Correlative Raman-SEM-EDX analysis of corroded components

In particular microbiologically induced corrosion (MIC) of steel and chlorid corrosion of concrete

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Introduction

Direct costs due to corrosion worldwide amount to 3% and in some countries up to 5% of the GDP (gross domestic product) [1][2]. Microbiologically influenced corrosion (MIC) is responsible for 20% of all corrosion damage [3]. In this context, there is great interest in understanding MIC especially, since it has been shown that some microbes slow down the rate of corrosion [4], while others speed it up [5]. Correlative microscopy can bring new insights here.

Another costly problem we can study with correlative microscopy is the neutralization of the passivation of concrete in reinforced concrete structures caused by road salt. The road salt (NaCl) leads to pitting corrosion in the embedded steel through various transport mechanisms in the concrete. These transport mechanisms need to be investigated and correlative microscopy can bring new insights.

Correlative microscopy combines the advantages of different microscopic and spectroscopic measurement methods at the same sample location. Electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, Micro-X-ray fluorescence spectroscopy (µrfa) and infinite focus microscopy (IFM) are used in this work.

Results MIC – Investigations

During experiments in the Koralmtunnel (1) iron oxidizing bacteria were found to be part of a biofilm (2) producing microbial community dominated by a variety of eubacterial methanotrophs. Microbial community analysis (16S profiling and metagenomic studies) from biofilm samples revealed the presence of different species from the family of Gallionellaceae (3). The flow of electrons from Fe^{++} is used by autotrophic bacteria such as *Ferriphaselus sp.* to generate energy e.g. for CO_2 fixation processes and concomitant production of biomass.

The corrosion rate and pitting corrosion determined by ASTM standard [6] showed that the MIC samples had 2-6 times lower corrosion rate but stronger pitting corrosion. This could be due to the fact that discontinuous sulfur layers formed on all MIC samples, which may have slowed the corrosion rate, but created vulnerabilities for pitting corrosion due to the discontinuities.

Rebar (reference)

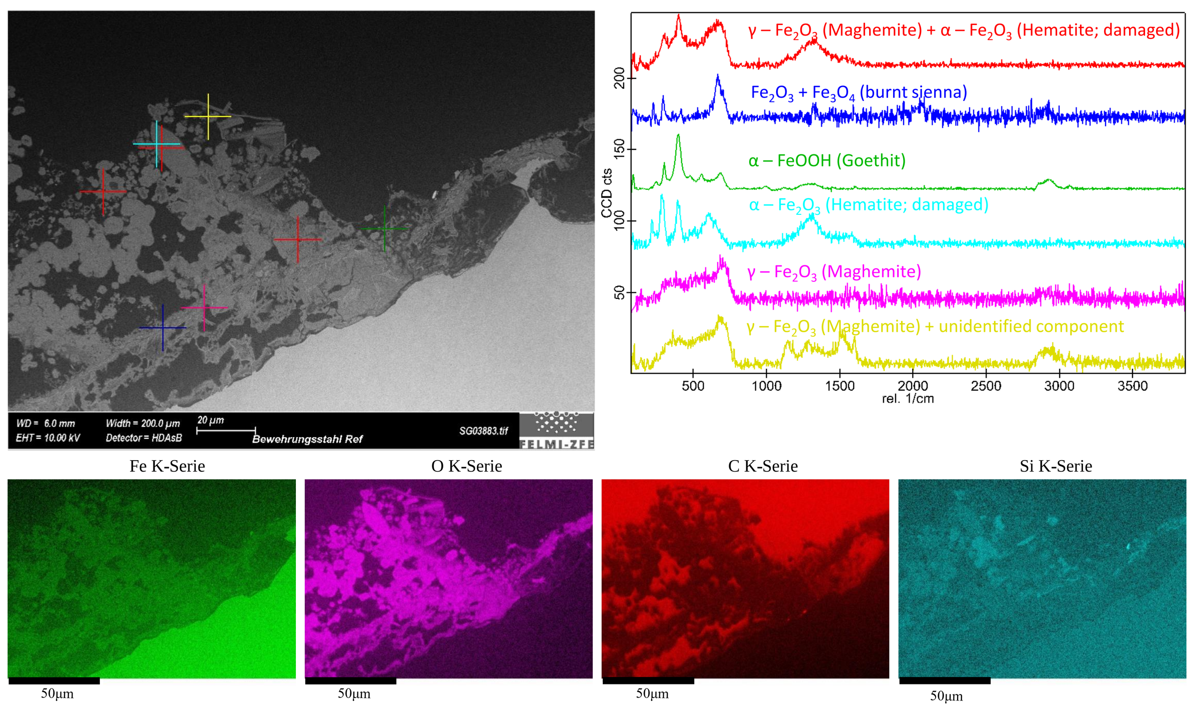


Fig.1: Left: Cross-section of the rebar sample (SEM). The crosses mark the Raman measuring positions.

Right: On the reference sample some typical iron-oxides/hydroxides are found (Raman-spectra).

Below: These are the most important elements found in the EDX-mapping.

Rebar (MIC)

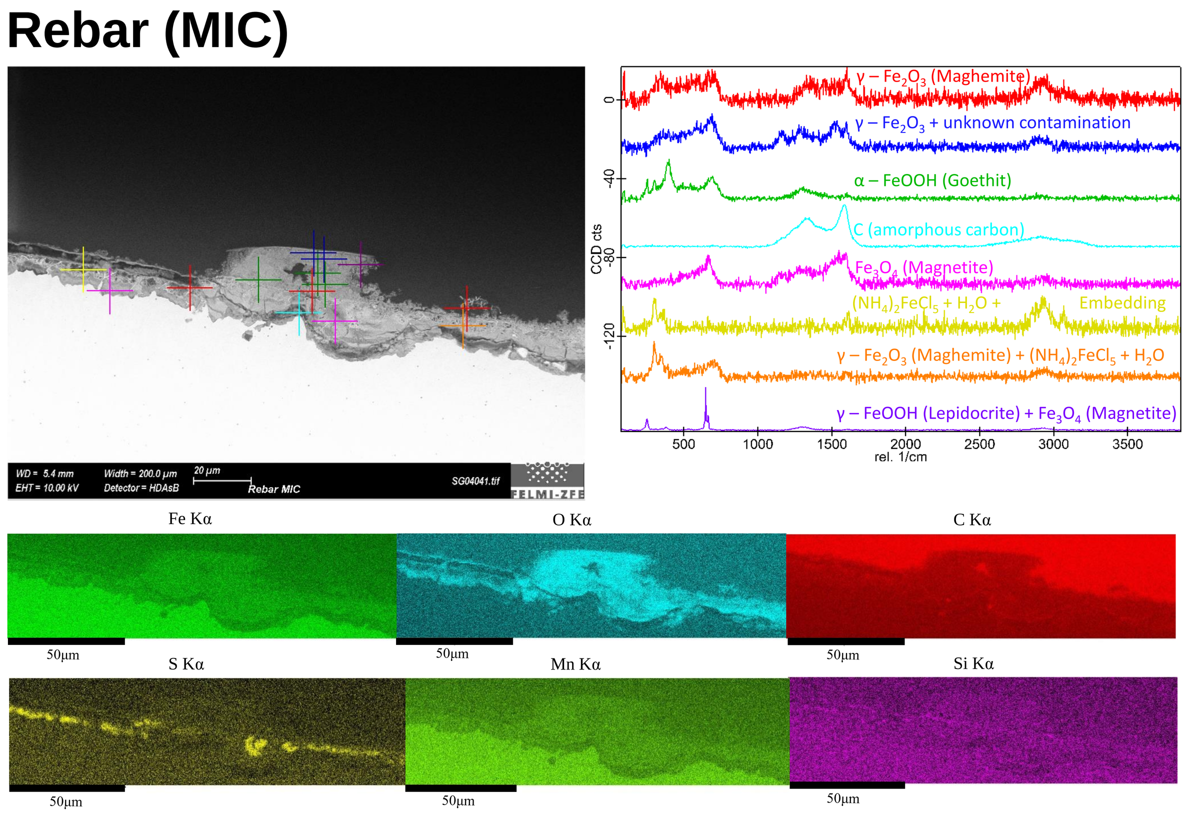


Fig.2:
In addition to the iron-oxides found on the reference *Magnetite, Lepidocrocite* and *amorphous carbon* could be detected on the MIC sample.

In the EDX-mapping a sulfur layer is clearly visible X that presumably formed due to MIC. In other measurements the sulfur layer was identified as Sulfur oxide by Raman.

Open question:
A Raman spectrum was measured that can best be identified as $(NH_4)_2FeCl_5$ but no *N* was found by EDX.

Chlorid corrosion – Investigations

Steel in reinforced concrete is basically very well protected against corrosion, since the steel forms a protective passivation layer in the alkaline concrete porous medium. However, due to environmental influences, signs of corrosion of the steel reinforcement still appear as the structure ages, since chlorides from the road salt or seawater and CO_2 from the air destroy the protective layer. Since the environmental influences and conditions in traffic structures are very different, the many mechanisms involved in chloride transport vary greatly.

With µrfa and correlative SEM/EDX/Raman spectroscopy, a deeper understanding of the transport mechanisms in hardened concrete should be developed. The cross-section of a platform concrete edge with embedded reinforced steel was used as a sample.

During the µrfa measurements (see Figure 3), an accumulation of chlorine was measured on the outside of the platform edge. This point was then examined with EDX and Raman. The aim is to obtain information about the spread of chlorine corrosion and the effect on the rebar. Since the chlorine transport has not yet progressed to the reinforcement steel in this sample, only the penetration of the chlorine into the concrete could be observed.

Concrete

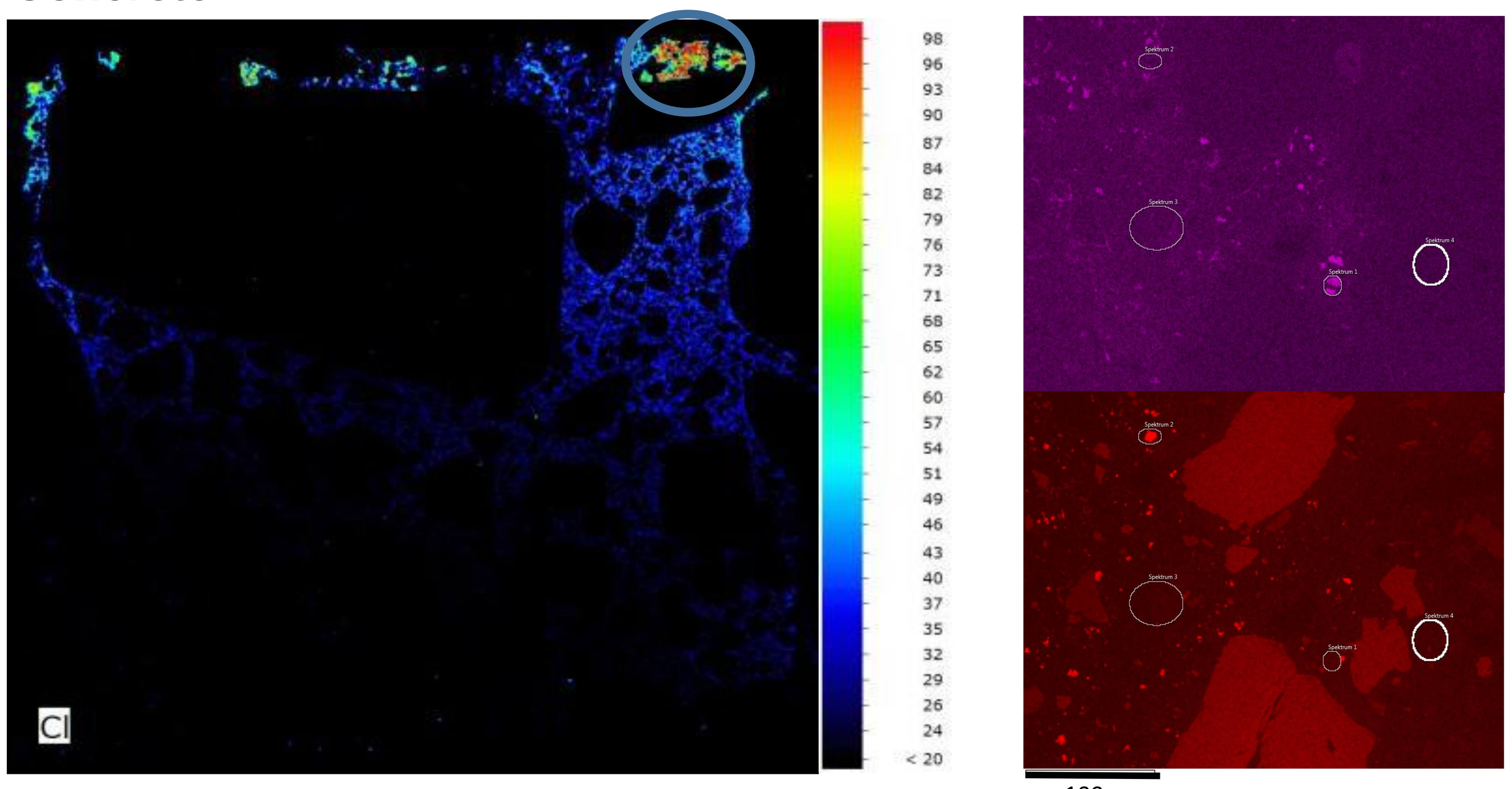
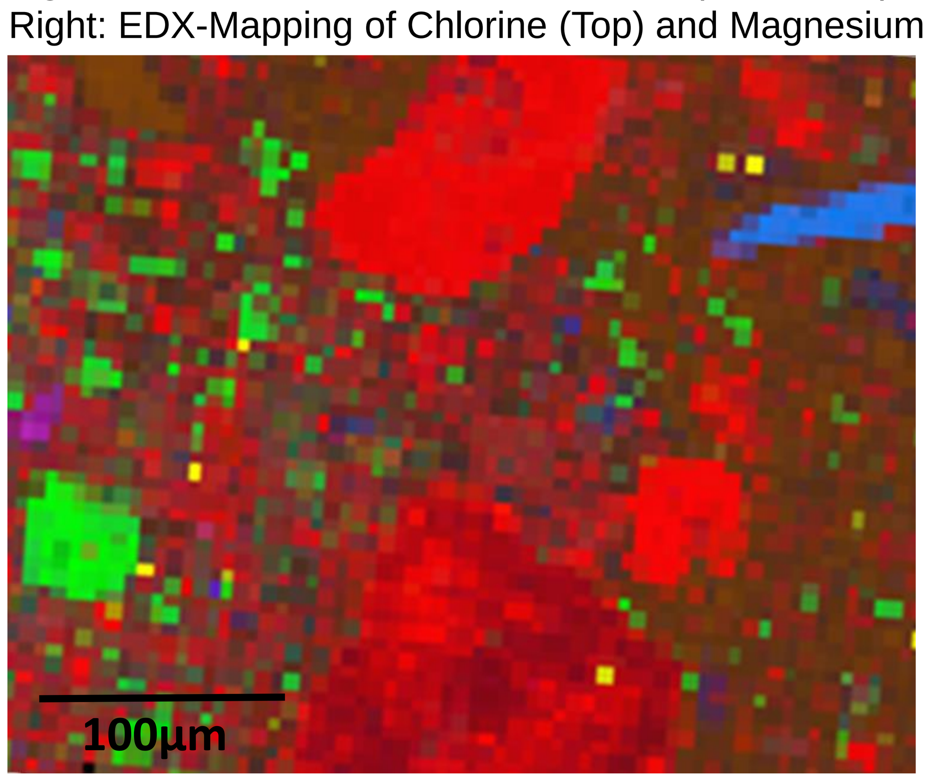


Fig.3: Left: Cross-section of concrete (Chlorine; µrfa-Spectrum). Right: EDX-Mapping of Chlorine (Top) and Magnesium (Mg)



– Quarz (SiO_2)
– Magnesite ($MgCO_3$) + Natriumcarbonate (Na_2CO_3)
Anatase TiO_2
– Calcite $CaCO_3$
– Andesine $(Na,Ca)AlSi_2O_8$
– Silicon Carbide SiC
– Rutile TiO_2

Fig.4:
Raman-mapping of region of interest according to Figure 3

Acknowledgements

"KorroNet – Projekt":
Avoidance of selective corrosion

"ChloridKorrosion – Projekt":
Reduction of damage caused by chloride-induced reinforcement corrosion on reinforced concrete components

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