Relating the formation factor to chloride diffusion in concrete based on low carbon binder types

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Abstract. The development and introduction of new types of binders are being driven by the desire to reduce CO_2 emissions in cement production. To use these binders as alternatives to Portland cement, their influence on the durability of concrete and reinforced concrete structures must be quantified. The test methods usually focus, for example, on resistance to the penetration of corrosive substances such as chloride through diffusion processes, carbonation resistance or frost resistance. These test methods often involve the use of chemical indicators, the chemical reaction of which can be influenced by the chemical composition of the pore solution contained in the tested concrete or mortar. Therefore, conventional test methods may not be fully applicable for new types of binders. An alternative is to assess the quality of mortars and concretes using electrical methods that are independent of indicator reactions. This article takes a closer look at the electrical resistivity of mortars and concretes and the formation factor as a microstructure parameter. Both, but the formation factor in particular, show great potential for providing meaningful assessments as a parameter for evaluating the durability of mortar and concrete.

1 Introduction

The enormous global demand for concrete is met almost exclusively by using types of cement produced with ordinary Portland cement (OPC) clinker. The manufacturing process results in high CO_2 emissions, firstly from the conversion of limestone to calcium oxide and secondly from the generation of high burning temperatures. Cement production therefore accounts for 8 - 9 % of global man-made CO_2 emissions [1-3]. In order to reduce this proportion, the development of alternative types of binders is being driven forward worldwide. The substitution of clinker with additives has made considerable progress in reducing the clinker factor in cements. In Europe, mainly Portland composite cements with granulated blast furnace slag (GBFS), fly ash or limestone powder are used, which are standardized in the CEM II class [4]. In CEM III/C cements, substitution rates of up to 95 % with GBFS are even possible [4]. Decades of practical experience have already been gained with these cements with regard to the durability and corrosion protection of the metallic reinforcement. However, the availability of fly ash and GBFS can only be ensured in sufficient quantities in the medium term, as the shutdown of coal-fired power plants and changes in the steel production process will result in fewer of these secondary raw materials [5, 6].

One current issue is therefore the search for alternatives as an additive in composite cement. In addition, approaches are also being pursued to produce binders without the use of OPC clinker.

In order to be able to safely use alternative binder types in reinforced concrete, reliable test methods are required to quantify the influence of the binders on the durability of the components. The rapid chloride migration (RCM) test, e.g. according to DIN EN 12390-18 [7], is usually used to test resistance to chloride penetration. In this test, chloride ions penetrate mortar or concrete test specimens in an accelerated manner by applying an electric field. At the end of the test, the test specimens are split and the penetration front of the chlorides is made visible using a sprayed-on chemical indicator based on silver nitrate. The reaction of the indicator is influenced by the chemical composition of the pore solution present in the mortar or concrete. This can differ from OPC-based systems in terms of its composition and pH value, meaning that the test may not be suitable for all binder types without validation [8-11]. One way of assessing the quality of mineral building materials without the use of indicator solutions is to use electrical methods. In the following, the electrical resistivity and the formation factor are explained and their suitability is demonstrated by means of comparisons with the chloride diffusion coefficient.

The electrical resistance of mineral building materials can be determined in different ways. One simple option is to measure the alternating current (AC) resistance, for example by connecting a drill core disk between two electrodes and recording the measured value in ohms with a resistance meter at a frequency of around 1000 Hz. As this measured value depends on the geometry of the sample, it must be multiplied by a geometry factor in order to obtain a comparable material characteristic value.

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$$\rho_{concrete} = R_{AC} \cdot k \quad (1)$$
with $$k = A \cdot l^{-1}$$

Where $\rho_{concrete}$ is the resistivity in Ωm, R_{AC} is the measured resistance value in Ω and k is the geometry factor with the unit m. A is the area of current flow and l the distance of the electrodes. The electrical conductivity of mortar and concrete is based on the fact that the pore system is filled with pore solution, which contains various positively and negatively charged ions that act as charge carriers. The solid phase of the mortar or concrete does not contribute to the conductivity. As a result, the ratio of the electrical resistivity of the concrete ($\rho_{concrete}$) to the electrical resistivity of the contained pore solution ($\rho_{pore\ solution}$) can be used to make statements about the pore structure, or more precisely about the connectivity of the pore paths [12]. For this purpose, the formation factor FF is determined according to equation (2) [13, 14]:

$$FF = \rho_{concrete} \cdot \rho_{pore\ solution}^{-1} \quad (2)$$

The formation factor can be used as a dimensionless parameter to characterize the pore structure. As it expresses the proportion of the total electrical resistivity of a porous material that cannot be explained by the electrical resistivity of the pore solution, it can be regarded as a structural parameter. A low porosity (φ) or connectivity (β) of the pores leads to a high formation factor. This can be expressed by equation (3) [12]:

$$FF = (\varphi \cdot \beta)^{-1} \quad (3)$$

In other studies, the formation factor as a structural parameter is associated with various transport processes such as chloride penetration [12, 15-17], oxygen diffusion [18], water absorption [19] or also with the duration of the initiation phase until the onset of corrosion of reinforcing steel [20].

2 Materials and methods

In order to test the applicability of the electrical resistivity and the formation factor to assess the chloride diffusion in various alternative binder types, both parameters were determined on concrete formulations based on novel binder types. In addition, the chloride diffusion coefficient of the concretes was determined and the correlation with electrical resistivity and formation factor was discussed.

2.1 Investigated concrete formulations

Concretes produced with alternative main components and alternatives that do not contain OPC at all were part of the investigation program. In addition, concretes based on CEM I and on CEM III/B were examined as reference concrete for comparison. All concrete formulations were produced with a w/b ratio of 0.4, a binder content of 350 kg/m³, a paste volume of 275 l/m³ and an A/B 8 grading curve. Superplasticizers were used to ensure workability. In the group of alternative main components, two calcined clays and a steel slag from the LD process were tested, each replacing 30 wt.% of the CEM I from the reference mix. A calcium sulfoaluminate (CSA) cement was also tested. CSA cements have been used in China for several decades and are known for their rapid hardening [21-24]. Therefore, tartaric acid was used here as a retarder. The test program was supplemented by a concrete produced with Celitement®. This binder contains C-S-H phases, that are produced in an autoclave and then mechanochemically activated [25-28]. Another group of alternative binders are the alkali-activated materials (AAMs), which are represented here by an alkali-activated GBFS. An overview of the binders used can be found in Table 1.

Table 1. Overview of the various binder types.

Identifier	Type of binder
Ref 1	CEM I 42.5
Ref 2	CEM III/B 42.5
CC I	70 % CEM I 42.5 + 30 % Metaillite
CC II	70 % CEM I 42.5 + 30 % Metakaolin
LD	70 % CEM I 42.5 + 30 % LD slag
CSA	Belitic Calcium Sulfoaluminate cement, tartaric acid as retardant
C-S-H	Celitement®
AAS I	GBFS activated by sodium silicate

2.2 Experimental

The electrical resistivity of the concrete formulations described above was determined on water-saturated samples aged 28 days. For this purpose, cubes with an edge length of 150 mm were produced and stripped and stored in water at an age of two days. At the age of 21 days, cores with a diameter of 100 mm were drilled and prepared into slices of 50 mm thickness. These were stored in water again until testing. The electrical resistance of three samples per formulation was measured at a frequency of 1000 Hz using the two-electrode method. It was converted into specific values on the basis of the sample geometry.

On additional cores produced in the same way the chloride diffusion coefficient was determined in accordance with DIN EN 12390-11 [29]. For this purpose, the outer surface of the cylinder disks was sealed with epoxy resin and cylindric containers were glued onto the top. These were filled with sodium chloride solution at the age of 30 days and secured with film to prevent evaporation. The test specimens with the cylindric containers were stored at 20 °C and >95 % relative humidity for 90 days. The concrete specimens were then ground in 2 mm slices, starting from the surface that was in contact with the chloride solution. The chloride content in the grinding powder was determined by laboratory analysis. Nine slices were taken from the chloride exposed side and one from the other side of the sample to determine the initial chloride content. The chloride diffusion coefficients (D_{nss}) were determined by fitting the chloride profiles to the diffusion equation according to DIN EN 12390-11 [29].

To determine the formation factors, the resistivities of the respective pore solutions are relevant in addition to the concrete resistivity. These can be determined either by expression due to very high pressure or by a leaching process, whereby the latter was used here. For this purpose, paste samples of the binders listed above were produced. At the age of 28 days, these were ground to a diameter < 100 µm in a disc vibrating mill, dried and then mixed with demineralized water at a ratio of 1:1 for 5 minutes. This mixture was centrifuged and the conductivity was measured in the clear supernatant.

3 Results and discussion

Table 2 shows an overview of the results. The concretes based on different binders show significantly different electrical resistivities at the age of 28 days. The lowest value was measured for the OPC composite with steel slag (LD) at 91 Ωm. The concrete based on Celitement® (C-S-H) showed the highest value with 2437 Ωm. Compared to the concrete resistivity ($\rho_{concrete}$), the pore solution resistivity ($\rho_{pore\ solution}$) is much lower. In addition, a clear difference is also noticeable here: In the case of CSA and C-S-H, the resistivity of the pore solutions is higher. The formation factors (FF) were calculated according to equation (2). The chloride diffusion coefficients (D_{nss}) are mean values of two specimens.

Table 2. Overview of the results.

Binder	$\rho_{concrete}$ [Ωm]	$\rho_{pore\ solution}$ [Ωm]	FF [-]	D_{nss} 10^{-12} m²s⁻¹
Ref 1	139	0.27	516	4.81
Ref 2	715	0.45	1594	1.33
CC I	355	0.36	984	1.99
CC II	1154	0.47	2458	0.60
LD	91	0.34	268	6.67
CSA	2437	1.75	1394	0.94
C-S-H	647	3.14	206	10.05
AAS I	150	0.23	644	2.43

The correlations of the diffusion coefficients with the concrete resistivities (see Fig. 1) and with the formation factor (see Fig. 2) show some differences: In principle, a trend can be recognized between resistivity and diffusion coefficient, which roughly follows a 1/x curve. Binders with a comparable resistivity of the pore solution follow the trend more closely. Binders with a higher pore solution resistivity, such as CSA and C-S-H, are positioned further away.

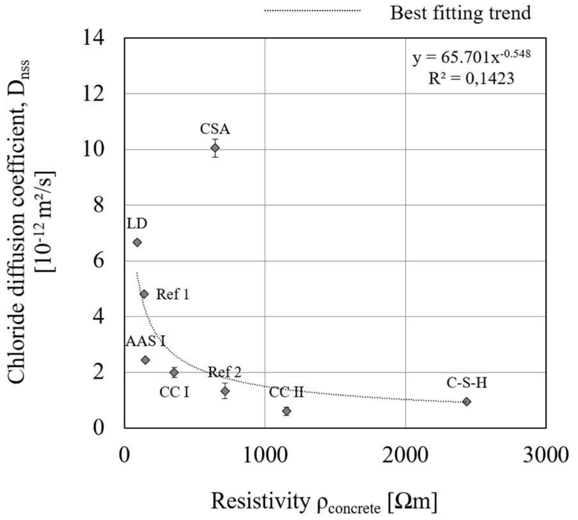

Fig. 1. Correlation between concrete resistivity and diffusion coefficient

If the deviating conductivity of the pore solution is now taken into account by calculating the formation factor (FF), the result is a better match (see Fig. 2.). For this dataset it is even possible to calculate the diffusion coefficient in porous media from the formation factor using the self-diffusion coefficient of chloride ($D_{0,Cl}$) [30]: The self-diffusion coefficient for chloride is 17.1 · 10^{-10} m²s⁻¹ at 18 °C and 20.3 · 10^{-10} m²s⁻¹ at 25 °C [31]. The dashed line in Fig. 2 is the graphical representation of equation (4) [30]:

$$D = D_{0,Cl} \cdot FF^{-1} \quad (4)$$

The measured values show good agreement with the calculated values.

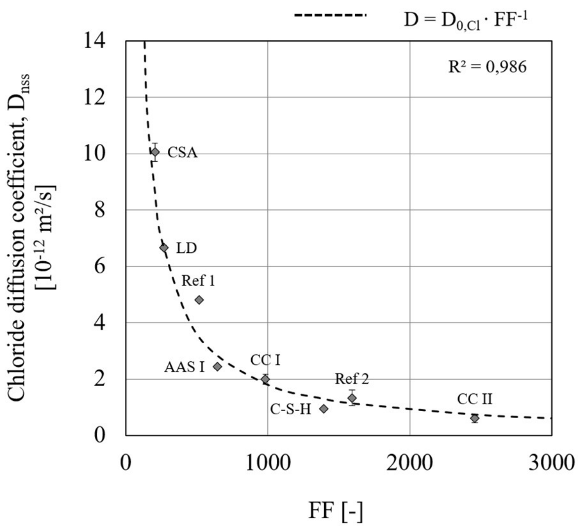

Fig. 2. Correlation between formation factor and diffusion coefficient

4 Conclusions

Based on the results shown here, the following conclusions can be drawn with regard to the suitability of electrical parameters for assessing the chloride penetration resistance of concrete:

- Electrical resistivity offers a simple way of assessing the durability of mortars and concretes. However, this statement is only valid to a limited extent for binder systems with a pore solution conductivity that deviates from OPC based materials.
- In order to assess binder types with different pore solution conductivities, the determination of the formation factor offers a more promising approach for assessing durability aspects.
- The application is particularly interesting for new types of binders, as the suitability of indicator-based test methods is unclear due to the sometimes unknown pore solution compositions.
- The calculation of chloride diffusion coefficients based on the formation factor of the concrete and the self-diffusion coefficient of chloride in solution shows good agreement with actual measured values. This shows that the formation factor also allows a quantitative assessment.

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