Correlative SEM, EDX and Raman microscopy of corrosive stressed components

In particular microbial corrosion (MIC), chloride induced corrosion (CIC) and alkalisilica reaction (AKR)

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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.

Free cutting steel,untreated (reference)

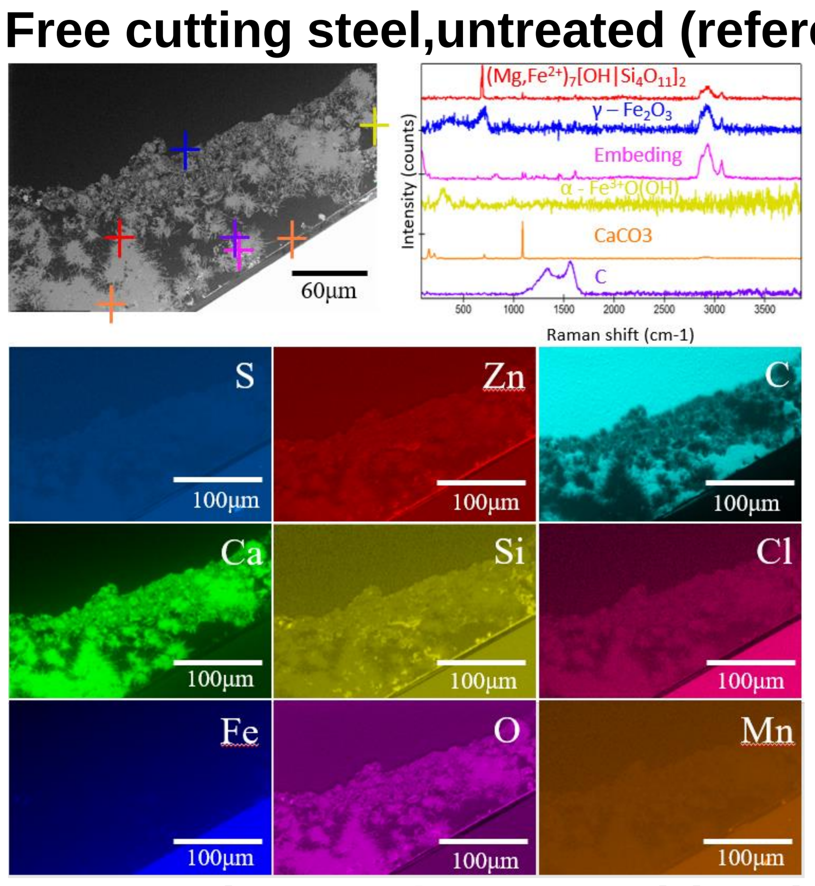

Fig.1:
Left: Cross section of free cutting steel, untreated Reference Sample (1.0711) (SEM). The crosses marks are the Raman measuring points.

Right: Fe-oxides were identified with raman spectroscopy as Magnetite (blue) and Goethite (blue). In addition, cumingtonite could be detected, a rare mineral that, according to literature, occurs in the Lavantal Alps in Carinthia, among other places.

Bottom: Edx measurements with most important elements: Sulfur, zinc, carbon, calcium, silicon, Chlorine, iron, oxgen and manganese.

Free cutting steel,untreated (MIC)

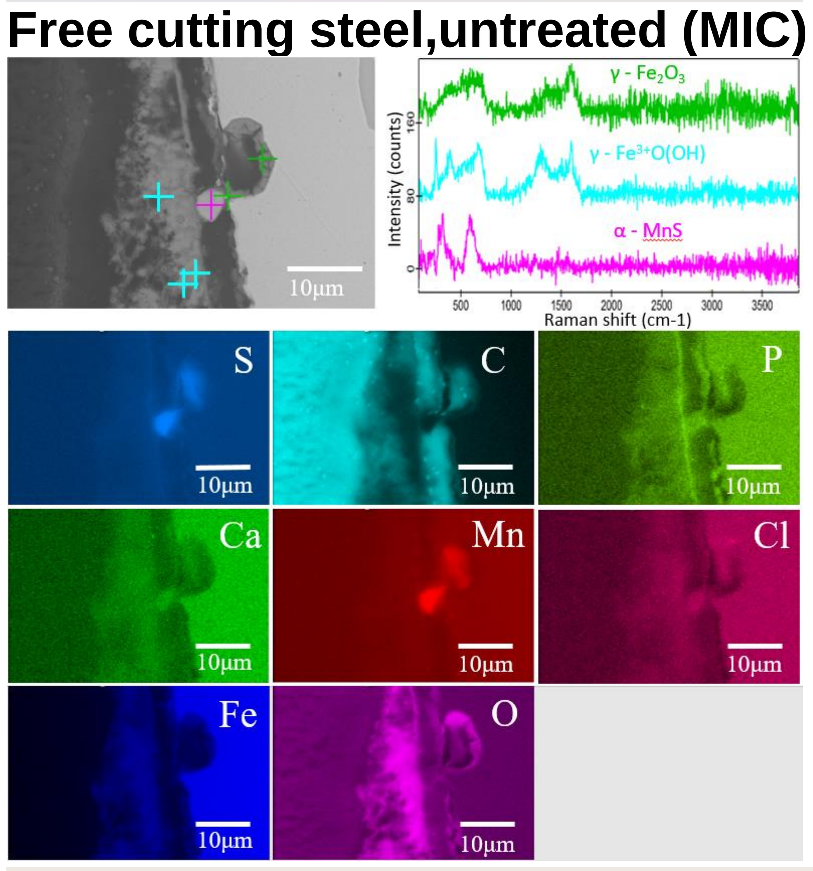

Fig.2:
Left: In the SEM-picture you can clearly see a pit caused by pitting corrosion.

Right: In addition to the iron-oxides found on the reference, Lepidocrocite and the Metal-sulfide Mangan(II)-sulfid could be detected on the MIC sample.

Bottom: In the EDX-mapping a sulfur layer is visible like in all MIC Samples that presumably formed due to MIC. In other measurements the sulfur layer was identified as Sulfur oxide by Raman.

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

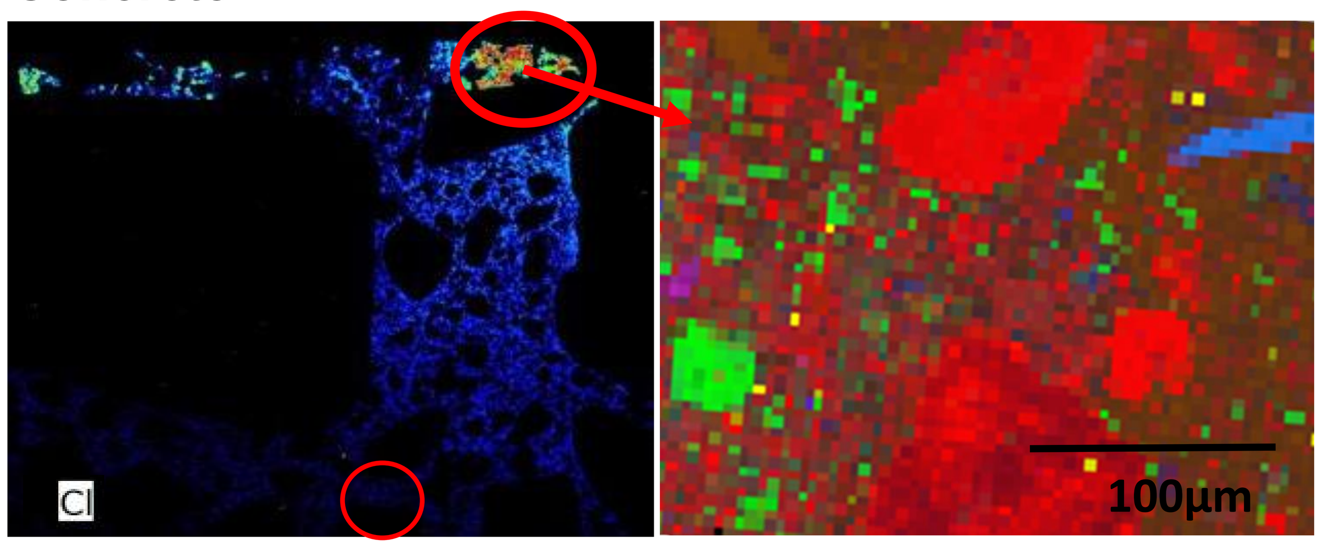

Fig.3: Left: Cross-section of concrete (Chlorine; µrfa-Spectrum). Right: Correlative raman mapping:

- 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

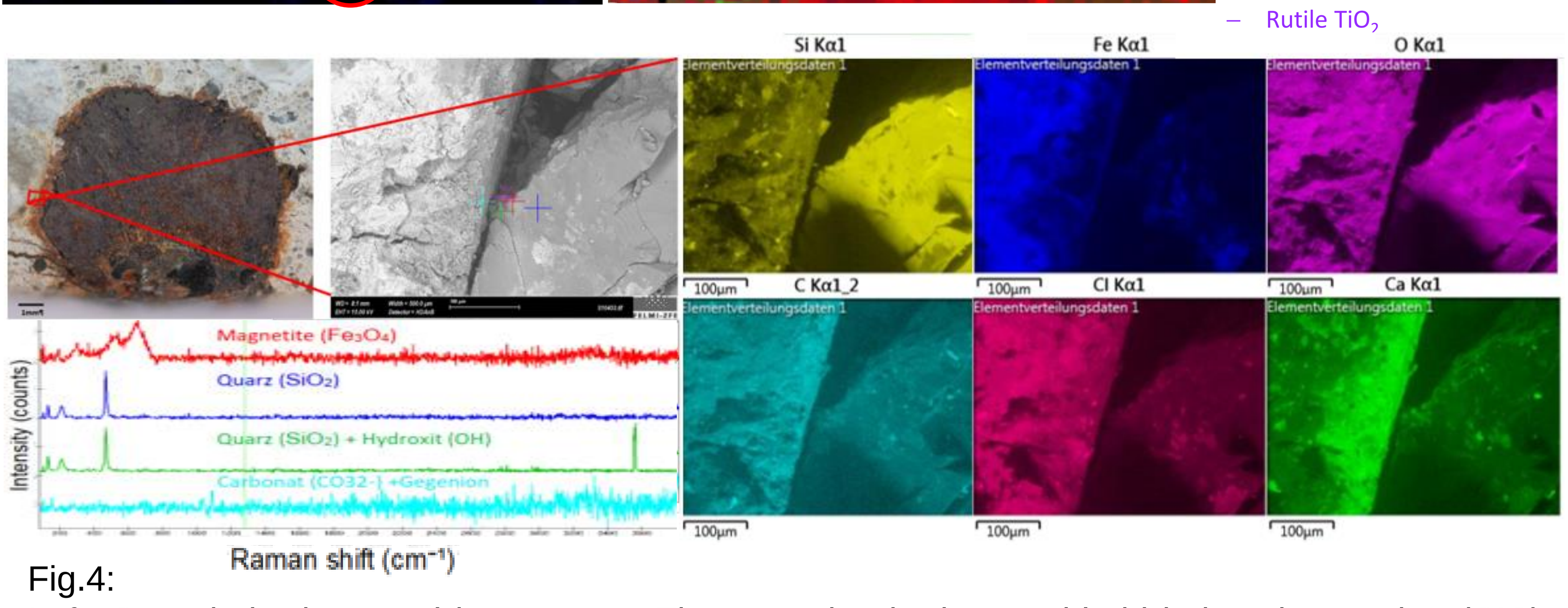

Fig.4:
Left: Corroded rebar steel in concrete. The corrosion is due to chlorid induced corrosion (CIC), The crosses in the SEM picture marks the Raman measuring points. Right: Edx measurements with most important elements: Silicon, iron, oxgen, carbon, chlorine and calcium. Bottom: Fe-oxides (Magnetite), si-oxide (Quartz), hydroxite and carbonate were identified with raman spectroscopy.

Results:

- Pitting corrosion quantitatively and qualitatively investigated.
- Corrosion rate lower with MIC. Pitting corrosion stronger with MIC.
- Interrupted sulfide layer S2- => sulfide oxide and magnesium sulfide (MnS). Sulfate layer $[SO_4]$2- identified (salts).
- Hydroxide and carbonate detected with Raman at the concrete-steel interface => carbonation => loss of passivation.
- Corrosion products such as iron oxide or hydroxides or carbonates distinguishable with Raman: Lepidocrocite (hydroxide), Maghemite (iron oxide), Magnetite (iron oxide), Geothite (hydroxide), Siderite (carbonate), Ferrihydrite (hydroxide), Wüstite (iron oxide), Hematite (iron oxide). Identification of sulfur-reducing bacteria (SRB) thanks to correlative measurements in connection with 16S ribosomal RNA analysis.

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

References/ Literature

[1] Hays, George F. "Now is the Time." *World Corrosion Organization* (2010).
[2] Biezma, M. V., and J. R. San Cristobal. "Methodology to study cost of corrosion." *Corrosion engineering, science and technology* 40.4 (2005): 344-352.
[3] Javaherdashti, Reza. "A review of some characteristics of MIC caused by sulfate-reducing bacteria: past, present and future." *Anti-corrosion methods and materials* 46.3 (1999): 173-180.
[4] Dubiel, M., et al. "Microbial iron respiration can protect steel from corrosion. " *Appl. Environ. Microbiol.* 68.3 (2002): 1440-1445.
[5] Javed, M. A., et al. "Effect of sulphate-reducing bacteria on the microbiologically influenced corrosion of ten different metals using constant test conditions. " *International Biodeterioration & Biodegradation* 125 (2017): 73-85.
[6] Standard, A. S. T. M. "G1-03 (Reapproved 2017). " *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*

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