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Removal of Concrete by Acidic Water

Usure du béton par de l'eau acide

Betonabtrag durch saure Wässer

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Horst Grube, geboren 1938, promovierte als Bauingenieur an der TH Darmstadt. Er leitete 12 Jahre das zentrale Baustofflabor einer Grossbaufirma und ist seit 8 Jahren stellv. Leiter der Hauptabteilung Betontechnik im Forschungsinstitut. Arbeitsschwerpunkte: Ausführung und Dauerhaftigkeit von Betonbauwerken, Durchlässigkeit gegenüber Flüssigkeiten und Gasen, Kriechen, Schwinden, Instandsetzung.

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Wolfram Rechenberg, geboren 1931, promovierte als Chemiker an der TU Hannover. Er war 5 Jahre als Entwickler für Gummiasbest und Klebebänder tätig. Seit 22 Jahren ist er wissenschaftlicher Mitarbeiter des Forschungsinstituts und betreut die chemische Analyse. Zu seinen Aufgabengebieten gehört der chemische Angriff auf Beton und die Erfassung von Zementwerksemissionen.

SUMMARY

The attack of acidic water must be assessed when planning durable concrete structures. The aggressiveness is generally expressed in terms of concentration of attacking acid. A protective layer built up by reaction products and its stability can have a much greater influence on the loss of material than the concentration of the attacking substances. Experiments, based on a calculation model, show how to estimate the loss of material (the amount of affected concrete) to be expected under practical conditions. Parameters are the type and the concentration of the acid solution, the composition of the concrete and the stability of the protective layer.

RÉSUMÉ

Il faut tenir compte de l'attaque possible des eaux acides lors de projet de structures en béton durables. Le degré d'attaque est en général donné par la concentration de l'acide. Une couche protectrice formée par des produits de réaction et sa stabilité peuvent avoir une influence plus importante sur le taux d'usure que la concentration de la solution attaquante. Des expériences basées sur un modèle de calcul montrent comment estimer le taux d'usure dans les conditions réelles de construction. Les paramètres sont le genre et la concentration de la solution d'acide attaquant, la composition du béton et la stabilité de la couche protectrice.

ZUSAMMENFASSUNG

Der Angriff saurer Wässer muss bei der Planung dauerhafter Betonbauwerke berücksichtigt werden. Der Angriffsgrad wird im allgemeinen durch die Konzentration der angreifenden Säure angegeben. Eine aus Reaktionsprodukten gebildete ungestörte Schutzschicht kann einen wesentlich grösseren Einfluss auf die Abtragsrate haben als die Konzentration der angreifenden Lösung. Versuche auf der Grundlage eines Rechenmodells zeigen, wie man die Abtragsrate unter baupraktischen Bedingungen abschätzen kann. Einflussgrössen sind Art und Konzentration der angreifenden sauren Lösung, die Zusammensetzung des Betons und die Stabilität der Schutzschicht.



1. INTRODUCTION

Water which contains diluted acid, e.g. lime-attacking carbonic acid, will affect concrete. The acid dissolves the calcium from its bonds. As a result, the concrete is progressively destroyed from the surface to the inside. The rate at which the hardened cement paste and possibly the aggregate are dissolved mainly depends on the concentration of the attacking acid in the water and on the chemical resistance of the concrete. Many standards determine the degree of attack primarily on the basis of the concentration of the aggressive substances, e.g. ISO standard /1/. Test results show /2,3,6/ that only a very small proportion of the aggressive substances in the running water reacts with the hardened cement paste. Beyond that the chemical resistance of the concrete against a solvent attack can be enhanced by using insoluble aggregates and cement with a higher SiO_2 content /4,5/ and by keeping the water cement ratio low ($w/c \leq 0,60$). The flow rate seems to have very little influence /7/ as long as we stay within the ground water range of flow rates. This behaviour is to be explained by the formation of a protective layer of SiO_2 gel which, with increasing duration of attack, acts as a barrier to the transport of aggressive substance to and removal of dissolved constituents from the concrete. The chemical resistance of the concrete against solvent attacks is thus essentially depending on the existence of that protective layer. Reference to these correlations was made by several authors /8-11/. However, in planning and designing concrete structures they are not yet generally considered. It was therefore the objective of our study to develop a mathematical model for estimating in advance the loss of concrete as a function of the concrete composition, the concentration of the aggressive solution and the stability of the protective layer.

2. COURSE OF REACTION

Tests have shown /11,12/ that carbon dioxide (CO_2) dissolved in water first leads to the formation of a thin layer of calcium carbonate (CaCO_3) in the areas of mortar or concrete which are close to the surface. Then additional CO_2 dissolves the CaCO_3 to form $\text{Ca}(\text{HCO}_3)_2$ which is removed by the water. Next in the same process calcium from the calcium silicates is dissolved and removed. What remains is a gel-like layer consisting of hydrous silicon dioxide which also contains iron and aluminium oxide /11,13/. The gel layer becomes thicker with progressing attack. If a solid material forms a protective layer, the rate of dissolution will become essentially independent of the flow rate of the solution. In that case it will only be determined by the thickness and the diffusion resistance of the protective layer. This dissolution process can be slowed down further by reducing the flow rate of the surrounding water towards zero and by increasing the diffusion resistance in the environment of the concrete by a tight soil.

3. DETERMINING THE CaO REMOVAL FROM MORTAR AND CONCRETE

Koelliker measured the rate at which CaO is removed by dissolution from $4 \times 4 \times 16 \text{ cm}^3$ Portland cement mortar prisms containing about 500 kg of cement per cubic meter and having a water-cement ratio of 0.50 /11,12/. Lime-dissolving carbonic acid was dissolved in the attacking water. The resulting pH value was about 4.4. The surface-related rate of dissolution decreased (following approx. a $1/\sqrt{t}$ law) with increasing exposure time. This indicates that, due to the effect of the lime-dissolving carbonic acid, a protective layer forms which gains in thickness in the course of time and thus increasingly blocks the diffusion of the dissolved CaO.

By means of a model based on Fick's first law equation 1 was developed /14/ which can be used for calculating the thickness d of the destroyed layer after any given exposure time t . The influencing variables are the diffusion coefficient, the mass of soluble matter per volume unit, the area percent of the soluble matter in the area of attack and the difference in $\text{Ca}(\text{HCO}_3)_2$ concentration:

$$d = \sqrt{\frac{2 D A_L}{m_L A_{\text{ges}}} (c_s^* - c_L)} \cdot \sqrt{t} \quad /1/$$

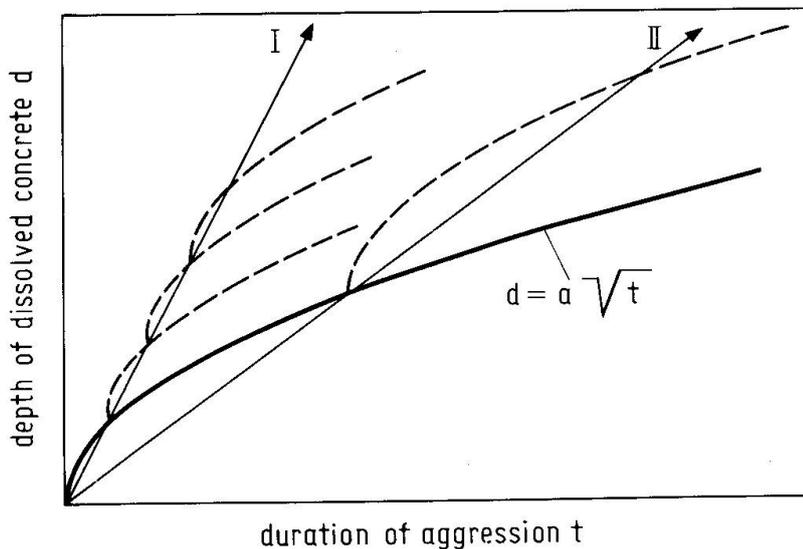
whereby

- d is the thickness of destroyed concrete layer in cm
- D $\text{Ca}(\text{HCO}_3)_2$ diffusion coefficient in cm^2/s of the protective layer (gel layer) ($D \approx 1.8 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ for SiO_2 gel of hardened Portland cement paste)
- m mass of soluble matter in g of CaO per cm^3 of concrete
- c_s^* CaO-concentration in g/cm^3 in the $\text{Ca}(\text{HCO}_3)_2$ -solution surrounding intact concrete
- c_L CaO-concentration in g/cm^3 in the $\text{Ca}(\text{HCO}_3)_2$ -solution which is unaffected by the concrete
- A_L/A_{ges} ratio of soluble matter area to total area in the cross section
- V_L/V_{ges} ratio of the volume of soluble constituents (if insoluble aggregate is used volume of hardened cement paste) to total volume
- $A_L/A_{\text{ges}} = V_L/V_{\text{ges}}$

Examples of computation including the determination of the concentration difference ($c_s^* - c_L$) are given in /14/.

The first root in equation 1 represents a constant valid in the respective case. Equation 1 can therefore be simplified to form equation 2.

$$d = a \cdot \sqrt{t} \quad /2/$$



The loss of mass which occurs with an intact protective layer and follows equation 2 is shown by the full bold line in Fig. 1. It had been assumed earlier that the loss of mass might follow a \sqrt{t} law /6, 8-10/. However, in the past it was not possible to describe different test periods by one function. This was due to the fact that the test specimens were dabbed with a moist cloth before being weighed. In this way part of the gel-like protective layer was re-

Fig. 1 Acceleration of a solvent attack when removing the protective layer periodically

moved so that the subsequent reaction occurred much faster than it would have done with an intact protective layer. If the protective layer is removed



regularly it is to be expected that the parabolic function turns to a linear one as shown by the straight lines I and II in Fig. 1. The "linear loss of mass" will be the steeper the more frequently the protective layer is removed (straight line I). It will be the flatter the less frequently the protective layer is removed (straight line II). This "linear loss of mass" has already been observed in connection with long-term tests /3/.

In order to verify this behaviour experimentally 4 x 4 x 16 cm prisms according to DIN 1164 were made with a 35 F Portland cement and a 35 L blast furnace slag cement. They contained 550 kg/m³ of cement and had a water-cement ratio of 0.50.

The prisms were produced and stored in water by the standard procedure. At the age of 7 days they were placed in tap water which was continuously enriched with CO₂ and renewed every week. The lime-attacking carbonic acid content was about 110 mg CO₂/l, the pH was 6.15 (mean values). The water flow rate was about 4.2 · 10⁻²² cm/s. The experimental setup is described in detail in /2/.

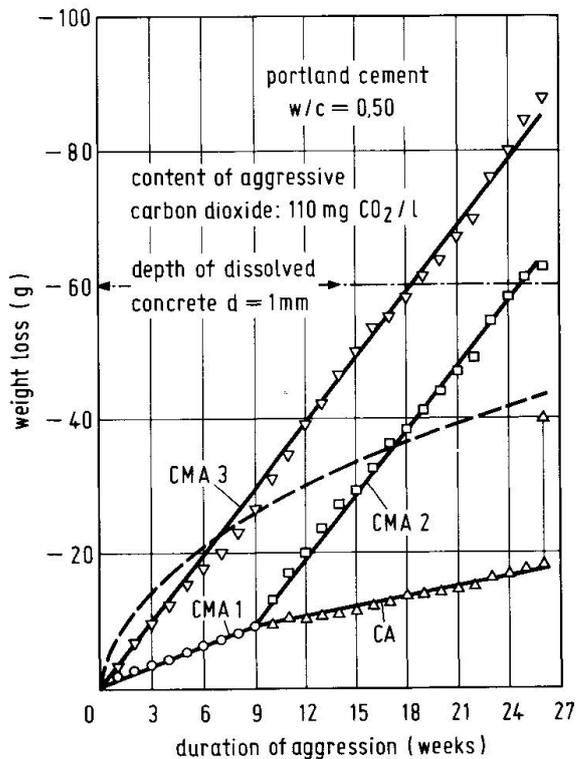


Fig. 2 Weight loss of PC-mortar prisms by aggressive carbon dioxide. Different intervals for removing the protective layer

the assumption that the higher content of silicon oxide and the resulting lower content of calcium oxide in blast furnace slag cement might be an explanation for this behaviour. The question, however, was not studied in greater detail.

The various losses of mass obtained in the tests are below the ones calculated using equation for, e.g., weekly losses, because brushing did not remove all of the SiO₂-gel from the pores. The longer the time period of an undistur-

The results for Portland cement mortar in Fig. 2 show that the weight loss resulting from the uniform chemical attack by 110 mg CO₂/l depends very much on the type and intensity of the additional mechanical treatment. In an initial series of tests the prisms were only dabbed once a week (CMA 1 in Fig. 2). After nine weeks some of the prisms were brushed once a week (CMA 2), the others were not subjected to any further mechanical treatment (CA). The prisms of the second test series were brushed three times per day throughout the test period (CMA 3).

The storage without any further mechanical treatment describes the chemical attack in slowly running water according to ISO DP 9690 /1/ with the diffusion being controlled by the protective layer. Dabbing presents a mild and brushing a vigorous additional mechanical treatment (M) of the protective layer.

The rate of concrete removal for CMA 3 was approx. 1 mm in 18 weeks or about 3 mm/a in the 4 x 4 x 16 cm prisms (a weight loss of 60 g corresponds to about 1 mm of loss of concrete). The rate of concrete loss was lower for the blast furnace slag cement mortars /14/ than it was for the Portland cement mortars. This leads to

bed gel layer was the better was the agreement between the calculated and the experimental results /14/. This can be seen from the dotted line in Figure 2, which shows the calculated depth of dissolved concrete according to equation 1. The first brush off at the age of 26 weeks shows the marked value slightly below the calculated value.

4. PRACTICAL APPLICATION

In addition to the construction cost the design engineer should include in his considerations the service life and the repair and maintenance cost of a structure. If concrete is exposed to acids the resulting loss of mass may be irrelevant to its use. This often is the case for structures like foundations or drilled foundation piles. In contrast, the practical use of a container or a water duct where the protective layer may be removed regularly can be considerably impaired by a constant loss of e.g. 0.5 mm of concrete per year. Therefore the design engineer, besides considering the acid concentration in the attacking water, should also pay attention to the external conditions on which the concrete is exposed to the water. For illustration Fig.3 shows the depth of concrete loss in mm after 20 years for different conditions of transport and different content of aggressive CO_2 . The conditions of transport are described in Table 1.

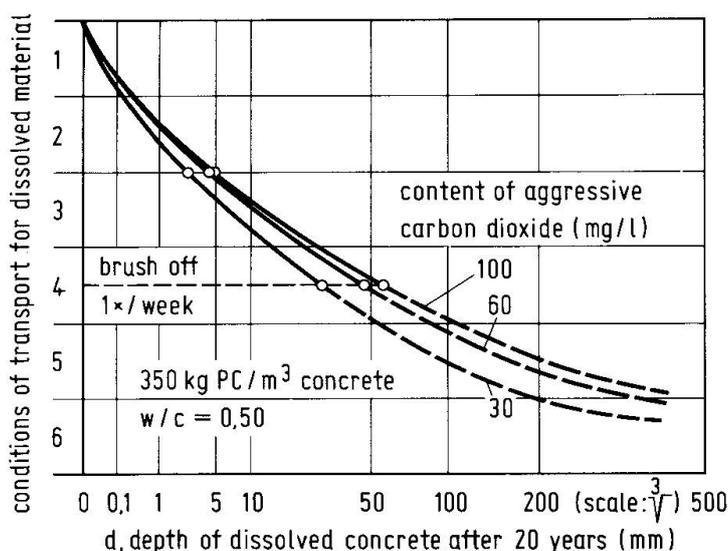


Fig. 3: Depth of dissolved (and removed) concrete after 20 years in different concentration of aggressive carbon dioxide at different conditions of transport (see below) for the products of the reaction

derably impaired by a constant loss of e.g. 0.5 mm of concrete per year. Therefore the design engineer, besides considering the acid concentration in the attacking water, should also pay attention to the external conditions on which the concrete is exposed to the water. For illustration Fig.3 shows the depth of concrete loss in mm after 20 years for different conditions of transport and different content of aggressive CO_2 . The conditions of transport are described in Table 1.

The dots in the figure represent the results of experiments and calculations. The dotted parts of the curves in the areas of TC 5 and 6 are extrapolations that can at present not be validated by test results.

CT 1	Compact deposited soil, permeability $k < 10^{-4}$ cm/s, very slowly moving or stagnant ground water, protective layer, Fick's 2. law.
CT 2	Permeable soil with $k \geq 10^{-4}$ cm/s, ground water moving slowly, protective layer, Fick's 1. law.
CT 3	Flowing free water, protective layer nearly undisturbed, Fick's 1. law
CT 4	Flowing free water, protective layer removed periodically, Fick's 1. law
CT 5	Flowing free water, high velocity of flow, no protective layer, approximation to specific velocity of dissolution.
CT 6	Flowing free water, very high velocity of turbulent flow, cavitation.

Table 1 Conditions of transport (CT) according to Fig. 3

5. CONCLUSIONS

- The diffusion model presented here and the tests described permit to arrive



at a quantitative estimate of the loss of mortar and concrete to be expected in case of a chemical attack by lime-dissolving carbonic acid.

- The exposure to lime-dissolving carbonic acid leads to the formation of a protective layer consisting of gel-like silicon dioxide.

- In the presence of an intact protective layer the loss of mass (the amount of affected concrete) follows a \sqrt{t} law.

- If the protective layer is mechanically destroyed the concrete is removed at an accelerated rate.

- A disturbance of the protective layer, even if it occurs at relatively long intervals, can have a much more damaging effect than an increase in the concentration of the aggressive acid.

- The tests described, i.e. the stripping of the protective layer at regular intervals, and the mathematical model permit a long-term estimate of the loss of mass also caused by other than lime-dissolving carbonic acid. Experiments with other acids can be made in about 3 months.

- It appears possible to consider more completely in future standards the factors which reduce and increase the loss of mass from concrete exposed to attacking acids. This would be to the benefit of concrete structures. It is suggested to define the degrees of attack by solved mass or the affected depth of concrete respectively.

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