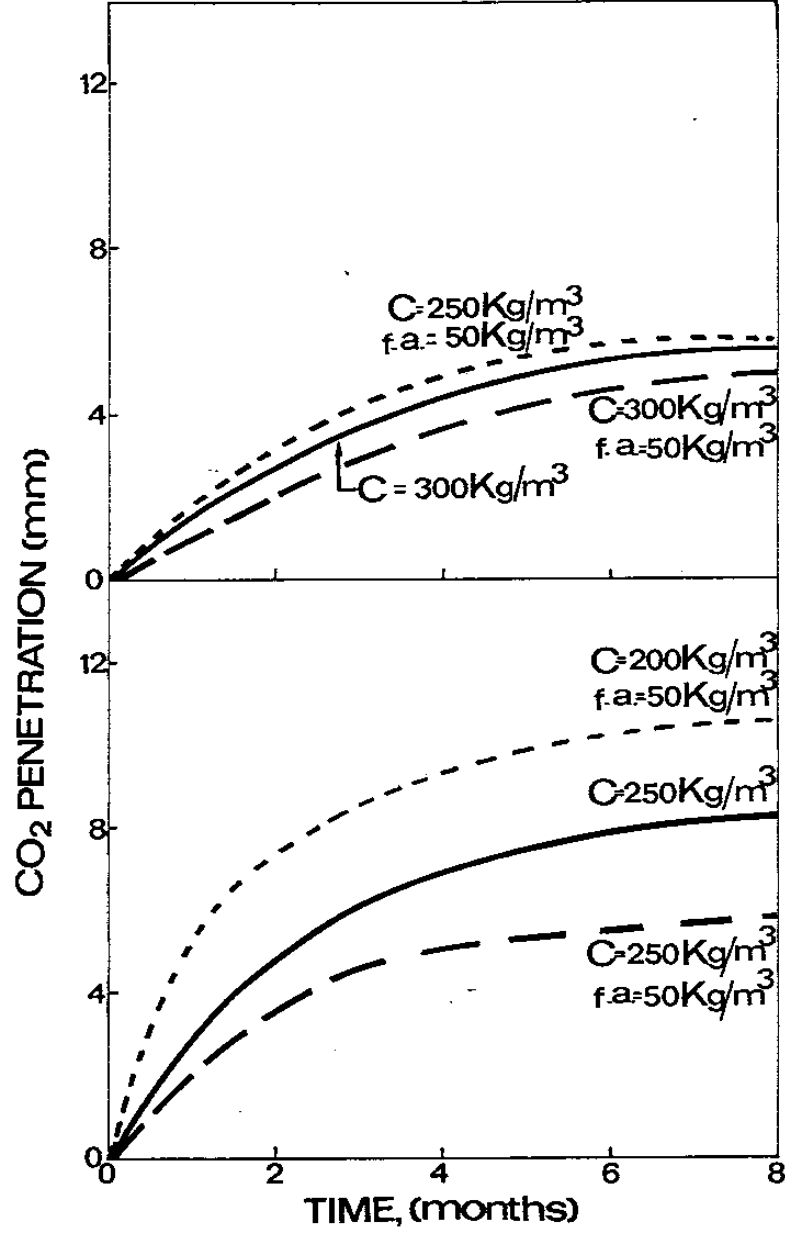


Fig. 1 Influence of fly ash (f.a.) addition, with and without reduction of portland cement content (C), on the CO₂ penetration through concretes with mixing water of 175 kg/m³ (T = 20°C; R.H. = 60%).

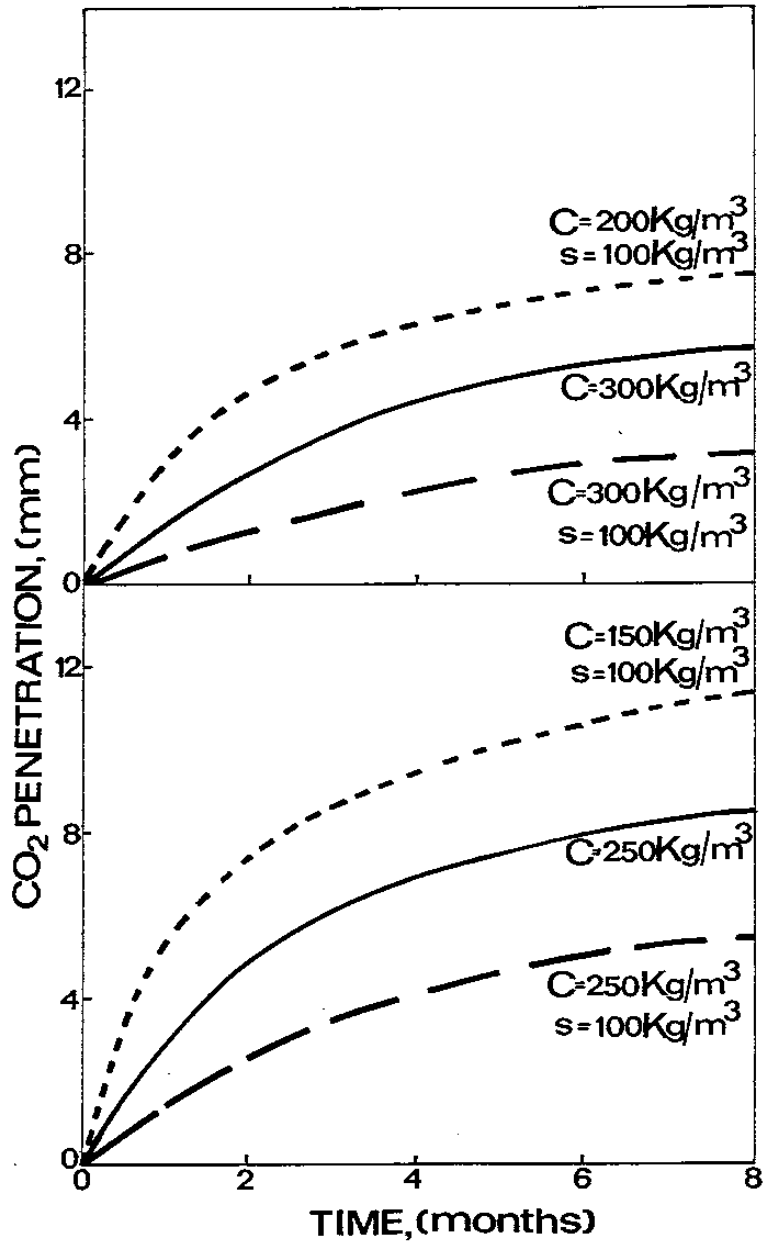


Fig. 2 Influence of fine ground slag (s) addition, with and without reduction of portland cement content (C), on the CO₂ penetration through concrete with mixing water of 175 kg/m³ (T = 20°C; R.H. = 60%).

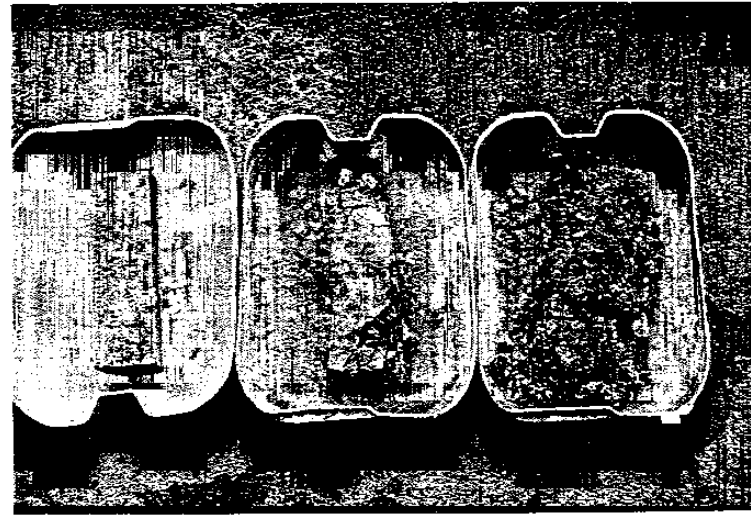


Fig. 3 Mortar specimens subject to sulfate attack: sound specimen, on the left; cracked specimen damaged by ettringite production, in the middle; destroyed specimen damaged by thaumasite formation, on the right.

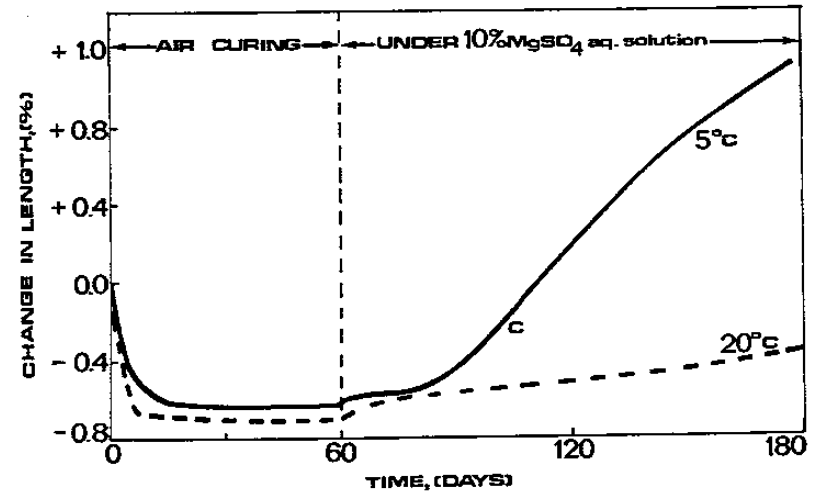


Fig. 4 Change in length of cement paste specimens in a 10% MgSO₄ aqueous solution at 5°C or 20°C. Cracking of specimens (C) is indicated on the 5°C curve (15).

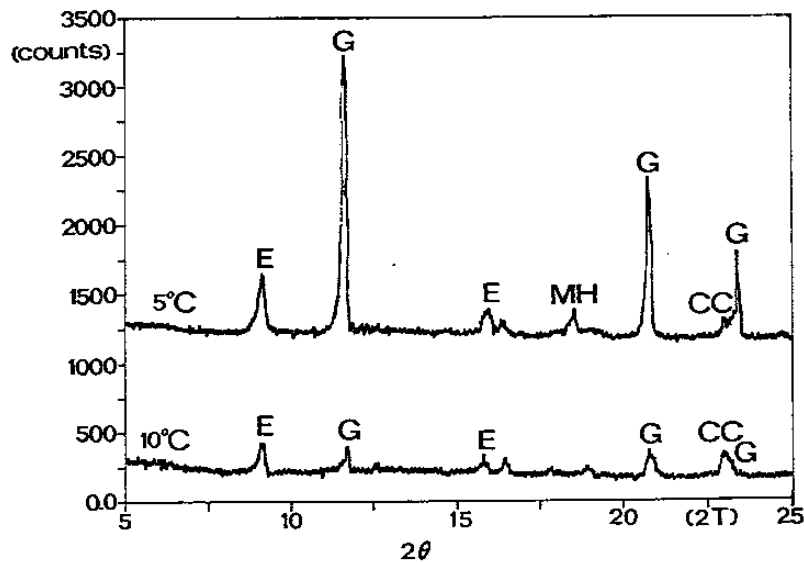


Fig. 5 XRD patterns of cement paste specimens (cured 2 months) after 4 months of immersion in a 10% $MgSO_4$ aqueous solution at 5°C or 20°C. E = ettringite; G = gypsum; MH = magnesium hydroxide; CC = calcite (15).

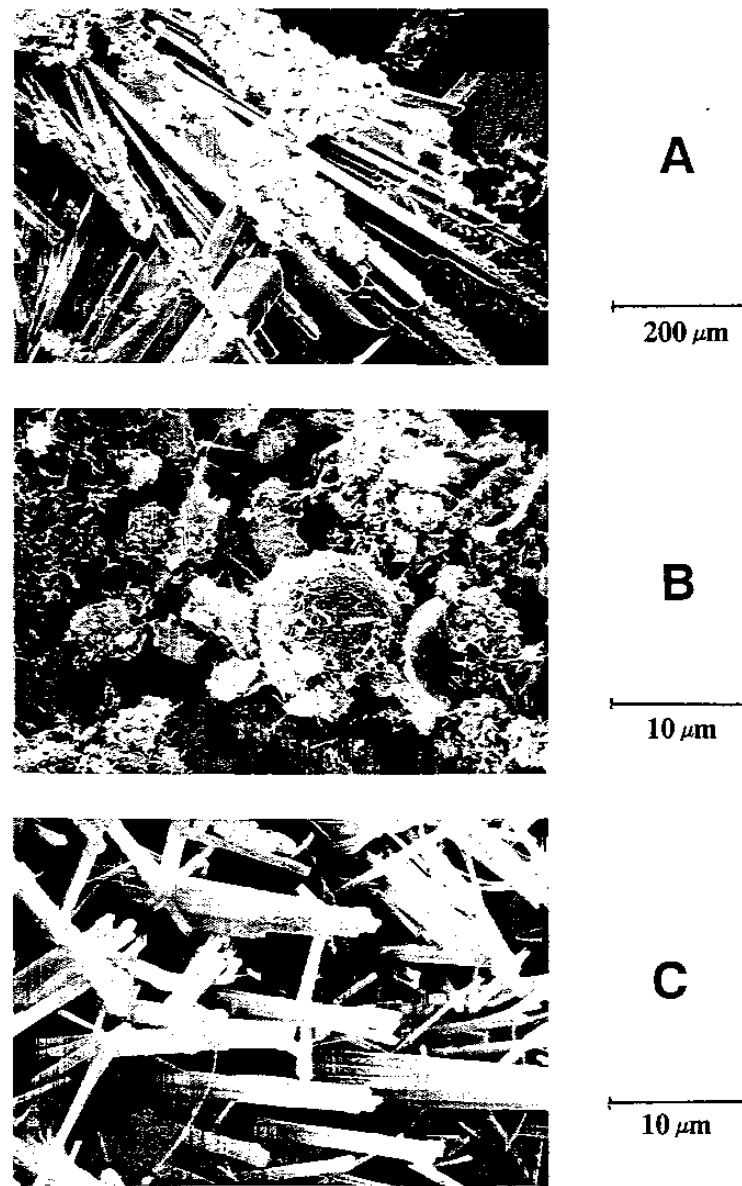


Fig. 6 Micrographs of cement paste specimens exposed to a 10% $MgSO_4$ aqueous solution at 5°C (A and B) or at 20°C (C). Very fine ettringite crystals are formed on large lath-like crystals of gypsum (A). At a larger magnification ettringite crystals formed at 5°C (B) appear to be much smaller than those (C) formed at 20°C (15).

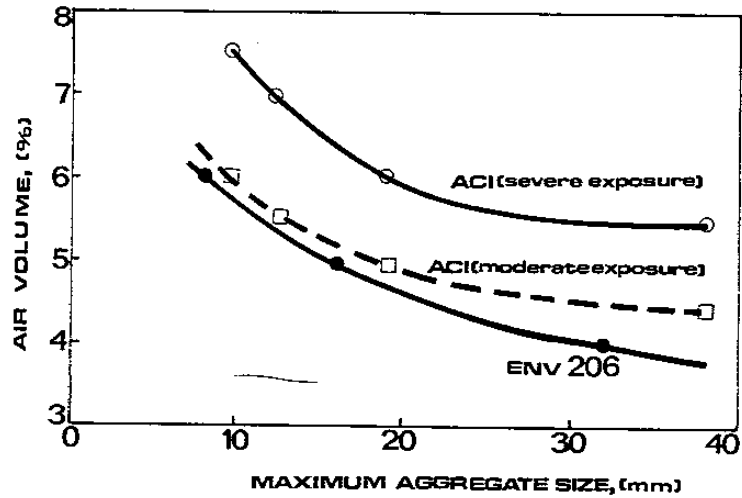


Fig. 7 Air volume requirements for durable concrete exposed to freezing-thawing (moderate exposure) or freezing-thawing with deicers action (severe exposure) according to ACI 201 (average values) and ENV 206 (minimum values).

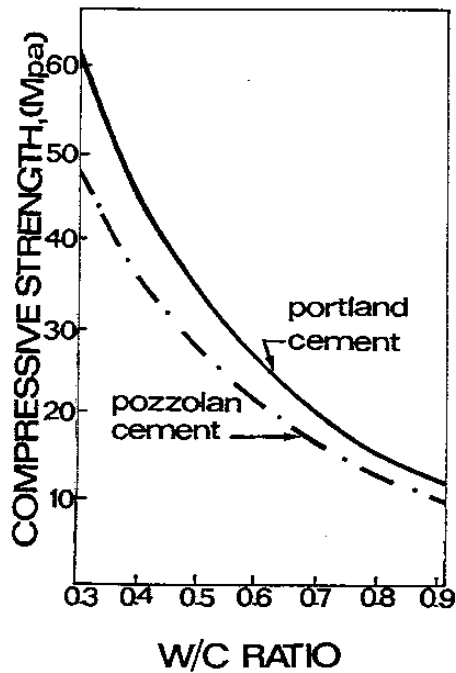


Fig. 8 28-day compressive strength (cylinder) versus w/c ratio in concrete with normal portland or pozzolan cement.