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Abstract

Metals embedded in porous media interact electrochemically with the liquid phase contained in the pores. A widespread form of this, adversely affecting the integrity of engineered structures, is corrosion of steel in porous media or in natural environments. While it is well-documented that the rate of this electrochemical dissolution process can vary over several orders of magnitude, understanding the underlying mechanisms remains a critical challenge hampering the development of reliable predictive models. Here we study the electrochemical dissolution kinetics of steel in meso-to-macro-porous media, using cement-based materials, wood, and artificial soil as model systems. Our results reveal the dual role of the pore structure, that is, the influence on the electrochemical behavior through transport limitations and an area-effect, which is ultimately due to microscopic inhomogeneity of the metal-porous material interface. We rationalize the observations with the theory of capillary condensation and propose a material-independent model to predict the corrosion rate.

Corrosion of steel in engineered materials such as ceramics[1,2], wood[3], and porous coatings[4], or in natural environments such as soils[5-7] and mineral ores[8] is one of the most relevant forms of electrochemical dissolution of metals. These cases are vital to various fields of science and technology such as civil and subsurface engineering, radioactive waste storage, oil and gas, or archaeology, where ultimately the quantification and control of the rate at which the corrosion processes occur is fundamental. Fig 1 shows that this electrochemical dissolution rate is strongly dependent on both the porosity and the moisture conditions of the porous medium surrounding the steel[9,10].

Even in virtually identical chemical composition of the liquid phase in the pore system, the measured corrosion rate can vary over more than 2 orders of magnitude. This finding is central to the design and selection of materials and to ensure long-lasting, safe, cost-efficient, and sustainable solutions. An example are concrete structures, where corrosion of the reinforcing steel embedded in a cementitious matrix greatly influences the service life and safety of the structure. Steel corrosion in concrete has received large attention in the literature, which can be traced back to the vast application of cementitious materials worldwide, and because steel corrosion in concrete is the by far most common deterioration process of concrete structures[2,11]. Motivated by the high greenhouse gas emissions in traditional production of cement, considerable research has recently focused on the development of cementitious binders with lower environmental footprint[12]. However, these modern cements differ from traditional ones in terms of compositional properties[12,13]. While continuously increasing in diversity, common features are differences in pore structure and the reduced capacity to buffer the pH in the alkaline range upon exposure to carbon dioxide[14,15]. Since the lower pH promotes active corrosion of the embedded steel, the traditional engineering approach of entirely relying on the alkaline environment to avoid corrosion is no longer possible. Instead, being able to quantify the rate at which the metal dissolution occurs is becoming increasingly important. However, this is a challenge, fundamentally because the mechanism controlling the electrochemical dissolution rate of steel in cement-based materials – and in porous materials in general – has remained unknown.

Long-held views regarding the mechanism controlling the corrosion rate include the assumption of the electrochemical dissolution rate being under Ohmic control or being limited by restricted supply of oxygen to the electrode surface (cathodic control)[10,16-18]. While these kinetic limitations may apply in selected special situations, there is broad experimental evidence showing that in most of the environmental exposure cases relevant in practice, neither Ohmic control nor limited availability of oxygen can explain the large variations in corrosion rate[10]. An aspect of particular controversy in the literature seems to be the role of oxygen. This is in detail discussed in Supplementary Note 1 on the basis of theoretical considerations combined with an assessment of literature data. While it is well-accepted that limited oxygen availability at the electrode surface reduces the rate at which the electrochemical iron dissolution reaction can occur[19,20], there are conflicting views about the conditions under which this may come into play. A common concept is to assume that an increase in degree of pore saturation inherently depresses the concentration of dissolved oxygen in the water[10,16]. However, the vast majority of literature data (Supplementary Note 1) of corrosion rates in soil and in cement-based materials generally shows an increasing corrosion rate with increasing degree of saturation, up to immersed conditions (suggesting highly saturated pore systems). This observation conflicts with the hypothesis of diffusional oxygen concentration control generally being the limiting process under elevated moisture conditions.

An alternative route to understand the effect of the degree of pore saturation on the corrosion rate can be found in an area-effect at the metal surface. The underlying idea is that the degree of pore saturation influences the fraction of steel surface area in contact with water-filled pores, and thus determines the fraction of steel area taking part in the electrochemical dissolution process[9,10]. Interestingly, already in the 1950s, Romanoff, in the conclusions of an extensive report describing a 17 years long study on corrosion of steel in soil[7], stated: "*(...) it appears that not enough attention was given to the amount of moisture at the [steel] surface (...) Water now appears to be important by itself, aside from its effects on the availability of atmospheric oxygen*". While Romanoff already seems to have suspected such an influence, and while also other studies later attributed key importance to the water distribution at the electrode surface[21-25], thorough mechanistic explanations have not been provided until today.

Here, we examine the electrochemical dissolution rate of steel electrodes embedded in cement-based materials and we validate the interpretation of the results for other porous materials, such as wood and artificial sandy soils. This allows to cover a wide range of porosities (16–72%). The results (Fig. 1, Supplementary Table 1) confirm the importance of the moisture state but also reveal that corrosion rates differ by a factor up to 5, depending on the porous systems. Thus, two parameters appear to be at the root of the electrochemical dissolution kinetics. These are i) the moisture state (degree of pore saturation) and ii) the pore structure.

Mechanistic model

On the basis of the experimental data (Supplementary Table 1, Fig. 1), we develop a quantitative model for the corrosion rate. This model considers all the relevant influencing factors – porosity, moisture conditions, and pore liquid chemistry –, yet retains a relatively simple form. As detailed in Fig. 2 (and Supplementary Figure 1), the following equation can reliably predict all experimentally measured corrosion rates – for different materials, porosities, and a wide variety of exposure conditions studied in this work:

$$i_{corr,app} = i_{corr,eff_{max}} \cdot \frac{1}{2}\left(1 + \frac{(P - P_{crit})}{\sqrt{k + (P - P_{crit})^2}}\right) \cdot P_{sat} \qquad (1)$$

Here, the term apparent corrosion current density, $i_{corr,app}$, corresponds to the corrosion rate, which is generally obtained by dividing the measured corrosion current, I_{corr}, by the exposed steel surface area, or that can be determined with weight loss measurements.

Equation 1 consists of two major terms (cf. Fig. 3), recognizing that $i_{corr,app}$ can be expressed as the product of the effective corrosion current density, $i_{corr,eff}$, that is, the corrosion current density occurring in those regions where the steel is in contact with liquid electrolyte, and the electrochemically active steel surface area fraction A_{active}, that is, the fraction of steel surface area on which electrochemical dissolution occurs:

$$i_{corr,app} = i_{corr,eff} \cdot A_{active} \tag{2}$$

This conceptual approach is schematically depicted in Fig. 3, where the two components of eq. 2 are shown as two branches. The left branch shows that the effective corrosion current density, $i_{corr,eff}$, is governed by the electrochemical behavior of the system, which ultimately depends on the capability of transport of ferrous ions away from the surface[26]. These influences are taken into account by the term $\frac{1}{2}\left(1 + \frac{(P-P_{crit})}{\sqrt{k+(P-P_{crit})^2}}\right)$ and by $i_{corr,eff_{max}}$, which will be discussed later in this article.

The right branch in Fig. 3 illustrates that the electrochemically active steel surface area depends both on the pore structure of the matrix and on the exposure relative humidity. The pore size distribution defines the quantity of liquid water that can be present at the steel surface when the porous material is exposed to a certain relative humidity. This is accounted for by P_{sat} in eq. 1, which is the water-filled porosity volume fraction. Ultimately, this controls the area fraction of metal surface that is in contact with electrolyte (as opposed to steel surface areas in contact with solid phases or with gas). We suggest that only this part of the steel surface areas is considered electrochemically active (Fig. 3, A_{active}).

This conceptual approach acknowledges that corrosion of steel in a meso-to-macro-porous medium is a non-uniform process. With eq. 2, the non-uniformity is translated into an averaged behavior across the entire steel surface[27]. This is needed to relate the non-uniform process in our model to experimental observations such as measured corrosion rates, which, with generally available techniques (weight loss measurements, electrochemical methods), can only be obtained at the macroscopic scale[28,29]. While our results (Fig. 2 and Supplementary Figure 1) indicate that this approach is adequate to consider the non-uniformity of the corrosion process in meso-to-macro-porous media, it should here be mentioned that this cannot be applied to other forms of non-uniform corrosion, such as pitting[30] or intergranular corrosion[31].

Electrochemically active area

In a material with no pores or with all pores air-filled, A_{active} would be zero. For a metal electrode immersed in an electrolyte (bulk solution), A_{active} becomes 1. In a porous material, A_{active} assumes a value between 0 and 1. At saturation of the porous medium, A_{active} is directly proportional to the total porosity. At a moisture state below saturation, A_{active} is proportional to the volume fraction of electrolyte in the porous material. The latter is here termed P_{sat} and can be defined as displayed in Fig. 3.

As explained in Supplementary Note 2, $P_{sat} = A_{active}$. P_{sat} can be obtained by taking into account the theory of water capillary condensation. This effect depends on the size of the considered pores and is described by the Kelvin-Laplace equation[32], defining the maximum pore radius r in which capillary condensation is possible at a given relative humidity (RH):

$$r = -\frac{2\gamma M}{\ln(RH)\rho RT} \tag{3}$$

Where γ is the surface tension, M is molar weight, and ρ is the density of water; R is the ideal gas constant and T the temperature. Supplementary Note 3 indicates how P_{sat} can be determined from r and porosity data.

Fig. 4 shows the experimentally determined corrosion rates, $i_{corr,app}$, versus the corresponding volume fraction of electrolyte, P_{sat}. These relationships are linear, with a different slope depending on the material. Extrapolating to $P_{sat} = 1$ yields the effective corrosion current density ($i_{corr,eff}$). This is the current density on the areas in contact with electrolyte, and thus determined by the electrochemical behavior of the system (Fig. 3). Apparently, $i_{corr,eff}$ depends on the material surrounding the steel, which affects the electrochemistry of the system.

Transport and precipitation of dissolved Fe^{2+} and the influence on the effective corrosion rate

Our hypothesis is that the pore structure influences the transport of ferrous ions, released at the steel surface in the anodic dissolution, into the matrix and thus controls the concentration of Fe^{2+} at the steel surface. This in turn affects the reversible potential of the reaction $Fe \rightarrow Fe^{2+} + 2e^-$, described by the Nernst equation:

$$E^{rev}_{Fe/Fe^{2+}} = E^{o}_{Fe/Fe^{2+}} + \frac{RT}{nF}\ln\left(c(Fe^{2+})\right) \tag{4}$$

Here, $E^{o}_{Fe/Fe^{2+}}$ is the standard potential and n is the number of electrons exchanged. An open (interconnected) pore structure would allow Fe^{2+} transport into the pore system, thus keeping the Fe^{2+} concentration at the steel surface on a lower level than in a denser pore system, where mass transport is impeded. Eq. 4 shows that a lower Fe^{2+} concentration depresses the reversible potential of the Fe/Fe^{2+} electrode. As shown in Supplementary Figure 2, based on well-established considerations regarding corrosion kinetics, this leads to an increase in the effective corrosion current density, $i_{corr,eff}$.

Experimental evidence for this hypothesis is apparent from the following observations. Transport of Fe^{2+} ions is only possible if the pores are interconnected. Thus, the distance to which corrosion products could travel (from the steel surface into the matrix) must be related to the interconnected pore fraction of the pore system. It has been reported that the interconnected pore fraction relates to the total porosity[33-37]. A detailed evaluation of SEM/EDX results (Fig. 5) on the basis of the diffusion length of iron ions reveals that the mortars studied in this work exhibit a clear relationship between matrix porosity and distance to which corrosion products could be transported. The detailed evaluation can be found in Supplementary Note 4, showing that the diffusion length increases from 42 µm to 158 µm for C-16.7% to C-28.4%. Thus, the higher the porosity, the farther corrosion products can diffuse. Since this property is directly related to the Fe^{2+} concentration at the steel surface, that is, higher porosity leads to lower Fe^{2+} concentration at the electrode surface[26], it affects the reversible potential of the anodic reaction (eq. 4) and hence has an impact on the effective corrosion rate, $i_{corr,eff}$ (Supplementary Figure 2).

Finally, this influence of the pore structure on $i_{corr,eff}$ can be seen from the plot in Fig. 6. A critical porosity, P_{crit}, of approx. 18.5% is estimated for cement-based materials. Here, P_{crit} is defined as the transition point between a condition of ion transport controlled by the pore structure, and one where the system tends to behave as in bulk solution, with transport properties defined by the diffusion coefficient of species in bulk water[38]. Such behavior resembles the dependence of diffusion on porosity (Supplementary Note 4), as it has been described in previous work[39,40].

The relationship between $i_{corr,eff}$ and total porosity, P, (Fig. 6) can be described with the following equation:

$$i_{corr,eff} = i_{corr,eff_{max}} \cdot \frac{1}{2}\left(1 + \frac{(P-P_{crit})}{\sqrt{k+(P-P_{crit})^2}}\right) \tag{5}$$

Here, $i_{corr,eff_{max}}$ is the maximum effective corrosion rate, mathematically defined as the upper asymptote of the fitting function. It describes the maximum corrosion rate that can be achieved in a completely open system, without any diffusion constraint by the porous structure. Note that the obtained asymptotic upper boundary of the S-shaped curves fitted in Fig. 6, $i_{corr,eff_{max}}$, finds good agreement with the value experimentally measured in bulk solution (Fig. 2).

The term $\frac{1}{2}\left(1 + \frac{(P-P_{crit})}{\sqrt{k+(P-P_{crit})^2}}\right)$ describes how the diffusion properties improve with increasing total porosity. At very low porosities, the probability of pore interconnection remains negligible, so that there is no significant increase of ion transport (proportional to $i_{corr,eff}$), until P approaches P_{crit}. At this point, a further small increase in porosity leads to a steep increase in diffusion. Finally, towards higher porosities the impact of the pore structure on the ion diffusion properties diminishes, and the system behaves as in bulk solution.

The constant k describes the shape of this function (Supplementary Note 5). Both k and P_{crit} are expected to be different depending on the type of microstructure. Figure 6 shows a substantially different P_{crit} between mortar and soil systems, while k remains unchanged. For the cement-based materials studied in this work, k and P_{crit} are 0.001 and 0.185, respectively. Whereas, for soil, P_{crit} becomes 0.335, due to the differences in the nature of the pore structure[41].

Outlook

In conclusion, we have proposed a theoretical model to predict the rate of electrochemical dissolution in carbonated concrete, soil, and wood, here used as model systems of meso-to-macro-porous media. In contrast to other empirical models proposed in the literature, the strength of the here suggested approach lies in the causality between the predicted variables and the input variables (Fig. 3). Supplementary Figure 1 shows that this model predicts the corrosion rate significantly more reliably than the common approach relying on the empirical relationship between corrosion rate and electrical matrix resistivity[10,42].

The concept will facilitate the implementation of the corrosion propagation phase in service life modeling of reinforced concrete structures, which is crucial for holistic sustainability considerations and to generate confidence in the durability of modern environmentally-friendly cement types. Additionally, the presented theory can successfully be applied to electrochemical dissolution problems in other meso-to-macro-porous media. Its applicability is also of interest for technically beneficial corrosion processes, such as degradable metallic medical implants, whose uniform dissolution mechanism still needs clarification[43-44].

Finally, it may be worth mentioning that we did not observe any influences of the precipitated rust on the corrosion process itself (Supplementary Note 6). Over a testing time of more than 1 year, corrosion rates remained constant as long as the moisture state in the porous medium was kept constant. Thus, possible time-dependent changes in corrosion kinetics that may arise from effects related to precipitated corrosion products acting as redox-couple or affecting the porosity (pore clogging, microstructural changes) were here not observed. However, future work may investigate this in studies over longer time spans, and, if needed, expand the here proposed model to take possible microstructural changes into account as well. Additional further developments may consider the influence of the chemical composition of the liquid phase in the porous material on the maximum effective corrosion rate, $i_{corr,eff_{max}}$. In our work, the chemical composition of the electrolyte was relatively constant throughout all tests to isolate the contribution of the pore system. However, depending on the nature of the porous media[45,46,47], the solution that is formed inside the pores may vary substantially and affect the electrochemical dissolution rate. This could be easily studied in laboratory tests for different species characterizing a certain porous system and it would be straightforward to implement this in the here proposed model.

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Methods

Mortar

Specimen design

We produced mortar samples with dimensions of 8 cm x 8 cm and a thickness of 6 mm. Each sample contained an embedded reference electrode (Ag/AgCl), 5 carbon steel electrodes of diameter 0.5 mm (with a cover depth from both exposure surfaces of 3 mm) and a counter electrode made of a stainless-steel mesh (Supplementary Figure 12)[48,49]. The advantage of the thin samples was to allow for complete carbonation within max. 3 weeks when exposed in 4% CO_2 and subsequently rapid moisture equilibration with the different tested exposure environments.

Materials

Two different cement types were used: an ordinary Portland cement (CEM I 52.5 R) and a cement with clinker replacement up to 35% by limestone and burnt oil shale (CEM II/B-M (T-LL) 42.5). The studied water/binder ratios (w/b) were 0.5, 0.6 and 0.85, the ratio sand to binder was 2, the maximum sand particle diameter was 1 mm. To ensure the fluidity needed to cast the thin specimens and at the same time maintain stability of the mix, a poly-carboxylate ether superplasticizer with a de-foaming agent was used (0.2% by weight of binder for the mix with w/b = 0.5). The samples were left in the mould for 1 day, and subsequently cured at 95% relative humidity (RH) for 7 days. After this, they were subjected to the carbonation procedure.

Carbonation procedure

The mortar samples were exposed to CO_2 at a concentration of 4% and 57% RH at 20°C. The exposure time was 2 weeks for the CEM II mortars and 3 weeks for the CEM I mortars. The phenolphthalein indicator spray test[50] was used on companion samples, that were split at different times, to ensure complete carbonation of all samples instrumented with electrodes before further exposure testing.

Exposure conditions

Constant relative humidity: The carbonated samples were exposed to different moisture conditions, namely 81% RH, 95% RH, and 99% RH (always at 20 °C).

Saturation: To achieve capillary saturation, two specimens per series were exposed to demineralized water with help of a pond mounted on the surface.

Time to moisture equilibration

The mass of the specimens was monitored to detect moisture equilibration, which could be achieved within maximum 2 weeks for all specimens and exposure conditions. The electrochemical measurements (see section below) were started after reaching moisture equilibrium. The results reported in this work, were obtained after 2–4 months of the different moisture exposure (after achieving stable values).

Mercury intrusion porosity (MIP) measurements

The MIP measurements were done with a porosimeter by Thermoscience (Pascal 140/440). Mortar specimens without embedded electrodes were produced and carbonated as described above. Subsequently, the samples were saturated with isopropanol with isopropanol replacement once a day during 1 week. This was done for reasons of microstructural preservation. Subsequently, the samples were transferred to a desiccator for drying under vacuum. MIP testing was performed with a pressure of 0.012 MPa, and then increasing to 400 MPa to allow for mercury intrusion into pores to a theoretical radius of 2 nm (here, we assumed 140° as contact angle). Replicate measurements indicated good reproducibility. The cementitious samples were labelled according to the obtained total porosity, e.g. C-16.7% indicates cementitious sample with total porosity of 16.7% (Supplementary Table 1).

SEM/EDX analysis

To study the spatial distribution of ferrous and ferric precipitates (corrosion products) in the porous cementitious matrix after terminating the exposure tests and the electrochemical measurements (described below), cross-sections were cut perpendicularly to the carbon steel electrodes from different samples. At this time, the samples had undergone exposure testing for 1.5 years (C-16.7%, C-17.6%, C-19.6%, and C-20.9%) or 9 months (C-24.8% and C-28.4%). The cut samples were embedded in a low viscosity resin under vacuum, and subsequently polished studied by scanning electron microscopy (SEM). The distribution of corrosion products was obtained through energy dispersive X-ray (EDX) mapping. More information is given in Supplementary Figure 7.

Artificial soil

Specimen design

Carbon steel wire electrodes (identical as the ones used in the cementitious samples) were embedded in the centre of a soil bed of thickness 2 cm. The counter electrode was a stainless-steel mesh, and an Ag/AgCl electrode was used as reference electrode.

Materials

Quartz sand was used as model for artificial soil. Different pore structures were simulated by combining different grain size distributions: <0.1 mm, 0.1-0.3 mm, 0.25-0.5 mm, and >0.5 mm.

Porosity measurement

To determine the porosity of the artificial soil, samples of the sand mixes were filled and compacted into a graduated cylinder and the pore volume was determined through measuring the amount of water that entered the sand upon water addition.

Exposure conditions

The samples containing the electrodes were saturated with a solution described in section “Bulk solution”. Electrochemical measurements were carried over time out as described below.

Wood

Specimen design

Carbon steel nails with a diameter of 1.5 mm were inserted in wood samples (with a cover depth from both exposure surfaces of 10 mm). The counter electrode was a stainless-steel mesh, and an Ag/AgCl electrode was used as reference electrode.

Materials

Four different types of samples of spruce were taken from regions exhibiting different arrangements of the growth rings, thus different contributions from earlywood and latewood.

Porosity measurement

The wood porosity was determined from the sample density and assuming a density of the cell walls of 1.5 g/cm^3 according to literature[51].

Exposure conditions

The wood samples containing the electrodes were saturated with a solution described in section “Bulk solution”. Electrochemical measurements were carried over time out as described below.

Bulk solution

Both the artificial soil and the wood samples were saturated with a solution with the following composition: saturated $Ca(OH)_2$, 0.01 M KOH, and 0.007 M $CaSO_4$. Prior to use, this alkaline solution was bubbled with CO_2, until it was carbonated and assumed a pH~8.5. The reason for selecting this solution was to ensure a similar chemical composition as the pore liquid in the carbonated cementitious samples in this work. By this, influences of the electrolyte composition could be minimized, which allowed to study the contribution from the pore system and the moisture content.

In addition to studying mortar, artificial soil, and wood samples, carbon steel electrodes were directly immersed in the described solution and electrochemical measurements performed.

Electrochemical measurements

The electrochemical measurements were performed with a potentiostat Metrohm Autolab PGSTAT30. The instantaneous (apparent) corrosion rate measurements were done in a 3-electrode setup, where always one of the carbon steel electrodes was the working electrode and the stainless steel electrode and Ag/AgCl electrode were the counter and reference electrode, respectively.

The instantaneous corrosion rate (current density) was determined from polarization resistance measurements. The polarization resistance was obtained from potentiodynamic sweep measurements (±10 mV from the open circuit potential, 0.1 mV/s sweep rate). To correct for the *IR*-drop in the porous medium, impedance measurements were done for each of the tested cases immediately after the potentiodynamic sweep tests (50 frequencies logarithmically spaced between 10^5 and 1 Hz). The instantaneous, apparent corrosion rate was calculated with the Stern Geary equation:

$i_{\mathrm{corr,app}}=B/R_{\mathrm{p}}$

Here, R_{p} is the *IR*-corrected polarization resistance and B was assumed as 0.026 V as recommended in the literature[52].

These electrochemical measurements were for each specimen and in each exposure condition repeated over time.

Data availability

The experimental data supporting the findings of this study are available in the main text or in the Supplementary Information. Additional data are available from the corresponding author upon reasonable request.

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Contributions

M.S. was the main investigator. He developed the experimental protocols and carried out the experiments. All authors designed the research, and contributed to the analysis and interpretation of the results and to the preparation of the manuscript.

Competing interests

The authors declare no competing interests.

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Figure captions

Fig. 1. Influence of porosity and moisture conditions on electrochemical dissolution kinetics. Measured corrosion rates of steel electrodes embedded in 14 different porous media (6 cement-based materials, 4 artificial soils, 4 woods) and in bulk solution (BS), all with comparable chemistry of the liquid phase (Supplementary Table 1). The whiskers represent the standard deviation based on at least 8 measurements per point.

Fig. 2. Master curve of corrosion of steel in porous media. It illustrates how the suggested theoretical model (Fig. 3) is capable of reliably predicting the measured corrosion rates, $i_{corr,app}$, irrespective of the environmental exposure conditions as well as irrespective of the type of porous material. The whiskers represent the standard deviation based on at least 8 measurements per point.

Fig. 3. Schematic representation of the proposed model. The two major influencing factors – pore structure and moisture state – are at the base of the mathematical description of the corrosion kinetics in dense porous media. The pore structure has a two-fold influence. First, it influences the transport of Fe^{2+} ions into the porous matrix and thus governs the Fe^{2+} concentration at the steel surface, which in turn affects the electrochemistry and ultimately the effective corrosion rate $i_{corr,eff}$ (left branch). Second, the pore structure, together with the moisture state of the porous material, determines the steel surface area in contact with electrolyte, A_{active} (right branch). The product of $i_{corr,eff}$ and A_active finally yields the measured (apparent) corrosion rate, $i_{corr,app}$.

Fig. 4. Measured corrosion rates ($i_{corr,app}$) as a function of the calculated volume fraction of electrolyte in the porous material (P_{sat}) (Supplementary Note 2). This relationship is different for different mortars. This can be traced to the differences in pore structure. More open pore systems show a higher slope. The effective corrosion current densities ($i_{corr,eff}$) are obtained from extrapolating current densities to $P_{sat} = 1$. The whiskers represent the standard deviation based on at least 8 measurements per point.

Fig. 5. Influence of matrix porosity on the distance to which corrosion products diffuse from the electrode. Examples of SEM/EDX iron mapping for sections of samples of steel (circles) embedded in cement-based systems of different total porosity (indicated percentages). (More images in Supplementary Note 4).

Fig. 6. Relationship between total porosity and the effective corrosion current density (Fig. 4). The fitted curve (solid line) corresponds to the mathematical expression displayed. The transition between different curvatures of the function, which corresponds to the steepest point, is the critical porosity (P_{crit}). The asymptotic value at porosity = 1 is the maximum effective corrosion current density ($i_{corr,eff_{max}}$) that can be achieved in an open pore system. The whiskers represent the standard deviation based on at least 8 measurements per point.