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Long-Term Influence of Fly Ash on Chloride-Induced Corrosion

by Peter Schießl and Udo Wiens

Synopsis: The durability of reinforced concrete structures has been acquiring an increasing degree of emphasis in research activities. The development of concrete mixtures with regard to different attacks imposed on concrete structures by climatic influences plays a decisive role in this context. Under certain conditions, the performance of these concretes can be increased by using pozzolanic additions, such as fly ash or blast-furnace slag, as cementitious components. This publication intends to summarise the influence of these cementitious components on important processes contributing to chloride-induced corrosion. Diffusion and corrosion cells were used to examine the diffusion resistance and corrosion rate of mortars and concretes clag in relation to the total content of cementitious binders. The results of pore structure investigations were also employed in order to clarify the influence of these cementitious components on the influence of these cementitious components on the concrete.

<u>Keywords</u>: Blast-furnace slag; chlorides; concrete; corrosion; diffusion; durability; fly ash; porosity.

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INTRODUCTION

The service life of concrete structures exposed to chlorides (see-water, deicing salts, etc.) strongly depends on the quality of concrete cover. Prolonging the time to initiation of the corrosion process and reducing the corrosion rate once the corrosion process has started should be one of the primary aims when designing concrete mixtures for structures exposed to chlorides.

It is well known that the use of fly ash or blast-furnace slag improves the corrosion resistance of portland cement concretes (1,2). The main beneficial effect of fly ash is related to the refinement of the pore structure by the pozzolanic reaction reducing diffusion rates and electrolytic conductivity of concrete (3). Some authors have reported an increase in the chloride binding capacity when fly ash is added to the portland cement concretes (4,5). Most of the investigations done until now concentrate on the influence of fly ash on chloride binding or chloride transport. In this paper an approach is made to valuate the effects of fly ash on the transport and the physisorptive binding of chloride and the consequences for the corrosion of steel in concrete. Diffusion coefficients were determined on the mortar specimens by means of a rapid-test method. In concrete corrosion cells time-dependent corrosion currents and electrolytic resistances were measured. Additionally, pore structure analysis were carried out to support the explanation of the chloride transport and chloride binding phenomena. Parameters varied in this test series were the fly ash content and the type of cement. The results were compared and correlated with the extensive published data about oxygen diffusion and resistivity measurements (3,6,7).

EXPERIMENTAL

Materials and mixtures

For the mortar and concrete investigations, a portland cement (C1) with low-alkali content and two blast-furnace slag cements containing 46 and 74 mass.% of slag respectively (C2 and C3) in compliance with the requirements of German cement standard DIN 1164 were selected. The chemical composition of the fly ash corresponds to a low-calcium class F fly ash in accordance with ASTM C 618. Table 1 shows the physical and chemical properties of the binding components.

Table 2 summarises the composition of the examined mortars and concretes. The influence of fly ash content was examined by the combination of portland cement (C1) and 0, 20, 40 and 60 mass.% in relation to (c+f) of fly ash. In the case of the blast-furnace slag cement (C2) 20 mass.% of fly ash was used. No fly ash was added to the cement with the high-slag content (C3). Concretes containing this type of cement are known to possess a very high resistance against the penetration of chlorides and sulphates. It is also known that the pozzolanic reaction of the fly ash in conjunction with high-slag blast-furnace cements is only weak which means that the fly ash will not make any substantial contribution to the density of the pore structure (7).

Composition and production of the mortar mixtures were based on EN 196-1, using standard 0.08/2 mm sand. After mixing, prismatic moulds of $70 \times 70 \times 300$ mm³ were filled with mortar, compacted and stored in the vapour chamber (20 °C/95 % R.H.) for 1 day. After demoulding, the storage was continued under water of 20 °C until testing.

The water content of all concretes was kept constant at 180 kg/m³. An efficiency factor for the fly ash of k = 0.5 was incorporated into the calculated w/(c+k·f) value throughout. In this way, nearly the same compressive strength at 28 days was attained for all the concretes, with the exception of the concrete containing portland cement and 60 mass.% fly ash (see Table 2). Sand and gravel from the River Rhine was used as the aggregate. The grain size distribution of the concrete aggregates corresponded to grading curve A/B 16, in accordance with German standard DIN 1045.

The composition of cementitious components and the water/binder for the mortar and concrete mixtures were identical. The storage of the test specimens and the compressive strength tests were carried out on the concrete in accordance with German standard DIN 1048 (150-mm cubes). The test specimens used to determine time-dependent development of the electrolytic resistance and the

corrosion currents were stored at 20°C/80% R.H. after 2 days in the vapour chamber (20 °C/95% R.H.) and were then connected to a data-acquisition system.

Test procedures

The chloride-diffusion coefficients were determined by means of a rapidtest method developed by Tang and Nilsson, which is described in (8). The experimental set-up (migration cell) is shown in Fig. 1.

Before testing, cylinders of $\emptyset = 50$ and h = 50 mm were drilled from the mortar prisms and inserted into the test set-up. A voltage of 30 or 40 V (DC) was applied between anode and cathode, depending on the expected diffusion resistance. No increase in temperature of the solutions or in the measured current was detected during the tests. The chloride concentration in the cathode chamber was c(NaCl) = 0.513 mol/L (in c(KOH) = 0.2 mol/L) in all the tests. After a specified time, depending on the expected diffusion resistance, the cylindric mortar specimens were split along their longitudinal axis and the chloride penetration depths were determined by a colorimetric method described in (9). The calculation of the migration coefficients from the chloride penetration depth (x_d) is presented in (8). The transport coefficient determined with the aid of the migration cell is called D_{CLM} (M = migration).

The experimental set-up to determine the electrolytic resistance is described in (10). In contrast to the description in (10), corrosion cells measuring $200 \times 110 \times 110 \text{ mm}^3$ were used in the course of these tests. One mild steel St-37 (DIN EN 10 025, material No. 1.0037) and one platinised titanium rod (fully coated with 2.5 µm platinum), measuring length 1 = 180 mm and diameter \emptyset = 16 mm served as electrodes (distance of electrodes: 20 mm). In all cases, one mass.% of chloride, related to the cement content, was added to the fresh concrete. A pore size distribution range between 1.8 nm and 150 µm was determined on mortar specimens by mercury intrusion porosimetry.

RESULTS AND DISCUSSION

Diffusion coefficients

The determination of diffusion coefficients for chloride by means of the rapid tests, whereby the chloride ions are driven into the test specimen via an electrical field, is a subject of controversy in the relevant literature (11,12). There is a lack of confirmed knowledge as to the precise processes which occur in such

migration tests. Charge transport in the electric field, for example, is effected not only via chloride ions, but also via other negatively charged ions (e.g. OH-ions). The question as to how chloride binding processes are affected by the electrical field also remains unanswered.

Compared to conventional diffusion tests the rapid-test method has the advantage that the influence of the time-dependent changes in pore structure are eliminated. This is of particular interest with regard to additions, such as fly ash or blast-furnace slag, reacting over a long period. The pore structure of concrete and mortar with these materials changes over a period of years. It is thus often very difficult to specify the time at which a steady state prevails in conventional diffusion cells for determining intrinsic diffusion coefficients. Fig. 2 shows the time-dependent development of D_{CLM} dependent on cement type and fly ash content. Using an efficiency factor of 0.5 for fly ash (w/(c+0.5 f) = 0.50), nearly the same migration coefficients as for the corresponding reference mixtures without fly ash are attained at an age of 28 days, irrespective of the fly ash content. While the migration coefficients for the portland cement (C1) remain virtually unchanged over the test period, the migration coefficients for the mixtures containing fly ash fall markedly as the fly ash content increases. The use of blast-furnace slag is also accompanied by a rise in the diffusion resistance (C2).

The results of these tests together with the migration coefficients published in the relevant literature (5,8) show that the rapid test is highly suitable for characterising the diffusion resistance of concretes containing different additions. It should be taken into account, however, that in the case of slowly reacting additions, such as fly ash or blast-furnace slag, a migration coefficient determined from rapid tests after 28 days or earlier is unsuitable to describe the long-term behavior of these materials, as the pore structure of the concrete is continuously changing over years as a result of the slowly progressing reactions.

Fig. 2 also illustrates that a further reduction of the migration coefficients is possible when combining blast-furnace slag cement (C2) and fly ash. The increase in the diffusion resistance is less for the blast-furnace slag cement (C2) than for the portland cement (C1) at the same fly ash content (20 mass.%), however. This is due to the lower reactivity of the fly ash in the blast-furnace cement mixtures, caused by a lower content of Ca(OH)₂, a lower alkalinity of the pore solution and a denser pore structure (7). With the blast-furnace slag cement (C3) migration coefficients of 2.3, 1.7 and $0.3 \cdot 10^{-12} \text{ m}^2/\text{s}$ at 28, 91 and 365 days were measured, respectively. This is in the range of the mixture with blast-furnace slag cement (C2) and 20 mass.% fly ash.

The results of the migration test are essentially confirmed by the conventional diffusion tests (7,13). Fig. 3 shows the intrinsic chloride diffusion coefficients determined via conventional tests in relation to the duration of precuring and the fly ash content (7). It needs to be taken into account that the

test duration of the conventional diffusion test is in the range of several weeks to some month until the steady state is reached, i.e. the measured values for D_{CI} are mean values over the test period.

When 20 and 40 mass.% portland cement is replaced by the same quantity of fly ash, the diffusion coefficients obtained in conventional tests fall by approximately one or more than one order of magnitude, after a precuring period of 365 days. The reductions measured in the migration test are in the same order of magnitude.

The higher reduction of the migration coefficients caused by the fly ash in the migration tests compared to the diffusion tests are accountable, among other things, to the fact that a fly ash efficiency factor k = 0.5 was incorporated into the water-cement ratio for the mixtures used in these tests (Fig. 2), resulting in a lower water/binder-ratio w/(c+f) compared to the mixtures presented in Fig. 3.

The results of these tests together with the migration coefficients published in the relevant literature (8) show that the rapid test is highly suitable for characterising the diffusion resistance of concretes containing different additions.

Influence of pore structure on migration coefficients

Several authors report that the increase in the diffusion resistance of concrete resulting from the addition of fly ash is not accountable solely to the reduction in the capillary pore volume (7, 14).

From Fig. 4 it can be derived, that at a given capillary pore volume (defined here as pores with a radius larger than 10 nm), a lower migration coefficient $D_{Cl,M}$ was usually determined as fly ash content increased. Even at relatively high capillary porosities as was measured for the mixture with 60 mass.% fly ash a significant reduction of the migration coefficients could be obeserved. The migration coefficient as well as the capillary porosity did not change for the reference mortar over the period of testing (28, 91 and 365 days), wheras the capillary porosity is reduced by fly ash on the behalf of the gel pore volume.

This behavior indicates a blocking of the pore channels connecting the capillary pore system due to the CSH-phases which are produced by the pozzolanic reaction. The pore parameter which should best reflect this effect is the threshold radius. This parameter determined by the mercury intrusion porosimetry characterises the pore radius below which a continuus network of pores exists. The smaller this value, the lower will be the continuity of the pore network. The good correlation between the migration coefficient and the threshold radius

confirms the model concept that permeability is reduced primarily through the reduction of this pore entry radius due to pozzolanic reaction of the fly ash (Fig. 5). The pozzolanic reaction of the fly ash distinctly reduces the threshold radius as compared to the reference mixture. The effect becomes more pronounced as fly ash content increases. This influence of fly ash occurs even with blast-furnace slag, but it is less significant with these cements, since the reaction of the slag has already densified the pore structure.

However, the movement of chloride ions in the microstructure of dense concrete is not solely restricted by the blocking of the pore channels. The sorptive binding of chloride in dense concrete is of decisive importance, too. To confirm this assumption the ratio oxygen diffusion coefficient/chloride migration coefficient, D_{02}/D_{CLM} , is plotted against the migration coefficient D_{CLM} in Fig. 6. In the range of 9 and 13.10⁻¹² m²/s for D_{CLM}, the ratio D_{O2}/D_{CLM}, nearly remains constant. As the resistance of the mortar to chloride diffusion increases, i.e. as D_{CLM} falls below 9.10⁻¹² m²/s, the D_{02}/D_{CLM} ratio grows disproportionately. Without restrictions by a porous medium, a ratio $D_{O2 air}/D_{Cl.solution}$ of $\approx 10^4$ is to be expected (15). This is confirmed for migration coefficients of D_{CLM} between 9 and 13.10⁻¹² m²/s, e.g. for cement paste of relatively high porosity (see dotted line in Fig. 6). If no interaction took place between the charged chloride ions and the pore walls, the D_{02}/D_{CLM} ratio would have to remain constant at $\approx 10^4$. even at low chloride migration coefficients, as the oxygen diffusion coefficient would then have to be influenced to an equal degree by the reduction in permeability. Instead, the D_{O2}/D_{CLM} ratio increases substantially.

In view of the densification of the pore structure by supplying additional CSH from the pozzolanic reaction of fly ash, it is to be suspected that chloride transport is very severely inhibited by interactions between the electrostatically charged pore walls and the negatively charged chloride ions. These observations are confirmed by investigations carried out by Ngala et al. (14). For cement paste of low capillary porosity (with or without fly ash), a very substantial difference between oxygen and chloride diffusion coefficients was found (14). A similar result would be obtained, if the diffusion coefficients from Fig. 3 for the graph, instead of D_{CLM} were used.

Importance of results for chloride-induced corrosion

Beside the transport of chloride ions the permeability of the pore structure is of decisive importance for processes involved in the corrosion of steel in concrete. One of the most important processes is the charge transport of hydroxile ions between anodic and cathodic steel surfaces, which is determined by the resistance of the electrolyte (in this case the concrete). Fig. 7 shows the timedependent development of the electrolytic resistance.

For the concretes mixed with fly ash and portland cement, a significant increase in electrolytic resistance is to be observed after approx. 20 days. Studies by Härdtl (3) and Sybertz and Wiens (16) show that, although a certain quantity of $Ca(OH)_2$ has been converted into hydration products by this time as a result of the pozzolanic reaction of the fly ash, the absolute quantity of hydration products can hardly be sufficient to reduce the capillary porosity to such an extent as to explain the marked rise in electrolytic resistance as the fly ash content increases. Rather, a thin layer of reaction products on the surface of the fly ash particles would appear sufficient to interfere with the continuity of the pore system. This "pore-blocking effect" together with the pore wall interactions, described in Fig. 6, are suspected to be the cause for the observerd drastic reduction in ion transport through the matrix.

As the age increases, the electrolytic resistance in the mixtures containing 40 and 60 mass.% fly ash exceeds both, of the reference portland cement mixture (C1) and the two mixtures with blast-furnace slag (C2 and C3). After approximately 1 year, the concrete with portland cement (C1) and 20 mass.% fly ash attains the same electrolytic resistance as the concrete with the blast-furnace slag cement (C3). At this age, the electrolytic resistances of the 20, 40 and 60 mass.% containing fly ash mixtures are 7, 19 or 30 times higer compared to the reference portland cement mixture (C1).

Concretes mixed with blast-furnace slag display the typical time-dependent course of resistance, with initially higher values giving way to a slower increase.

Fig. 8 shows the corresponding macrocell currents for concrete mixtures with cement (C1) and 0, 20, 40 and 60 mass.% fly ash. The high overall macrocell currents at the beginning of the measurement are mainly due to the anodic polarisation by the use of a platinised titanium rod as the anode. At the beginning of the measurement, the macrocell current of the fly ash containing mixtures exceeds the values of the reference mixture. At about 10 days the macrocell currents for all mixtures yield roughly the same value. Corresponding to the increase in electrolytic resistance for the fly ash containing mixtures at about 20 days due to the starting of the pozzolanic reaction, a significant drop of the macrocell currents with increasing fly ash content from this date on is observable. From experience it is known that 1 mass.% added chloride is in the range of the critical chloride content for the test conditions given after more than about 365 days. For this reason the polarisation resistances overrule the influence of the electric resistance. Additionally the 1 mass.% chloride are related to the cement content, that means reduced chloride contents related to (c+f) with increasing fly ash content.

As previously explained, ion transport, and in conjunction with this, the corrosion rate of steel in concrete is determined to a decisive degree by the geometric limitations in the pore structure. Fig. 9 shows the interrelationship

between the electrolytic resistance of concrete and the median of the pore size distribution of mortar and cement paste for mixtures with and without fly ash or blast-furnace slag.

The median characterises the radius of a pore size distribution corresponding to a mercury intrusion volume of 50 %, and represents a simple parameter for characterising the pore structure. As the pore structure becomes increasingly finer due to hydration of the cement or the pozzolanic reaction, the median values generally decrease. Especially pore blocking effects cause a significant shift of the median value.

In Fig. 9, the results of these investigations are compared with the results obtained by Härdtl (3), Raupach (6) and Wiens et al. (10) for normal and highstrength concretes with and without fly ash or blast-furnace slag. Since a decreasing median radius, e.g. caused by the pore blocking effect of fly ash or an increase of the surface of hydration products, resulting in a drastic reduction of ion movement, an exponential interrelationship to the electrolytic resistance is to be expected and confirmed by the graph of Fig. 9.

The lowest median radii and the highest electrolytic resistances for normal strength concretes are observed for the mixture with 60 mass.% fly ash or for mixtures with blast-furnace slag cement.

CONCLUSIONS

Chloride migration coefficients can be determined for concretes mixed with portland cements containing fly ash or blast-furnace slag by means of the migration test developed by Tang and Nilsson (8). When applying this rapid-test method, changes in pore structure over the time of testing do not occur.

The increased resistance to chloride transport in comparison to portland cement concretes which was observed when adding fly ash to concrete is accountable to the densification of the pore structure due to the formation of additional CSH phases. As the pore structure densifies, the interactions between the electrically charged pore walls and the chloride ions acquire a decisive influence, as a result of which chloride transport is inhibited. Another primary reason for the increase in diffusion resistance resulting from the use of fly ash is the effective disruption of the pore system's continuity by reaction products which form on the surfaces or in the vicinity of the fly ash particles. A relatively thin hydrate layer (corresponding to a relatively low level of reaction of the fly ash) appears to be sufficient to effectively seal up the pore channels.

Due to the pozzolanic reaction of the fly ash and the required reduction in the w/(c+f) which is necessary in order to attain the same strength levels, a substantial increase in electrolytic resistance and a subsequent reduction of corrosion rates is attainable. In concretes containing fly ash, a further increase in electrolytic resistance levels is still to be expected beyond the age of 365 days.

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