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Experience from the Netherlands

Concrete with great resistance to chloride penetration

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A descriptive strategy for concrete durability is utilised in the current version of concrete standard EN 206, whereby proof of durability is furnished through compliance with the limit values of the provisions regulating concrete properties and concrete composition. However, these do not sufficiently take the action of each type of cement or of the concrete additive into consideration. Furthers developments of the future EN 206 European concrete standard are envisaged with, amongst other things, the application of performance strategies for concrete, in which these as well as the development of actions and resistances over time are better taken into account. With these matters, the resistance of concrete against chloride penetration is one of the most important properties of concrete with great relevance for durability.

A major influence on the resistance of concrete to chloride penetration is exerted by the selection of raw materials for concrete and the definition of its composition. One technical measure for increasing chloride penetration resistance in concrete is to employ fly ash and blast furnace slag as components of the binding agent or as concrete additives. In the Netherlands, long-term experience has been gained with the utilisation of concretes with great resistance to chloride penetration. Test results are available that permit assessments in relation to how this resistance depends on concrete composition and age as well.

At the current time, stipulations as regards concrete durability are defined by exposure classes in EN 206, the European concrete standard [1]. Concrete durability is safeguarded by means of descriptive stipulations regarding concrete composition, e.g. water/cement value (w/c value). Stipulations concerning the durability of concrete, its testing and assessment are regulated at national level in every European country. It has not yet been possible to attain a uniform European basis for assessing concrete durability up to date. This is where the strategy for safeguarding the durability of concrete structures through a European definition of resistance classes can be applied [2].

The penetration speed of the carbonation or chloride front into concrete is based [3] on this strategy of resistance classes, which has been derived from life span design and is particularly suited to reinforcement depassivation induced by carbonation and chloride. Evidence of compliance with the stipulated resistance class criteria can be provided through performance testing.

The action of chloride is found amongst the most common causes of damage to concrete building structures. The necessary resistance to chloride penetration in concrete is basically achieved by increasing concrete density. Chloride penetrates into concrete especially through capillary pores. Interrupting and minimising pore space is the key to attaining good resistance to chloride penetration in concrete.

It is well known that fly ash makes its own contribution to improving essential hardened concrete properties through the pozzolanic reaction, in which amorphous silica oxide and aluminium oxide from fly ash react with calcium hydroxide from cement hydration to create strength-forming calcium silicate hydrate phases (CSH) and calcium aluminate hydrate phases (CAH). A positive contribution is made to concrete durability through the formation of these additional phases. Their delayed reaction, in comparison with Portland cement, generates CSH phase growth in the free spaces of the concrete micro-structure. Chemical densification and a reduction in capillary pores occur. When compared with pure Portland cement concretes, there tends to be a shift towards pore distribution in the direction of finer pores by employing fly ash, [4]. Thanks to the latent hydraulic reaction, blast furnace slag furnishes a similar contribution to concrete durability [5].

Chlorides mainly penetrate into concrete by means of diffusion. At the beginning of the 1970s, it was determined that this process can be described by Fick's second law [6]. Since this time, many developments have taken place regarding modelling, testing and assessing chloride penetration into concrete e.g. DuraCrete [7], Fib Model Code [8] and CUR Leidraad 1 [9]. Since 2015, with EN 12390-11 [10], there exists a standardised European testing procedure for determining the resistance of concrete to chloride penetration by diffusion. An assessment of chloride penetration resistance has not yet been standardised in Europe.

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■ Dr Gert van der Wegen studied chemical engineering at the Eindhoven University of Technology, gaining his doctorate at the Faculty for Applied Physics at the University of Groningen. In 1982, he joined today's SGS INTRON B.V., Sittard as head of the concrete laboratory and has been the company's managing director since 1991. He is responsible there, amongst other matters, for investigations into the utilisation of secondary raw materials in concrete. In 2012, he became chairman of Stutech, the Dutch Association for Concrete Technology Experts. Gert van der Wegen is member of the Dutch standardisation committee for concrete technology and chairman of the working group for implementing European Standard EN 206 in the Netherlands.

■ Prof Dr Rob B. Polder studied inorganic chemistry at Utrecht University, gaining his doctorate at Wageningen University. From 1984 until 2017, he conducted research in the area of construction materials and structures at The Netherlands Organisation for Applied Scientific Research (TNO) in Delft. From 2009 until 2017, he was professor of Materials for Sustainable Development at the Delft University of Technology. Since 2013, he has been chairman of the Dutch Knowledge Centre concerning cathodic corrosion protection of steel in concrete. The main focus of his research is the durability, protection and rehabilitation of concrete structures.

Modelling and Assessing Chloride Penetration Resistance in Concrete

Modelling

Chloride diffusion in concrete can be described by Fick's second law [6, 7].

$$\partial C / \partial t = D\,(\partial^2 C / \partial x^2) \qquad (1)$$

In DuraCrete[7], the European research project, this differential equation was modified through taking into account: a time-dependent diffusion coefficient, a coefficient for ambient conditions (Fig.1) and the duration of post-treatment for the concrete:

$$C(x,t) = C_s - (C_s - C_i)\ \mathrm{erf}\{x/2\sqrt{[K_{tot}\ D(t)\ t]}\} \qquad (2)$$

$$D(t) = D_0\,(t_0/t)^{n_{Cl}} \qquad (3)$$

with

$C(x,t)$ = Chloride content at a certain depth (x) at a certain time (t)

C_s = Chloride content at the concrete surface

C_i = Original chloride content of the concrete

erf = Gaussian error function

K_{tot} = k_e (Ambient coefficient) x k_c (Post-treatment coefficient)

D_0 = Chloride diffusion coefficient at the age of t_0
n_{Cl} = Age exponent [-], exponent taking into account time dependency with the effective chloride diffusion coefficient of concrete at the time of observation

On account of more recent findings and knowledge [10], the Dutch VC81 CUR Commission "Designing structural concrete in relation to durability" has further elaborated the DuraCrete model. The most important new aspects are:

- Ambient coefficient (k_e)
- Age exponent (n_{Cl})
- Critical chloride content

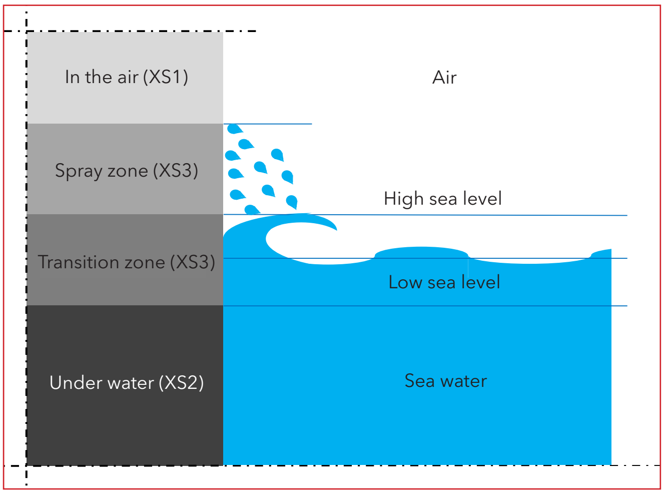

Fig. 1: Ambient conditions and the exposure classes arising from them

Ambient Coefficient

The DuraCrete model only makes provisions for the ambient coefficient with CEM I und CEM III cements containing > 65 % blast furnace slag (BFS). The VC81 CUR Commission has also laid down k_e values for binding agents with fly ash (FA) (20 % to 30 %) and low blast furnace slag content (25 % to 50 %) (Table 1).

Critical Chloride Content

The DuraCrete model only lays down the critical chloride content for CEM I. This above mentioned content varies in relation to ambient conditions and the water/binding agent value (w/c value) of 0.5 % - 2.3 % in respect of binding agent content. In the light of new findings [11], the VC81 CUR Commission has decided to lay down critical chloride content uniformly for all binding agents at 0.6 %.

Verifying the Model Computations in Practice

The VC81 CUR Commission compared the values computed with the model with findings in practice (Table 3). The computed values for penetration depth in concrete at 0.5 % chloride content in relation to binding agent content agreed in most cases with the measured values.

Requirements regarding the chloride migration coefficient in respect of concrete covering and durability

The modified model can be employed to compute the maximum value for the chloride migration coefficient in relation to concrete covering in order to attain a certain service life (i.e. the age at which critical chloride content will be exceeded at the reinforcing steel's surface). Such computations were

Table 1: k_e value in relation to binding agent type and exposure class

Exposure Class	XS2, XS3			XD1, XD2, XD3, XS1		
Binding Agent Type	CEM I	CEM with > 50 % HSM	CEM with 20 % to 30 % FA or 25 % to 50 % HSM	CEM I	CEM with > 50 % HSM	CEM with 20 % to 30 % FA or 25 % to 50 % HSM
k_e Value	0.27	0.78	0.53	0.68	1.97	1.33

Age exponent (n_{Cl})
The VC81 CUR Commission has also redefined the values for the age exponent (n_{Cl}) (Table 2).

Table 2: Age exponent in relation to binding agent type

Binding agent type	Determined Value	
	XD2, XS2, XS3	XD1, XD3, XS1
CEM I	0.40	0.60
CEM I with 25% to 50% BFS CEM II/B-S, or CEM III/A with <50% BFS	0.45	0.65
CEM III with 50% to 80% BFS	0.50	0.70
CEM I with 21% to 30% FA	0.70	0.80
CEM V/A (25% HSM + 25% FA)	0.60	0.70

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Table 3: Comparison of results from model computations with values in practice for penetration depth at 0.5 % chloride content in relation to binding agent

Binding agent type	Object Information	Depth 0.5 % m/m Cl (mm)		Notes
		Object	Model	
CEM I	Pier Scheveningen; 41years; DCl,0 = 5.10^{-12} (m^2/s); Precast concrete slab	30	30	CUR report 215 [12]
	Idem; Precast concrete beam	38	30	
CEM III/B	Pier Scheveningen; 41 years; DCl,0 = 6.10^{-12} (m^2/s); Ready-mix concrete	38	35	
	Bruinse sluice; 16 years; DCl,0 = 4.10^{-12} (m^2/s); Ready-mix concrete	18-27	22	CUR report 100 [13]
	Vlissingen sluice; 26 years; DCl,0 = 7.10^{-12} (m^2/s); Ready-mix concrete	30-32	33	
	Zandkreekdam sluice; 18 years; DCl,0 = 4.10^{-12} (m^2/s); Ready-mix concrete	25-30	22	

carried out for various binding agent types and ambient conditions (exposure classes).

The computations were carried out using the mean values of all parameters. This creates a 50 % risk that the actual service life will be lower than the computed one. Increasing concrete coverage by 20 mm for steel reinforced concrete (risk < 10 %) and by 30 mm for prestressed concrete (risk < 5 %) is necessary in order to reduce this risk. Table 4 lists the results of such computations for a service life of 100 years.
The chloride migration coefficient of concrete should only exhibit a value of maximum $12 \cdot 10^{-12}$ m^2/s after 28 days to attain a 100 year service life using steel reinforced concrete with CEM 1 cement of exposure class XD1 with a concrete coverage of 50 mm.

Action of the W/C value on the resistance of concrete to chloride penetration at an age of 28 days

Investigations in the Netherlands [9] concerning the chloride migration coefficient (rapid chloride migration coefficient – RCM value) into more than 150 different concrete mixes show that a linear correlation exists between the chloride migration coefficient in concrete at an age of 28 days and the w/c value (Fig.2). Comparable findings are illustrated in [15].

The RCM value for concrete with CEM I cement displays a very strong relationship to the w/c value and is substantially greater than that of concrete with CEM III cement. The RCM value for fly ash concrete is less dependent on the w/c value than the RCM value for concrete with CEM I cement.

Table 4: Computed maximum value for the chloride migration coefficient in relation to concrete covering for a service life of 100 years

Concrete Coverage [mm]		Max. Value D_{RCM} [10^{-12} m^2/s]							
Reinforcing steel	Prestressing steel	CEM I		CEM I + III 25% to 50% HSM		CEM III 50% to 80% HSM		CEM II/B-V CEM I + 20% to 30% FA	
		XD1, XD2, XD3, XS1	XS2, XS3	XD1, XD2, XD3, XS1	XS2, XS3	XD1, XD2, XD3, XS1	XS2, XS3	XD1, XD2, XD3, XS1	XS2, XS3
35	45	3.0	1.5	2.0	1.0	2.0	1.0	6.5	5.5
40	50	5.5	2.0	4.0	1.5	4.0	1.5	12	10
45	55	8.5	3.5	6.0	2.5	6.0	2.5	18	15
50	60	12	5.0	9.0	3.5	8.5	3.5	26	22
55	65	17	7.0	12	5.0	12	5.0	36	30
60	70	22	9.0	16	6.5	15	6.5	47	39


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The RCM value for fly ash concrete is already lower than that of concrete with CEM I cement with a w/c value of approx. 0.45.

Long-term investigations into the resistance of concrete with fly ash and blast furnace slag to chloride penetration

Blast Furnace Slag

The following is a report concerning the findings from two test series in the Netherlands regarding the influence of blast furnace slag on resistance to chloride penetration (RCM value). The first series of tests was carried out on mortar samples (w/c = 0.50) between the ages of 1 and 28 days using CEM I cement and CEM III/B cement [16]. Testing times were shortened in deviation from the NT Build 492 regulation [14] on account of the samples' very young age. The samples were stored in a lime solution and not saturated in a vacuum. Other findings originated from earlier work by the Netherlands Organisation for Applied Scientific Research (TNO) on concrete samples (w/c = 0.45) of an age between 28 days and 3 years [17]. The testing duration complied with the NT Build 492 regulation.

Fig. 3 shows clearly that the results from testing with CEM III/B cement up to an age from 7 days exhibit a greater chloride migration coefficient than samples with CEM I cement. At an age of 7 days, the chloride migration coefficient of samples with CEM III/B cement is comparable with the chloride migration coefficient of samples with a CEM I cement. After 28 days, the chloride migration coefficient of samples with CEM III/B cement is already substantially less than with the chloride migration coefficient of samples with a CEM I cement. It decreases constantly even up to 3 years of age. An age exponent at an age of 28 days (mortar) of 0.62 was determined from the curve's gradient with samples using CEM I cement and of 1.5 with samples using CEM III/B cement and at an age of 28 days up to 3 years (concrete) correspondingly of 0.19 and 0.37.

Fig. 3 confirms previously known differences in concrete micro-structure make-up over time, when using CEM I cement and CEM III cement, caused by the latent-hydraulic reaction of blast furnace slag in the CEM III cement.

Fly Ash

The following presents the findings from the latest test series in the Netherlands regarding the influence of fly ash on resistance to chloride penetration over a period of time. The values determined for the age exponents of concretes containing fly ash are greater than those of other binding agent compositions (Table 2).

Since the age exponent exerts a great influence on the service life computed for concrete, SGS INTRON carried out on behalf of Vliegasunie – a Dutch fly ash manufacturer – a research project scheduled to run for five years into determining the age exponents of concretes containing fly ash [18].

Three Dutch fly ashes (FA1, FA2, FA3) were utilised with three cements CEM I 52.5 N (Z1, Z2, Z3) as binding agents in the concrete. The reference concrete was made with a CEM III/B 42.5 N (Zref) cement as binding agent. Binding agent content was 360 kg/m^3 in every case; with binding agents with fly ash and cement, the fly ash content was 120 kg/m^3 and CEM I 52.5 N content was 240 kg/m^3. The w/c value was 0.45 in each case. Dutch river sand and gravel (0/16 mm) were employed as aggregates.

The chloride migration coefficient in relation to concrete age is illustrated in Fig.4. After 28 days, the reference concrete with CEM III/B cement displayed a lower chloride migration coefficient with $2 \cdot 10^{-12}$ m^2/s than the concretes containing fly ash. Concretes containing fly ash exhibit the same chloride migration coefficient after 1½ years as the reference concrete. At an age of three years, however, the chloride migration coefficient of concretes containing fly ash was two times lower than that of the reference concrete. At an age of five years, no significant changes were observed in comparison with the findings after three years.

Age exponents for concretes were calculated using equation (3). The results are given in Table 5. The age exponents for fly

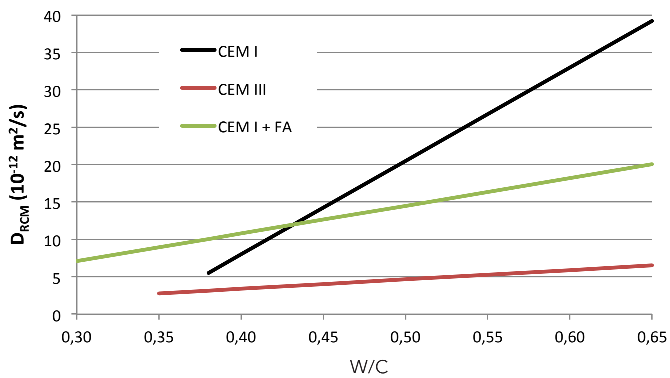

Fig. 2: RCM value at an age of 28 days in relation to w/c value

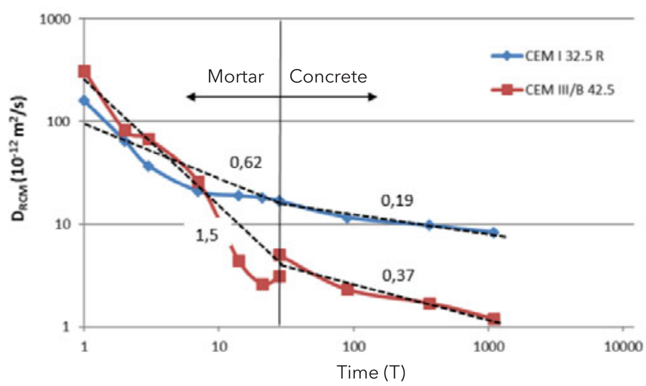

Fig. 3: RCM values and curve gradient between 1 day and 3 years

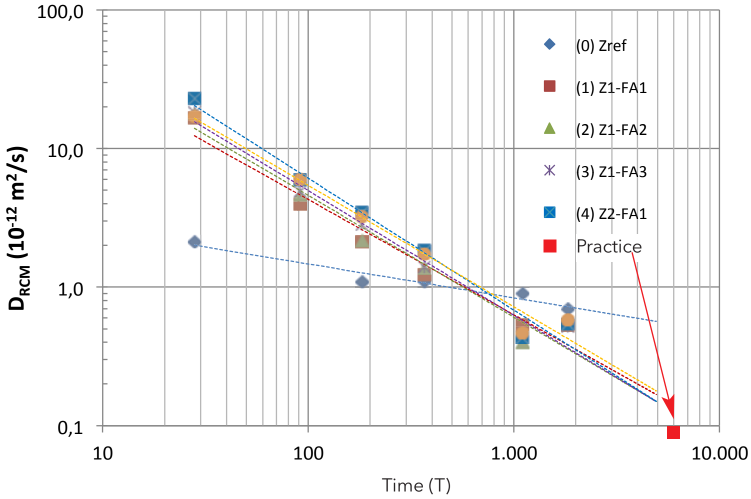

Fig. 4: Chloride migration coefficient in relation to concrete age

ash concretes were 0.9 to 1.0. These test results show clearly that the age exponents of concretes containing fly ash given in Table 5 represent a sound basis for computing the development of resistance to chloride penetration over time.

Experience gained from practice

Blast Furnace Slag

Investigations into chloride transport were undertaken at the outset of the 21st century on concrete structures erected using CEM III/B cement in sea water surroundings [19]. Six concrete structures aged between 16 and 40 years were examined and samples taken (drill cores).

Only one concrete structure exhibited corrosion. This was caused by insufficient concrete covering. The depth of carbonation was very low – mainly at 2 mm (only occasionally 5 mm). All concrete structures displayed considerable chloride penetration with a relatively wide dispersion within individual testing areas. It turned out that the chloride content at the concrete surface up to 7 m above sea level is approx. 3 % in relation to cement content; above 7 m, it greatly depends on whether the concrete surface was exposed to rain. In sheltered zones, the value could reach 5 %; in areas exposed to rain, chloride content was mainly under 1 %. All diffusion co-

Table 5: Age exponents of concretes investigated at the age of 1 to 5 years

Concrete	Cement	Fly Ash	Age Exponent (-)		
			After 1 year	After 3 years	After 5 years
0	CEM III/B 42,5 N – Zref	–	0.28	0.24	0.28
1	CEM I 52,5 N – Z1	FA1	1.02	0.93	0.81
2	CEM I 52,5 N – Z1	FA2	1.02	1.02	0.83
3	CEM I 52,5 N – Z1	FA3	0.99	1.01	0.89
4	CEM I 52,5 N – Z2	FA1	0.98	1.05	0.94
5	CEM I 52,5 N – Z3	FA1	0.89	0.97	0.85

Fig. 5: The tidal barrage in Haringvlietdam (built 1970) is one of the six structures investigated

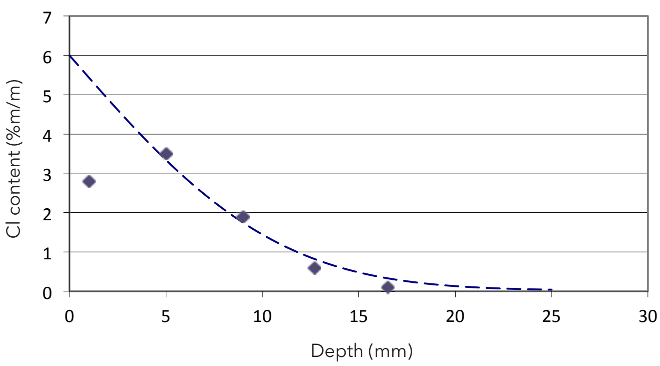

Fig. 6: Chloride profile of a motorway's concrete road covering after 14 years impact with de-icing salt

efficients determined were very low and were found in a range between 0.1 und $0.3 \cdot 10^{-12}$ m²/s. An age exponent of the diffusion coefficient of about 0.48 was determined with test specimens [20] stored under water in the North Sea for 16 years. This value agrees with the value of 0.45 for concrete with CEM III/B cement given in literature [15].

It may be summarised that concrete manufactured with cement containing a large proportion of blast furnace slag – and thus corresponding to modern CEM III/B cement – exhibits great resistance against chloride penetration in concrete structures constructed between 1960 and 1985. This concrete possesses a moderate age exponent of about 0.5. The chloride content at the concrete surfaces in the water transition and spray zones is similar to the values found in literature for concretes manufactured with Portland cement [9]. In the atmospheric zone (in the air), it depends on the height above sea level and on the leaching effect of rain.

Fly Ash

The results gained in practice regarding the durability of concrete with fly ash were compiled in CUR report 2000-2 [21]. Amongst other things, this includes the results from investigations into chloride penetration resistance on the 14 year old concrete of a motorway. This concrete road covering was produced with 350 kg/m³ Portland fly ash cement (CEM II/B-V 32.5 R). The w/c value was 0.42. After 28 days, the fresh concrete displayed an air void content of approx. 4 Vol.-%. The concrete strength after 28 days was 48 N/mm² and 83 N/mm² after 14 years. The motorway was strewn with salt during winter in accordance with weather conditions. The chloride penetration profile after 14 years can be viewed in Fig.6.

Chloride content at a depth of 1 mm is reduced due to carbonation and was not taken into account in determining the chloride profile. The chloride diffusion coefficient of $0.08 \cdot 10^{-12}$ m^2/s computed from this chloride profile with equation (2) correlates very well with the value determined in [18] (Fig. 4).

Conclusion

In the Netherlands, experience in assessing and utilising special concretes with great resistance to chloride penetration has already been gained over a number of years. The model for computing chloride diffusion, taking the ambient coefficient, age exponent and critical chloride content into account, was developed still further and tested in practice. Critical chloride content was laid down uniformly at 0.6 % for all binding agent types.

A rapid procedure, which enables the penetration of chlorides to be determined under the influence of an electrical field, was approved by the authorities in the Netherlands alongside the diffusion procedure.

It was confirmed that a linear correlation exists between the chloride migration coefficient of concrete at an age of 28 days and the w/c value. This relationship of the chloride migration coefficient to the w/c value is greatly influenced by the binding agent type.

Long term investigations into the resistance of concrete with fly ash and blast furnace slag to chloride penetration have shown that an appreciable improvement in chloride penetration resistance occurs with increasing age due to the pozzolanic reaction of fly ash and the latent-hydraulic reaction of blast furnace slag. The chloride migration coefficient of concrete with blast furnace slag at an age of 28 days is already lower than with concretes with pure Portland cement or with concretes with fly ash. At an age of three years, the chloride migration coefficient of concrete containing fly ash is two times lower than that of concrete with blast furnace slag. At an age of five years, no significant changes were observed in comparison with the findings after three years.

Experience gained from practice confirms this great resistance of concretes with fly ash and blast furnace slag to chloride penetration. The chloride diffusion coefficients determined in practice exhibit good correlation with computed chloride diffusion coefficients and those determined on a laboratory scale.

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FURTHER INFORMATION

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