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Corrosion of Potential Canister Materials During Oxic to Anoxic Transient in Compacted Bentonite

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ABSTRACT

The long-term performance of the engineered barrier system is crucial for the safe, long-term disposal of high-level radioactive waste in a deep geological repository. This study examines the corrosion behavior of cast iron with spheroidal graphite and copper in contact with compacted bentonite under laboratory conditions, as well as that of copper in contact with compacted bentonite following exposure in an underground research laboratory (URL; MaCoTe experiment at Grimsel Test Site). In the laboratory experiments, bentonite was saturated with an artificial water composition from a crystalline rock and exposed for 1 and 4 months at 60°C under transient oxic conditions. The results indicate minor material degradation in the laboratory samples and suggest a redox-transient state at the metal–bentonite interface. Copper speciation in the bentonite from the MaCoTe experiment indicates a dependence on exposure time and bentonite dry density. Overall, the study highlights the importance of combining laboratory and URL studies to improve the understanding and prediction of long-term stability of metal–bentonite interactions for the safe disposal of HLW.

1 | Introduction

High-level radioactive waste (HLW) requires long-term, safe disposal to minimize its potential impact on the environment. Although Germany has phased out nuclear power plants, the existing HLW must eventually be transferred from interim storage facilities to a deep geological repository (DGR). Therefore, in 2017, the German Site Selection Act was enacted to regulate the site selection process for a DGR in Germany [1].

Internationally, the well-established “KBS-3” concept represents a widely accepted multi-barrier approach for the safe disposal of HLW [2]. It comprises geological (host rock) and engineered (canister and buffer) barriers designed to isolate the waste from the bio- and geosphere. The design of the repository and the canister largely relies on the host rock, as crystalline, clay or salt host rocks each have different mechanical, chemical

and physical properties and thus require different properties of the barrier materials (e.g., the canister).

In Sweden, Finland and Canada, a crystalline rock was chosen to host the repository and copper was selected as the outer canister material for corrosion protection. Designs in Sweden and Finland rely on an individual copper overpack, whereas Canada uses a copper coating applied on a carbon steel container [3–5]. The insert of the Swedish and Finnish canister design is made of cast iron with spheroidal graphite, which provides primarily mechanical strength and radiation shielding. Cast iron with spheroidal graphite is also used in the German interim storage and transport containers “CASTOR” and was proposed as a material for the “Pollux” container, originally designed for a repository in salt rock [6].

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Finland, Sweden, Canada, and Switzerland consider bentonite, a natural clay material, as the buffer material. Bentonite is mainly composed of smectite, in particular montmorillonite, which has a strong swelling capacity and low hydraulic conductivity [7]. Upon saturation with water from the surrounding host rock, bentonite is, therefore, expected to tightly enclose the canister and establish a stable hydro-geochemical environment. Since the canister will be in direct contact with the buffer, the surrounding chemical environment is important for assessing the long-term performance of the engineered barrier system (EBS).

Over the lifetime of a DGR, the near-field conditions will evolve from initially oxic and unsaturated to anoxic and saturated conditions. These changes must be considered when evaluating the degradation of the EBS. Oxic to sub-oxic conditions are assumed to prevail for a few months to a few years due to initially trapped oxygen in the repository [2, 8]. For copper as an outer material, uniform corrosion yields copper oxides (e.g., CuO or Cu₂O) or copper salts (e.g., CuCl) formation. Under anoxic conditions, sulfide is the main concern for copper corrosion since it can convert the initial protective Cu₂O layer on the canister surface to a sulfide layer [8]. Sulfide may originate from the transformation of sulfur-bearing minerals, such as pyrite (e.g., FeS₂), or from the metabolic activity of sulfate-reducing bacteria (SRB). The latter gains energy by reducing sulfate, for instance from the groundwater or sulfate-bearing minerals in the sealing system (e.g., FeS₂ or CaSO₄ · nH₂O), to hydrogen sulfide (H₂S) which can further corrode copper at the canister surface [9]. Using highly compacted bentonite around the canisters, serves different safety functions, one of which is suppressing microbial activity and thereby reducing sulfide production and transport towards the canisters [4, 10].

Several studies have investigated the interaction of copper with compacted bentonite. Tully et al. [11] examined the corrosion of cold-sprayed, electrodeposited and oxygen-free, phosphorous-doped copper in highly compacted Wyoming MX80 bentonite (dry densities of 1.1, 1.4, and 1.6 g·cm⁻³). During the exposure times (1–18 months) an uneven saturation of the bentonite was observed which led to different exposure conditions between the different dry densities. Despite the presence of attached bentonite on the copper coupon surfaces, copper, oxygen and sulfur-rich corrosion products were identified. A thicker corrosion layer was observed on the samples exposed to the lower bentonite dry density (1.1 g·cm⁻³) which is linked to either increased microbial activity or a faster saturation of the bentonite. Also, more compact corrosion layers were observed on the higher compacted bentonite (1.6 g·cm⁻³) as compared to the lower dry density (1.1 g·cm⁻³). An enrichment of copper within the adjacent bentonite was observed, whereby the Cu-speciation remains unclear.

The studies of Martinez-Moreno et al. [12, 13] focus on the microbial influence on oxygen-free high conductivity copper corrosion in highly compacted bentonite (1.7 g·cm⁻³). After exposure for 1 year at 30°C under anoxic conditions, copper sulfides were found on the copper surface, while at 60°C no copper sulfides were present at the surface. In general, the copper coupons remained largely unaffected by corrosion. Enhanced SRB activity is observed at exposure conditions of 30°C, whereas their activity decreased at 60°C. Under both exposure conditions no influence of microbial activity on the smectite properties were reported.

For cast iron with spheroidal graphite, oxic corrosion will predominantly yield uniform corrosion upon the formation of iron oxyhydroxides (FeOOH) or ferrihydrite (Fe(OH)₃). Under anoxic conditions, Fe₃O₄ will become the dominant corrosion product, which potentially leads to a protective layer, slowing down the corrosion [14]. However, in the presence of bentonite, the nature of the formed corrosion products also depends on dissolved silicon (Si) content [15].

Muñoz et al. [16] investigated the corrosion behavior of cast iron with spheroidal graphite under hydrostatic pressure in synthetic Opalinus clay pore water. It has been reported that higher hydrostatic pressure favors the corrosion of spheroidal graphite cast iron. Cathodic water reduction produces hydrogen, which further promotes anodic iron dissolution by weakening its crystal structure. Additionally, the authors report the preferential dissolution of ferrite from the cast iron matrix, along with the release of silicon. Additional studies by Muñoz et al. [17] investigated the effect of γ-radiation on the corrosion behavior of cast iron in a bentonite suspension. Their main findings suggest an enhanced catalytic activity of the graphite nodules, promoting the dissolution of the iron matrix. This results in increase of pH, which leads to a modification of the smectite structure [17]. It's worth noting that physico-chemical processes may not be directly comparable between bentonite suspensions and compacted bentonite. Compared with compacted bentonite, bentonite suspensions provide higher water availability at the metal–bentonite interface and facilitate ion or solute transport due to the absence of compaction and less restricted pore space. Corrosion studies in compacted bentonite provide a detailed understanding of interfacial reactions between metal and bentonite, which is the focus of the present study.

Other laboratory studies performed by Mota-Heredia et al. [18, 19] investigated the corrosion behavior of carbon steel in contact with bentonite under hydrothermal gradients (1.5–0.4 bar, 100°C (steel plate) and 40°C (upper bentonite)). Carbon steel materials embedded in two distinct bentonites, FEBEX and MX-80, (dry density: 1.65 g·cm⁻³) were exposed to a synthetic Na-Cl-SO₄-type groundwater under inert N₂ atmosphere over time periods ranging up to 27 months (steel grade TStE 355, which is the selected canister material in the Spanish DGR concept). The main corrosion products were identified as Fe₃O₄, γ-Fe₂O₃, α-Fe₂O₃, green rust and ferri-chlorite as well as a chloritized smectite. Different material behavior regarding iron migration into the bentonite was observed for Ca- and Mg-rich bentonite (FEBEX) which was higher as compared to Na-rich bentonite (MX-80). Additionally, MX-80 bentonite shows a higher Fe incorporation in the interlayer of the smectite and an increase in cation exchange capacity (CEC). The authors emphasize the redox-transient state as Fe²⁺ and Fe³⁺ phases were observed.

The laboratory studies discussed above suggest that the conditions established during short exposure times may not fully reflect long-term repository conditions. Consequently, several international in situ experiments have been conducted in underground research laboratories (URLs), where experiments are performed under repository-relevant conditions. These studies provide valuable insights into the long-term behavior of materials and complement laboratory experiments, while also serving as a foundation for coupled thermo-hydraulic models. The Material Corrosion Test

(MaCoTe) at the Grimsel Test Site, is a long-term in situ experiment in a crystalline rock designed to assess the effectiveness of engineered barrier components exposed to subsurface groundwater conditions [20]. First results after 1 year exposure time indicate the highest corrosion rates, independently of bentonite dry density (1.25 or 1.50 g cm^{-3}), for carbon steel ($\sim 2 \mu\text{m year}^{-1}$) and lower corrosion rates for copper (wrought, electrodeposited, cold sprayed) ($\sim 0.13\text{--}0.32 \mu\text{m year}^{-1}$). The bentonite in contact with carbon steel shows a discoloration and a distinct enrichment of iron along the interface. Bentonite in contact with copper shows minor black discoloration after dismantling and an enrichment of copper determined by SEM-EDS. The authors report no significant differences regarding corrosion behavior of the tested materials with the bentonite dry density after 1 year of exposure.

The "Mini Can" field test was implemented by the Swedish Nuclear Fuel and Waste Management Co (SKB) in 2006 to investigate the influence of bentonite on the corrosion behavior of KBS-3 canisters (miniature canister made of a cast iron insert and a copper outer shell) [21]. Three setups were installed: one surrounded by bentonite with a dry density of 1.3 g cm^{-3} , another with a dry density of 1.6 g cm^{-3} and a third one without bentonite allowing direct contact between groundwater and the copper canister. Cast iron exhibited high corrosion rates (up to several hundred μm per year) with a heterogeneous corrosion behavior. In contrast, copper showed significantly lower corrosion rates (max. $0.15 \mu\text{m year}^{-1}$), primarily characterized by pitting and surface roughening. For both metals, the canister surrounded by high-density bentonite showed the lowest corrosion extent and the lowest SRB activity. SRB is supposed to have predominantly influenced cast iron corrosion by forming FeS and only to a limited extent copper corrosion upon forming copper sulfides.

As described above, extensive research has been conducted to optimize the design of the EBS and to evaluate the long-term evolution of DGR's. Laboratory studies performed under close to repository-relevant conditions are essential, as they provide initial insights into potential corrosion mechanisms. This study addresses a first experimental approach to analyze the corrosion behavior of cast iron and copper in compacted bentonite using an artificial water composition from a German crystalline rock under transient oxic conditions. In addition, the study entails a detailed investigation of the effect of exposure time on potential bentonite alteration due to copper corrosion, as limited information is currently available on copper speciation within bentonite under repository-relevant conditions. This is of particular interest, since bentonite alteration and precipitation of secondary phases within the buffer may alter its properties. To this end, the analysis of samples from laboratory experiments is complemented with analyses of samples from the MaCoTe experiment after up to 7 years exposure time.

2 | Materials and Methods

2.1 | Laboratory-Based Exposure Experiments

Corrosion experiments were performed in tailor-made corrosion cells (Supporting Information S1: Figure S1). The design was based on the reaction cells used in the MaCoTe experiment and modified to achieve similar conditions in laboratory experiments [20]. The cells are composed of an inner filter (stainless-steel (316L), sintered to an average $15 \mu\text{m}$ porosity)

with a diameter of 4 cm, two lids and an outer case made of stainless steel (grade 316L) and built around the inner filter. Holes in the outer case allow water inflow, whereas the inner stainless-steel filter ensures the compaction of the bentonite.

Cast iron with spheroidal graphite (thereafter abbreviated CI) (type: EN-GJS-400-15-C, purchased at Marks GmbH, Germany) cut into disks (20 mm diameter, 3 mm height), cold rolled copper (99.999%), and cold rolled, phosphorous-doped copper ($P = 0.018 \text{ wt.}\%$) both cut into rectangular shape ($2 \times 50 \times 150 \text{ mm}^3$) (purchased at HMW Hauner GmbH & Co. KG, Germany) are used for the exposure experiments (details on composition and microstructure see [22]). Prior to the experiments, all coupons were ground with 600-, 800- and 1200-grid SiC paper using a grinding and polishing machine (QATM Qpol 250 A2-ECO, detail is provided in supporting information) and subsequently cleaned with isopropanol.

The experiments were set up in three steps. First, Wyoming-type bentonite (composition see [22]) is compacted to 1.50 g cm^{-3} dry density under air. While compacting the bentonite, two metal coupons were emplaced in separate layers. In the second step, the cells were mounted and pre-saturated in artificial water (composition see Table 1) for 14 days in a glovebox system. Subsequent to pre-saturation, the cells+water were placed in individual anaerobic containers at 60°C for 1 (only cast iron) and 4 months (cast iron and copper). After exposure the cells were dismantled under anoxic conditions in a glovebox system. The metal coupons were carefully removed from the bentonite without disturbing the surface of the coupons and the interface with the bentonite and dried within the glovebox for further analysis.

2.2 | Compacted Bentonite From MaCoTe Field Experiment

Bentonites in contact with wrought copper (WC) from the MaCoTe field experiment were studied as complementary samples to the lab-based experiments. A detailed description of the experimental design is documented in [20]. Briefly, the corrosion modules are filled with coupons made of different candidate canister materials embedded within MX-80 bentonite at a dry density of 1.25 or 1.50 g cm^{-3} . The corrosion modules were assembled and transported under anoxic conditions before insertion in a vertical borehole in which they were exposed to granitic pore water for varying time periods. Only the bentonite in contact with the metal coupons was analyzed, not the metal itself. The interface between compacted bentonite and WC of four samples with varying exposure times (4.5 & 7.1 years) and dry density of the bentonite (1.25 & 1.50 g cm^{-3}) were studied. All steps following module retrieval from the borehole until transport to the laboratory for analysis were performed under anoxic conditions. In the laboratory, the samples were stored and dried in a glovebox system. After drying they were embedded in epoxy resin under vacuum conditions and polished for analysis.

2.3 | Analytical Methods

2.3.1 | Laboratory Analytics

Digital microscopy (KEYENCE 3D Digital Microscope VHX5000) was used to characterize the initial surface state of the metal

TABLE 1 | Ionic composition of the water from a crystalline host rock in Germany with the corresponding salt composition used for preparing the artificial water for this study. The final pH of the artificial water was adjusted by adding NaOH and HCl. Data is based on [23].

Ions	Ionic concentration c [mol/L]	Salts	Salt composition m [g]
Na ⁺	8.35×10^{-2}	Na ₂ SO ₄	0.76
K ⁺	2.38×10^{-3}	NaHCO ₃	1.16
Mg ²⁺	9.25×10^{-4}	NaCl	3.45
Ca ²⁺	4.40×10^{-3}	KCl	0.18
Cl ⁻	7.26×10^{-2}	MgCl ₂ × 6 H ₂ O	0.09
HCO ₃ ⁻	1.37×10^{-2}	CaCl ₂ × 2 H ₂ O	0.49
SO ₄ ²⁻	5.35×10^{-3}		
pH	6.7		
TDS (mg/L)	6117.6		
I (mol/kgw)	9.5×10^{-2}		

coupons. After exposure, macro scale surface changes were investigated by digital microscopy and light optical microscopy (LOM) using a Carl Zeiss AX10 Scope A1 microscope. Elemental distribution on the metal surfaces was obtained by micro-X-ray fluorescence spectroscopy (μ -XRF) (Bruker M4 Tornado spectrometer, Ag-tube, 50 kV, 200 μ A, 20 μ m pixel size) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) (Hitachi TM4000+, operated at 15 kV and with 0.21 μ m pixel size). Complementary analyses were performed, under ambient conditions, by confocal micro-Raman spectroscopy (Horiba XploRA PLUS, 532 nm, calibrated on Si before measurements) and X-ray diffraction (XRD) (Malvern Panalytical Empyrean diffractometer with Co-K α radiation operated at 40 kV/40 mA with a X'Celerator detector). μ -Raman spectra were collected with a maximum of 1% laser-intensity, resulting in an average laser power density of $3.5 \cdot 10^3$ W/cm² on the sample. Regions of interest for XRD were identified by using an optical microscope above the sample stage. Diffraction data were treated with High Score Plus v.4 [24].

For cross section analysis, the metal coupons were embedded in epoxy resin (Buehler). They were ground and polished according to Supporting Information S1: Table S1 and subsequently investigated by LOM, SEM-EDS and μ -Raman spectroscopy. Focused ion beam (FIB)-SEM-EDS (FEI Versa 3D operated at 5 kV) analysis was performed on cast iron with spheroidal graphite after 1 month of exposure. One region of interest was stabilized by a platinum deposit, cut and characterized by EDS.

Dried bentonite powder from the laboratory studies was characterized by X-ray powder diffraction (Malvern Panalytical X'Pert³ Powder diffractometer with Cu-K α radiation operated at 45 kV/40 mA with a Pixcel detector) to investigate secondary phases in the bentonite close to the contact zone. Fused tablets of the bentonite from the interfacial region (bentonite-coupon) were prepared to investigate the chemical composition by quantitative wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) (Rh-tube, analytics & system software SPECTRAplus V3) (Bruker S8 Tiger). The standard deviations (1 σ and 2 σ) were used as a measure of data quality in the WD-XRF analysis.

The dried bentonite, was embedded in epoxy resin (Buehler) under vacuum conditions to ensure full saturation within the

pore space of the bentonite. The surface was then dry-ground up to 2500-grid SiC paper to ensure a smooth surface state. Digital microscopy and LOM were used for imaging the metal-bentonite interface. μ XRF (Bruker M4 Tornado spectrometer, Ag-tube, 50 kV, 600 μ A, 20 μ m pixel size) was used to investigate the elemental distribution along the interface. The bentonite from the MaCoTe field experiment was investigated by field emission gun – scanning electron microscopy (FEG-SEM, operated at 20 kV and with a pixel size ranging from 0.197 to 1.69 μ m) (Tescan Clara) to analyze the elemental distribution along the interface in more detail and to select areas of interest for complementary analyses with synchrotron-based techniques.

2.3.2 | X-Ray Absorption Spectroscopy

Cross sections of the dried bentonite from the MaCoTe experiment were investigated by synchrotron- μ -XRF (sy- μ -XRF) and information about Cu speciation was provided by micro-X-ray absorption near-edge structure (μ -XANES) spectroscopy. Measurements were carried out at the mySpot beamline at the BESSY II electron storage ring operated by the Helmholtz-Zentrum Berlin für Materialien und Energie [25]. The storage ring energy was 1.7 GeV and the ring current was 300 mA (top-up mode). The incoming X-ray beam was monochromatized using a pair of Si (111) crystals and energy calibrated using a Cu foil. A beam size of ~20 μ m was achieved using a pinhole. The samples were mounted in an airtight sample holder having a polyimide window (Kapton) and oriented at 45° with respect to the incoming X-ray beam. The fluorescence radiation was recorded by a RaySpec Sirius SD silicon drift detector (SDD) (RaySpec LTD).

Overview μ -XRF maps with 100 μ m step size and 2 s dwell time were collected along the interface at an excitation energy of 9279 eV. Subsequently, regions of interest were identified to be measured in detail with 20 μ m step size and 5 s dwell time. μ -XRF data was treated with the PyMCA toolkit [26]. On the detailed μ -XRF maps, points for the collection of Cu K-edge (8978.9 eV) μ -XANES spectra were selected to achieve good counting statistics at each selected point, 2–3 spectra were recorded and averaged. Additionally, XANES spectra were recorded with a standard beam size (~200 μ m) on relevant reference compounds, based on pre-characterization: CuS (covellite), Cu₂S (chalcocite), Cu₉S₅ (digenite), CuO (tenorite), Cu₂O (cuprite), Cu₂(OH)₃Cl (atacamite) and

Cu-adsorbed on bentonite (2 g/L in 0.3 M NaClO₄, [Cu]_{tot} = 80 μmol/L, pH = 7.05) (reference spectra see Supporting Information S1: Figure S2). The Cu K-edge XANES spectrum of digenite was recorded at the ID21 beamline at European Synchrotron Radiation Facility (ESRF) (Grenoble, France) [27]. At this station, the incoming X-ray beam was also monochromatized using a pair of Si (111) crystals and energy calibrated using a Cu foil. The μ-XANES data was analyzed using Athena implemented in the IFEFFIT software [28]. Steps of the data processing include energy calibration and normalization. Linear combination fitting (LCF) was performed by using Athena to reconstruct the sample spectrum using a combination of model compounds spectra. The R-factor (R_f) is a quality factor for the LCF. It describes the differences between the measured and fitted data. The lower the R_f the better the fit.

3 | Results

3.1 | Surface Characterization of Corroded Metal Coupons

3.1.1 | Cast Iron With Spheroidal Graphite (EN-GJS-400-15-C)

Cast iron shows distinct surface changes after exposure for 1 and 4 months at 60°C. After 1 month of exposure, the surface shows a brownish to black discoloration with local hotspots of a black surface coverage (Figure 1a). The samples exposed for 4 months also show a brownish to black discoloration and additionally areas with a green appearance. After both exposure times, the surface covering appears homogeneous; however the original metal surface is still visible and therefore either no continuous corrosion layer was formed or parts have remained sticking to the removed bentonite. By light optical microscopy patches of dark brown minerals with varying shape and size, brownish-orange and dark grey phases were identified on the metal surface.

The brownish discoloration on the sample surface shows a high contrast in the μ-XRF maps of aluminum, calcium, and silicon. It is therefore assumed to be attached bentonite on the surface. Local enrichment of sulfur is observed (see Supporting Information S1: Figure S3).

The mineralogical phase composition at the metal surface was characterized by XRD and μ-Raman spectroscopy.

By μ-Raman spectroscopy of the 1-month sample (solid symbols in Figure 1b), Fe₃O₄ presence was evidenced from the band at 670 cm⁻¹, however the modes at ~ 90 and ~530 cm⁻¹ are not present [29]. The Raman band at 283 cm⁻¹ refers to FeS. After 4 months of exposure (open symbols in Figure 1b), spectra contain additional bands at 428 and 500 cm⁻¹ corresponding to a green rust phase [Fe^{II}_{1-x}Fe^{III}_x(OH)₂]^{+x} · [(x/n)An⁻ⁿ · mH₂O]^{-x} and at 710 cm⁻¹ to γ-Fe₂O₃. The prominent band at 1089 cm⁻¹ refers to CaCO₃ [30, 31]. Figure 1c shows the Raman spectrum of FeS in more detail. A change in Raman peaks after 1 and 4 months is observed. As described by El Mendili et al. [32], the Raman bands present at 210 and 283 cm⁻¹ (strong) can be assigned to poorly crystalline FeS, whereas the shoulders at 258 and 376 cm⁻¹ can be assigned to more crystalline FeS. The bands at 122, 173, 258, 308 (strong) and 358 cm⁻¹ refer to a partially oxidized FeS which was identified after 4 months of exposure [33]. Some Raman spectra (not shown here) exhibit two modes at 250 and 380 cm⁻¹ which can be assigned to γ-FeOOH [29].

After 1 month, the main peaks identified by XRD measurements correspond to α-iron (bcc-lattice) at 2θ = 52.4° and 77.2°, representing the base material (see Figure 2). The peak at 2θ = 31.0° refers to spheroidal graphite as present in the base material and α-SiO₂ from bentonite. Additionally, γ-FeOOH (2θ = 16.6°) was identified. At 2θ = 19.1° [Fe_{1-x}S] · [(M²⁺, M³⁺) (OH)₂] (Tochilinite-like phase) was assigned based on available reference data [34]. Considering the structural variability and possible non-stoichiometry of Fe-S and layered hydroxide systems, the exact composition of the phase in this sample can slightly differ. After 4 months of exposure, only minor reflections of γ-FeOOH (2θ = 16.6°) were identified. Additionally, peaks at 2θ = 23.1° corresponding to montmorillonite, the main component of bentonite, and at 2θ = 34.7° corresponding to magnesium-bearing CaCO₃ were identified. The reflections at 2θ = 31.0° correspond to spheroidal graphite (base material) and α-SiO₂ (bentonite) (see Figure 2). The used reference spectra are listed in Supporting Information S1: Table S2.

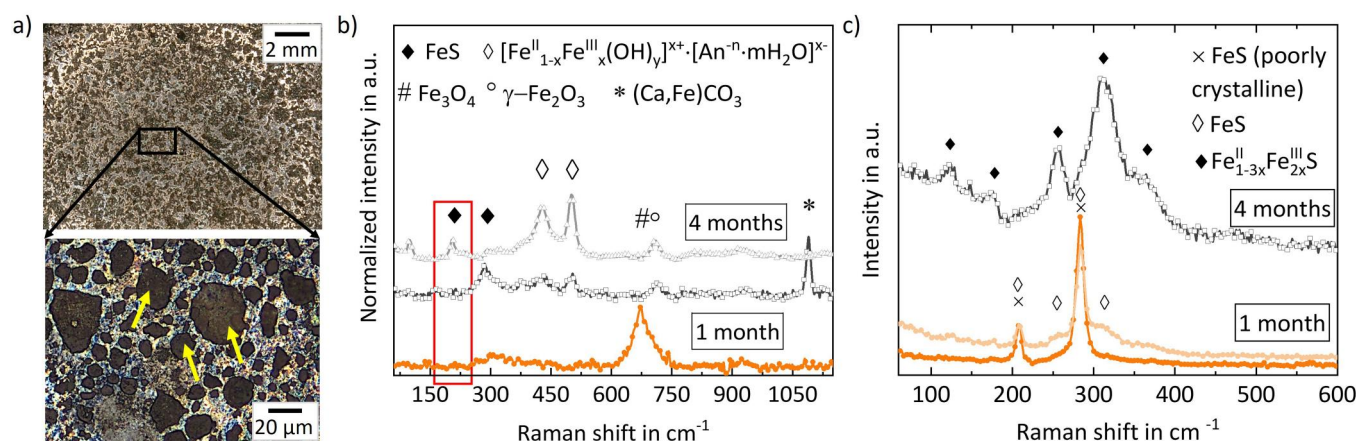


FIGURE 1 | (a) Digital microscopic image of cast iron with spheroidal graphite after 1 month exposure (a, top) and LOM image of the same sample (a, bottom). The yellow arrows indicate the phase Fe_xS_x. (b) μ-Raman spectra of cast iron after 1 (closed symbols in orange) and 4 months (open symbols in grey) exposure. The red square in (b) indicates the area of the main Raman bands of Fe_{1-x}S enlarged in (c) using new, more detailed measurements. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

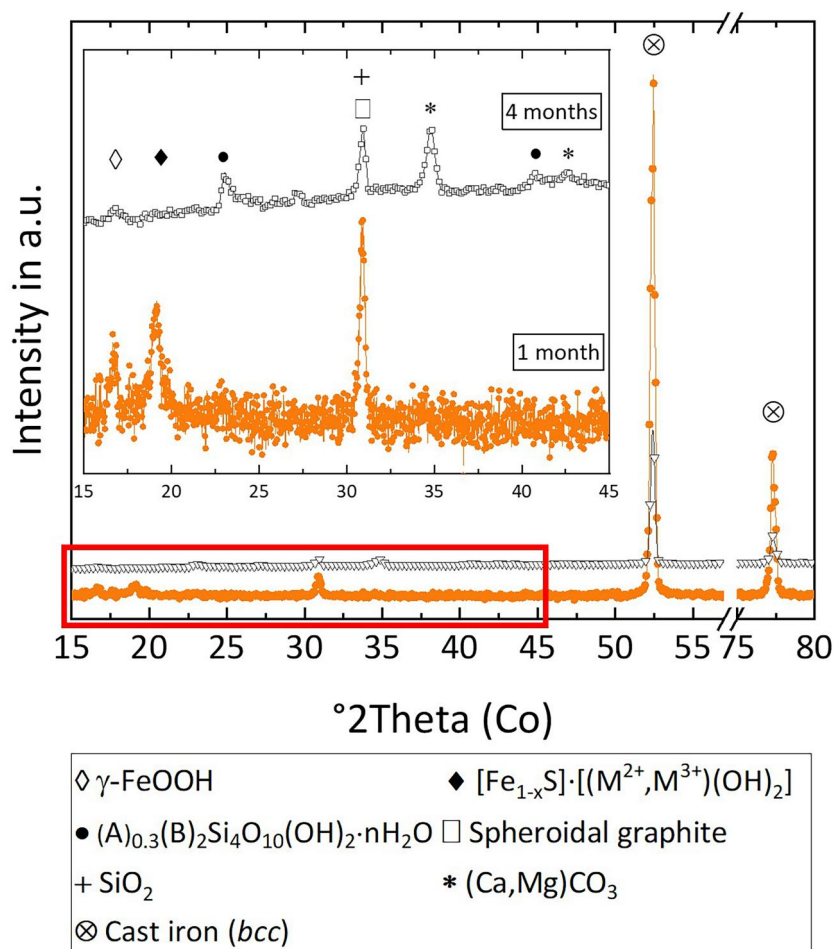


FIGURE 2 | X-ray diffractograms of cast iron with spheroidal graphite after 1 (closed symbols in orange) and 4 months (open symbols in grey). The diffraction pattern mainly shows *bcc*-reflexes of the base material (iron) at $2\theta = 52.5$ and 77.5° and individual peaks in the range of 15 to 45° 2θ . The close up of this region (marked by the red square) indicates γ -FeOOH at $2\theta = 16.6^\circ$, $[\text{Fe}_{1-x}\text{S}] \cdot [(\text{M}^{2+}, \text{M}^{3+})(\text{OH})_2]$ at $2\theta = 19.3^\circ$ and spheroidal graphite plus α - SiO_2 at $2\theta = 31.1^\circ$ after 1 month exposure. γ -FeOOH, spheroidal graphite and α - SiO_2 were also identified after 4 months. Additionally, at $2\theta = 23.1^\circ$ $(\text{A})_{0.3}(\text{B})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (montmorillonite, representing bentonite) and a mixed $(\text{Ca}, \text{Mg})\text{CO}_3$ at $2\theta = 34.8^\circ$ were identified after 4 months. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

Complementary to XRD and μ -Raman spectroscopy, SEM-EDS measurements were performed on the sample surfaces. The brown, round-shaped minerals identified by LOM (see Figure 1a) coincide with an enrichment of sulfur by SEM-EDS analysis. It is therefore concluded that these minerals refer to iron sulfide as it was identified by μ -Raman spectroscopy. Additionally, after 4 months of exposure calcium is locally enriched on the sample surface. The calcium enrichment shows a partial overlap with sulfur, potentially being $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$. Further calcium enriched areas may correlate with carbon, therefore suggesting a CaCO_3 phase. Even though carbon cannot unequivocally be determined by SEM-EDS, the results are in great accordance with the $(\text{Mg})\text{CaCO}_3$ phase identified by XRD after 4 months of exposure.

3.1.2 | Copper (Pure, Phosphorous-doped)

After the exposure of pure and P-doped copper, distinct surface alterations can be observed. For both types of copper materials, the original surface is preserved, which is seen by the characteristic copper color on the surface as well as by the presence of grinding marks from sample preparation. Light grey to darker

grey and black spots are evenly distributed on the copper surface (Figure 3a).

By μ -XRF analysis the darker grey surface covering is characterized by a higher aluminum and silicon content, which can be attributed to bentonite attached on the surface (see Supporting Information S1: Figure S4). An enrichment of sulfur and chlorine is also observed.

On all samples the XRD pattern display the characteristic copper 111 and 200 Bragg reflections at $2\theta = 50.8$ and 59.4° (Figure 3b). In the close-up of the region between 20 and 45° 2θ (see Figure 3b) at $2\theta = 23.1^\circ$ montmorillonite and at $2\theta = 24.4$ and 31.1° α - SiO_2 are identified. Cu_2O is identified by the reflections present at $2\theta = 34.5$ and 42.6° . Some diffractograms exhibit a shoulder at the Cu_2O 42.6° 2θ peak (Figure 3b). This coincides with CuO which shows its main reflection at $2\theta = 41.5^\circ$. All samples exhibit a more or less broad reflection at $2\theta = 33.1^\circ$. This can be attributed either to CuCl , which shows an additional reflection at $2\theta = 55.7^\circ$ or to Cu_xS , which shows its main reflection around $2\theta = 31.8$ to 34.4° . Some diffractograms show a sharp peak at 32.3° 2θ which corresponds to the main reflection of CuS . Low crystallinity and/or small phase

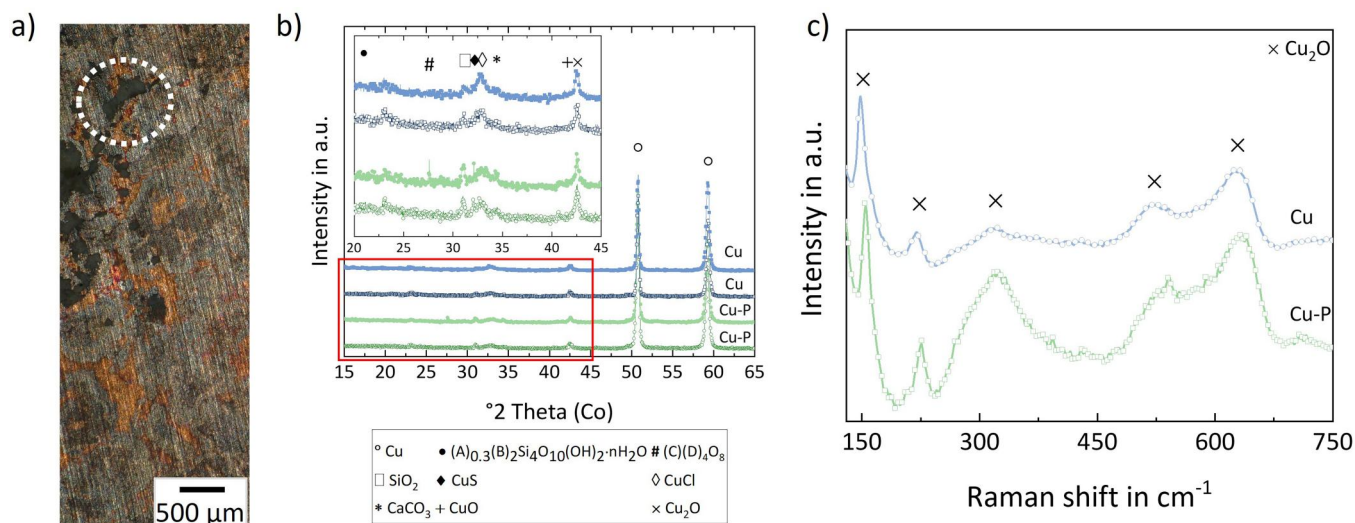


FIGURE 3 | (a) Digital microscopic image of pure copper exposed for 4 months. The dashed, white circle indicates attached bentonite. (b) X-ray diffractograms of two individual spots measured on pure (top in blue) and phosphorous-doped (bottom in green) copper. All diffractograms show main peaks of copper at $2\theta = 50.1$ and 59.4° . The close up between 20° and 45° 2θ reveals individual peaks of $(A)_{0.3}(B)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ (montmorillonite, with $A=Na$, Ca and $B=Al$, Mg) at $2\theta = 23.1^\circ$, $(C)(D)_4O_8$ (feldspar, with $C=Na$, K , Ca and $D=Al$, Si) at $2\theta = 27.6^\circ$ and $\alpha-SiO_2$ at $2\theta = 31.1^\circ$, all representing bentonite. At $2\theta = 32.3^\circ$ and 33.2° CuS and $CuCl$ were identified, respectively. Additionally, $CaCO_3$ at $2\theta = 34.3^\circ$, CuO at $2\theta = 41.7^\circ$ and Cu_2O at $2\theta = 42.6^\circ$ were identified. (c) Shows the μ -Raman spectra of pure (top in blue) and phosphorous-doped copper (bottom in green) which both show Cu_2O as the solely identified phase with the following bands assigned to: 143, 213, 322, 519, and 624 cm^{-1} . [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.70260)]

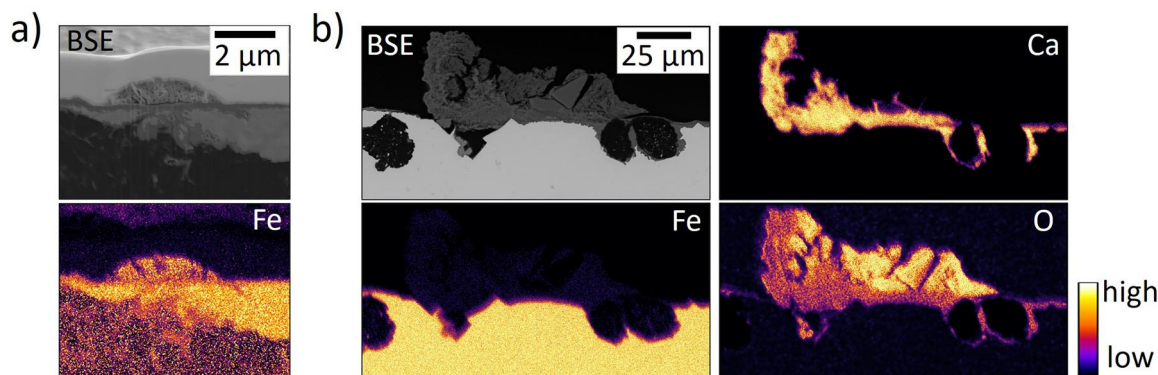


FIGURE 4 | SEM-EDS analysis of cross sections of cast iron with spheroidal graphite after (a) 1 month and (b) 4 months. The dashed white line in the BSE images represents the original sample surface. (a) BSE image collected by FIB-SEM shows the graphite nodule in black and a supporting platinum layer in bright color on top. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.70260)]

fractions lead to the observed broadened reflections. Thus, the XRD results indicate that the shape of the reflection around 33° 2θ depends on both the crystallinity and the relative abundance of CuS and/or $CuCl$. By μ -Raman spectroscopy only Cu_2O was identified on all three samples (see Figure 3c). Raman bands assigned to Cu_2O are: 150, 220, 325, 523, and 620 cm^{-1} [35].

3.2 | Cross Sectional Analysis of Corroded Metal Coupons

3.2.1 | Cast Iron With Spheroidal Graphite (EN-GJS-400-15-C)

FIB-SEM-EDS analysis of the coupon after 1 month exposure (see Figure 4a) shows the beginning of material degradation along the graphite nodules (black shape in Figure 4a), which is identified by a contrast changing (lighter grey in BSE) towards the iron as the original matrix. The newly formed phase is

characterized by a higher oxygen concentration and a lower iron concentration compared to the bulk. Additionally, a thin iron oxide layer ($<1\text{ }\mu\text{m}$) was identified at the metal surface, along with a locally developed porous iron oxide region of approximately $1\text{--}2\text{ }\mu\text{m}$ thickness. After 4 months of exposure, material degradation proceeds along the graphite nodules (see Figure 4b). A depletion of iron around the graphite nodules and an enrichment of oxygen and calcium are observed by SEM-EDS. However, the attack of the graphite nodules is only locally present and not homogeneously distributed along the whole interface.

3.2.2 | Copper (Pure, Phosphorous-doped)

Analysis of the cross sections by SEM-EDS indicated an enrichment of aluminum, silicon and oxygen, which corresponds to attached bentonite (see elemental distribution maps in Supporting Information S1: Figure S5 and S6). Locally, calcium and oxygen were enriched, which do not coincide with silicon, therefore, suggesting it to

be a calcium carbonate phase. Copper and oxygen EDS maps were post-processed with ImageJ [36]). The original maps were denoised (non-local mean denoiser) and combined by using the “AND” - operator which aims for the pixels that are included in the oxygen as well as in the copper map. By applying a threshold on the output image, the copper- and oxygen-rich layer was extracted with a layer thickness of $2.4 \pm 0.6 \mu\text{m}$ for pure copper and $1.2 \pm 0.1 \mu\text{m}$ for phosphorous-doped copper. It has to be emphasized, that local layer thicknesses may not represent the overall corrosion rate as determined, for example, by gravimetric loss measurements.

3.3 | Corrosion Induced Bentonite Changes

To characterize changes in the bentonite due to corrosion, phase composition and bulk chemical analysis were investigated on cross sections.

3.3.1 | Bentonite From Laboratory Experiments

After exposure for 1 and 4 months at 60°C bentonite was separated from the metal coupons and dried in a glovebox system. One part of the bentonite was used to prepare fused tablets for quantitative WD-XRF analysis. The second part was embedded in epoxy resin and further prepared for microscopy and $\mu\text{-XRF}$ analysis.

3.3.1.1 | Cast Iron-Bentonite Interface

After 1 month of exposure a brownish halo at the metal-bentonite interface extends about $600 \mu\text{m}$ into the bentonite (see Figure 5a). The surface shows a very thin black discoloration, which cannot be imaged by the digital microscope. After 4 months, a dark-grey

region of $\sim 300 \pm 100 \mu\text{m}$ is observed directly at the contact zone of cast iron and bentonite. A brownish-orange halo is extending $\sim 2 \text{ mm}$ ($\pm 120 \mu\text{m}$) inwards the bentonite (see Figure 5a).

By $\mu\text{-XRF}$, the sample exposed for 1 month shows an iron enrichment of $\sim 260 \pm 140 \mu\text{m}$ into the bentonite. After 4 months of exposure, this iron enrichment exceeds $\sim 300 \pm 140 \mu\text{m}$ depth. Additionally, FeS_2 , as naturally present in the bentonite, shows as bright green spots in the iron $\mu\text{-XRF}$ map. The brown halo shows a brighter contrast in the $\mu\text{-XRF}$ map, evidencing a higher Fe content, as compared to the bulk material (see Figure 5b).

The elemental composition in the bentonite after exposure was determined by WD-XRF. At first the SiO_2 to Al_2O_3 ratio was selected to represent the bulk bentonite composition as it is thought to be the most stable towards variations. Additionally, the ratio of Fe_2O_3 to $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$, as iron being the main factor influenced by corrosion of cast iron, was calculated. The results are shown in Table 2. The SiO_2 to Al_2O_3 ratio for the bulk material was calculated based on five measurements, being fairly constant at $3.23 (\pm 0.01)$ (1σ) which relates to a relative standard deviation of 0.20%. All measurements for cast iron (3.22 (1 month), 3.21 (4 months)) lay within 2σ therefore it is assumed not to be affected by corrosion. The iron content increases from 1 to 4 months exposure with respect to the bulk bentonite. However, the Fe_2O_3 to $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ ratio for the bulk material and the exposed bentonite is constant with 0.06 (0.01). Therefore, no distinct increase of iron within the bentonite upon corrosion was determined by WD-XRF.

X-ray powder diffraction showed no changes in the diffraction pattern of the dried bentonite after exposure.

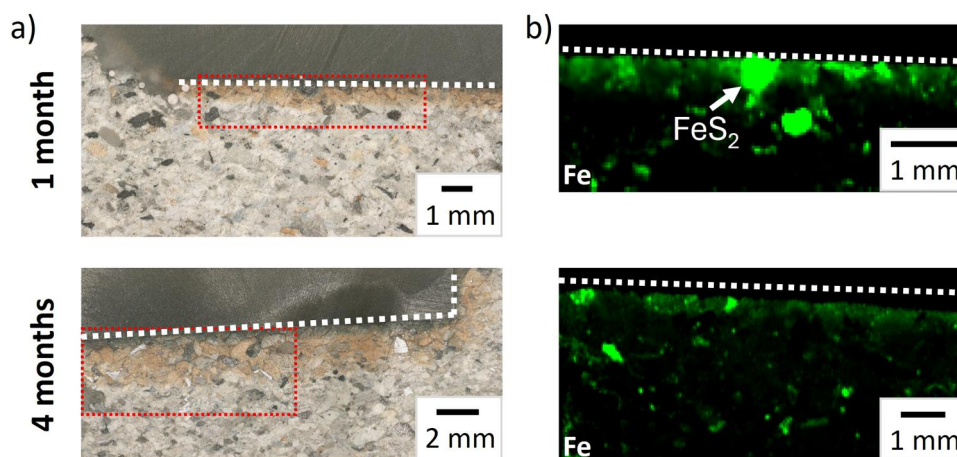


FIGURE 5 | (a) Digital microscopic images of bentonite exposed to cast iron after 1 month exposure (top) and 4 months exposure (bottom). (b) shows the corresponding $\mu\text{-XRF}$ elemental distribution map of iron. The location of (b) is indicated by the red square in (a). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 2 | Chemical composition of the bentonite (5 measurements) as determined by WD-XRF results and bentonite in contact with cast iron for 1 and 4 months. Numbers in brackets indicate the standard deviation.

	Time [month]	SiO_2 [mass-%]	Al_2O_3 [mass-%]	Fe_2O_3 [mass-%]	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$
Bulk bentonite		50.62	15.68	3.87	3.23 (0.01)	0.06 (0.01)
Cast iron	1	62.7	19.46	5.09	3.22 (0.01)	0.06 (0.01)
Cast iron	4	63.66	19.83	5.38	3.21 (0.01)	0.06 (0.01)

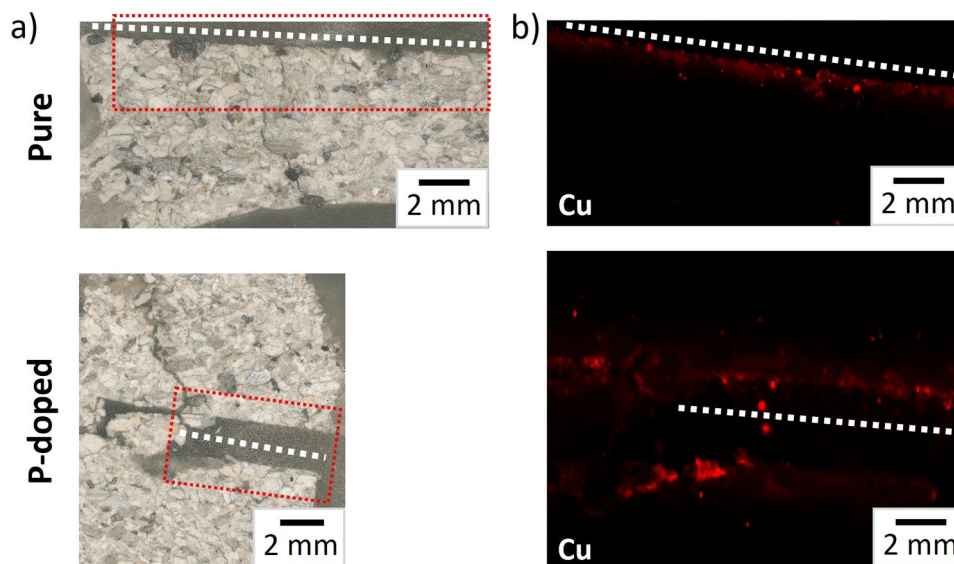


FIGURE 6 | (a) Digital microscopic images of bentonite exposed to pure copper (top) and phosphorous-doped copper (bottom). (b) shows the corresponding μ -XRF elemental distribution map of copper. The location of (b) is indicated by the red square in (a). The white, dotted line indicates the former copper-bentonite contact zone. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.20250)]

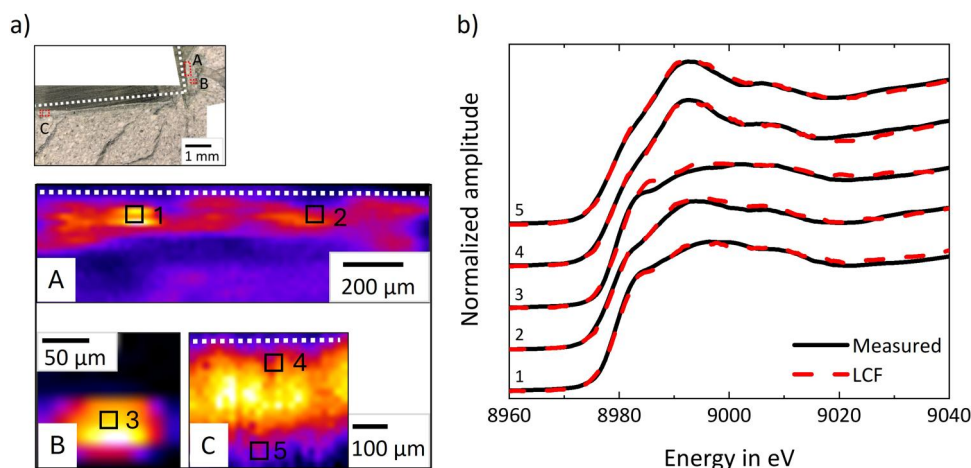


FIGURE 7 | Compacted bentonite from the MaCoTe experiment after exposure for 4.5 years at 1.25 g cm^{-3} . (a)-top digital microscopic image of dried bentonite embedded in epoxy resin. The white dotted line represents the former metal-bentonite interface and A, B, C represent the location of the sy- μ -XRF maps of copper in (a)-bottom. (b) Shows the μ -XANES spectra of selected measurement points (numbers 1–5 in a), whereas the black line corresponds to the measured data and the red-dotted line to the LCF. Fit results are presented in Supporting Information S1: Table S3. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.20250)]

3.3.1.2 | Copper (Pure, Phosphorous-doped)-Bentonite Interface

The copper-bentonite interface of pure and P-doped Cu does not show any changes observable by digital and light optical microscopy (Figure 6). By μ -XRF a slight enrichment of copper was observed. Similar to the cast iron-bentonite interface, quantitative analysis by WD-XRF was performed. However, the CuO to $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ ratio calculated out of the bulk shows a relative standard deviation of 41.75% and was therefore not further considered.

No changes in the diffraction pattern of the dried bentonite were observed by X-ray powder diffraction.

3.3.2 | Bentonite From MaCoTe Field Experiment

The bentonite from MaCoTe field experiment was prepared according to the bentonite samples from the laboratory as

described in Section 3.3-1. Before drying, all bentonite samples showed a blue to black discoloration along the former contact zone. After drying, the interface region was imaged by digital microscopy, SEM-EDS (see Supporting Information S1: Figure S7), sy- μ -XRF, and Cu K-edge μ -XANES spectra were recorded. The metal-bentonite interface in each sample is marked by the dotted line (see Figures 7–10).

3.3.2.1 | Copper-Bentonite Interface 4.5 Years; 1.25 g cm^{-3}

The bentonite sample after 4.5 years of exposure with 1.25 g cm^{-3} dry density shows a partial green discoloration at the metal-bentonite interface (Figure 7a). SEM-EDS indicates an enrichment of copper along the interface which correlates with an enrichment of sulfur (see Supporting Information S1: Figure S7a). Figure 7a shows sy- μ -XRF maps which reveal an enrichment of copper along the metal-bentonite interface. A discrete hotspot of copper

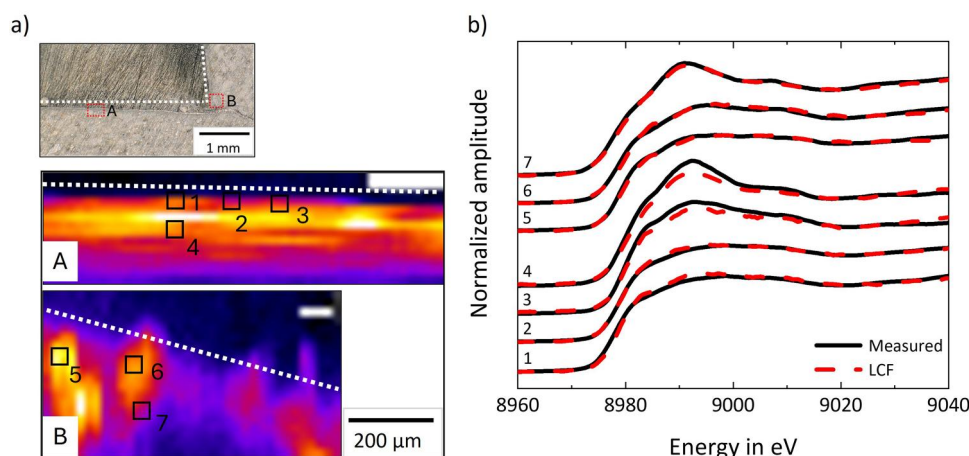


FIGURE 8 | Compacted bentonite from the MaCoTe experiment after exposure for 4.5 years at 1.50 g cm^{-3} . (a)-top digital microscopic image of dried bentonite embedded in epoxy resin. The white dotted line represents the former metal-bentonite interface and A, B represent the location of the sy-μ-XRF maps of copper in (a)-bottom. (b) Shows the μ-XANES spectra of selected measurement points (numbers 1-7 in a), whereas the black line corresponds to the measured data and the red-dotted line to the LCF. Fit results are presented in Supporting Information S1: Table S3. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.70250)]

enrichment $\sim 440 \pm 40 \mu\text{m}$ away from the interface is shown in Figure 7a-B. Five Cu-K-edge μ-XANES spectra were recorded at three independent locations (spectra 1-5 in Figure 7a). Except spectra 4 and 5 bearing similarities, all spectra look different (see Figure 7b). The XANES spectrum can be used as fingerprint of the local chemical environment of Cu, implying that different Cu species are present in that sample. Among the reference compounds selected in this study, the spectrum of Cu sorbed to bentonite has a high intensity rising edge, or white line, in agreement with reported spectra [36]. In contrast, copper sulfide compounds have a very low intensity and rather broad rising edge. Consequently, fits to the experimental spectra will unambiguously identify whether Cu is present as solid copper sulfide compound or as surface sorbed Cu. Results of fits to the μ-XANES spectra collected on the bentonite indicate the presence of several species, mainly CuS and Cu_9S_5 and lower amounts of copper adsorbed on bentonite in individual spectra (Figure 7b and Supporting Information S1: Table S3). Copper adsorbed on bentonite is predominantly found in the spectra which are further away from the interface. One spectrum (No. B-3) was recorded on the detailed map located $440 \pm 40 \mu\text{m}$ away from the interface. Result of the fit to this spectrum (No. B-3) indicates the presence of only CuS, suggesting that Cu migrated within bentonite before reacting with sulfide.

3.3.2.2 | Copper-Bentonite Interface 4.5 Years; 1.50 g cm^{-3}

Bentonite with higher dry density (1.50 g cm^{-3}) exposed for 4.5 years shows minor green discoloration at the former contact zone by digital microscopy (Figure 8a). SEM-EDS maps recorded along the interface show a discrete enrichment of copper and sulfur (see Supporting Information S1: Figure S7b).

By sy-μ-XRF a continuous layer of copper enrichment was measured along the interface (see Figure 8a). Five μ-XANES spectra were recorded along the interface, in areas having a high Cu content (see Figure 8). Results of fits to the spectra provide evidence for the presence of CuS or Cu_2S and Cu_9S_5 . Spectra 4 and 7 show a stronger white line intensity which

hints at the presence of adsorbed copper on bentonite (Figure 8b). The detailed Cu speciation obtained from modeling of the spectra is shown in Supporting Information S1: Table S3. One area of higher Cu content $600 \pm 20 \mu\text{m}$ away from the interface shows a spectrum composition (Spectrum 1) of $54\% \pm 7\% \text{ Cu}_2\text{S}$ and $46\% \pm 7\% \text{ Cu}_9\text{S}_5$ which indicates local precipitation or agglomeration of copper sulfides.

3.3.2.3 | Copper-Bentonite Interface 7.1 Years; 1.25 g cm^{-3}

The bentonite exposed for 7.1 years with 1.25 g cm^{-3} dry density shows a continuous grey/green discoloration along the former metal – bentonite interface (see Figure 9a). No discrete enrichment of copper and/or sulfur at the former metal-bentonite contact zone was observed by SEM-EDS. In contrast, distinct zones of copper enrichment are observed at varying depths from the interface (see Supporting Information S1: Figure S7c).

The μ-XRF map shown in Figure 9a indicates a pronounced copper enrichment within $360 \pm 40 \mu\text{m}$ from the interface.

By μ-XANES four spectra with increasing distance from the contact zone were measured (spectra 1-4 in Figure 9b). All four spectra could be adjusted to data recorded on CuS and Cu_9S_5 . Spectrum 5 shows minor amounts ($6 \pm 1\%$) of adsorbed copper, while the remaining fraction is assigned to Cu_9S_5 .

3.3.2.4 | Copper-Bentonite Interface 7.1 Years; 1.50 g cm^{-3}

Bentonite with 1.50 g cm^{-3} dry density shows after 7.1 years exposure a thin and homogeneous dark discoloration along the bentonite-metal interface (see Figure 10a). For this sample an enrichment of copper and sulfur along the interface is observed by SEM-EDS. Additionally, a local hotspot of copper and sulfur enrichment is observed below the interface (see Supporting Information S1: Figure S7d).

The μ-XRF maps show discrete enrichments of copper along the metal-bentonite interface. The highest copper enrichment can

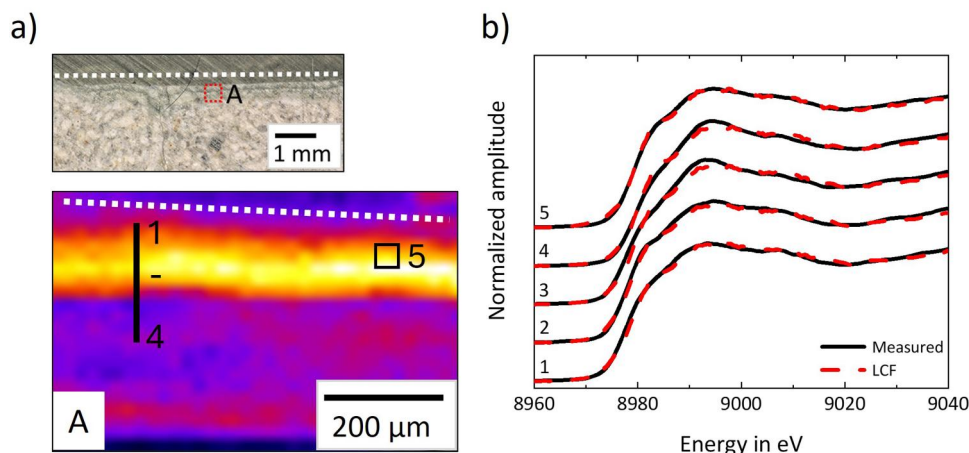


FIGURE 9 | Compacted bentonite from the MaCoTe experiment after exposure for 7.1 years at 1.25 g cm^{-3} . (a)-top digital microscopic image of dried bentonite embedded in epoxy resin. The white dotted line represents the former metal-bentonite interface and A represents the location of the sy- μ -XRF map of copper in (a)-bottom. (b) Shows the μ -XANES spectra of selected measurement points (numbers 1-5 in a), whereas the black line corresponds to the measured data and the red-dotted line to the LCF. Fit results are presented in Supporting Information S1: Table S4. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

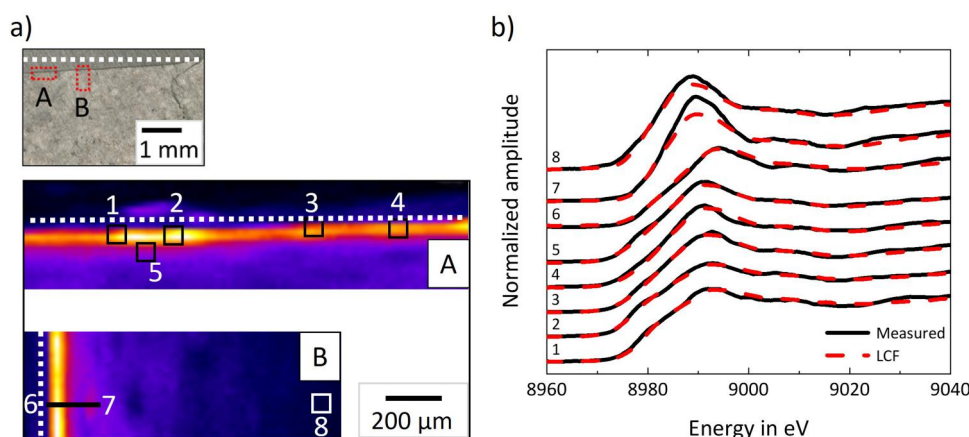


FIGURE 10 | Compacted bentonite from the MaCoTe experiment after exposure for 7.1 years at 1.50 g cm^{-3} . (a)-top digital microscopic image of dried bentonite embedded in epoxy resin. The white dotted line represents the former metal-bentonite interface and A, B represent the location of the sy- μ -XRF maps of copper in (a)-bottom. (b) Shows the μ -XANES spectra of selected measurement points (numbers 1-8 in a), whereas the black line corresponds to the measured data and the red-dotted line to the LCF. Fit results are presented in Supporting Information S1: Table S4. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

be observed along the interface ($280 \pm 60 \mu\text{m}$), whereas minor copper enrichment can be detected up to $\sim 2 \text{ mm}$ from the interface (Figure 10a).

The copper speciation was characterized by μ -XANES measurements (Figure 10b). Results from fits to the spectra recorded horizontally along the interface indicate the presence of copper adsorbed on bentonite and CuS or Cu_9S_5 (spectra 1-5 in Figure 10c). Additionally, μ -XANES spectra were recorded in the direction perpendicular to the interface in order to provide Cu speciation information as a function of increasing distance from the contact zone. The LCF of spectrum 6 in Figure 10b indicates a composition of adsorbed copper and CuS , which is in agreement with the observed moderate and broadened white line intensity. After $60 \mu\text{m}$ the spectrum changes, which can be recognized by a stronger white line intensity. The LCFs indicate that these spectra only consist of copper adsorbed on bentonite (see spectra 7 and 8 in Figure 10b). The detailed components of

the spectra after comparison to the reference samples and LCF is shown in Supporting Information S1: Table S4.

3.3.2.5 | Comparison Between Exposure Time and Dry Density

The sy- μ -XRF with the elemental distribution of copper in the four bentonite samples with different dry densities are displayed for comparison in Figure 11. The bentonite and resin are labeled as B and R, respectively. All samples show an enrichment of copper along the former metal bentonite contact zone, which is displayed by the bright colors in Figure 11. However, the samples with 1.25 g cm^{-3} dry density show copper enrichment to a larger extent along the interface than in samples with 1.50 g cm^{-3} dry density. The reason behind this observation might be due to solid copper sulfides remaining adhered on the bentonite surface.

For bentonite with a dry density of 1.25 g cm^{-3} exposed for 4.5 years, copper concentrations do not reach steady state levels

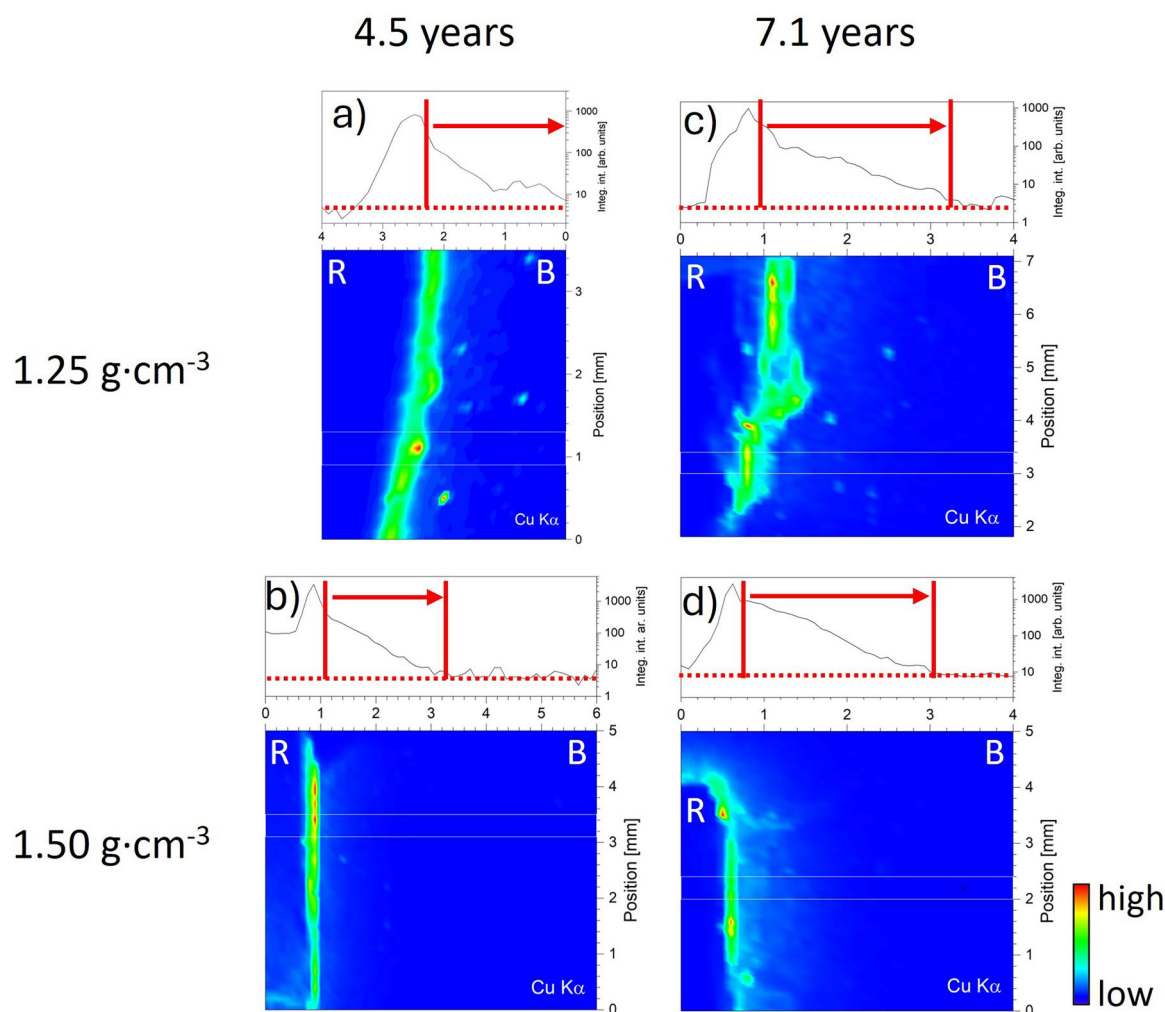


FIGURE 11 | Depth profiles of the MaCoTe bentonite of Cu-K α measured by sy- μ -XRF. R = resin, B = bentonite. The red dotted lines indicate the background level of copper within the bentonite. The solid red lines indicate the area of copper enrichment within the bentonite. (a) Shows the bentonite exposed for 4.5 years with 1.25 g·cm⁻³ dry density. (b) Shows the bentonite exposed for 4.5 years with 1.50 g·cm⁻³ dry density. (c) Shows the bentonite exposed for 7.1 years with 1.25 g·cm⁻³ dry density. (d) Shows the bentonite exposed for 4.5 years with 1.50 g·cm⁻³ dry density. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

within approximately 2 mm of the interface. In contrast, the sample with a dry density of 1.50 g·cm⁻³ exposed for same durations reaches background copper levels at approximately 2.5 mm from the interface. After 7.1 years of exposure, both dry densities exhibit copper enrichment extending to approximately 2.5 mm from the interface.

When comparing the copper phases in dependency of the distance from the contact zone, differences can be observed. The samples exposed for 4.5 years show predominantly CuS, Cu₂S and Cu₉S₅ as determined by LCF and subordinately copper adsorbed on bentonite (see Supporting Information S1: Table S5). The sample exposed for 7.1 years with 1.25 g·cm⁻³ dry density shows an increased fraction of copper adsorbed on bentonite with increasing distance from the contact zone. Yet, both spectra are mainly composed of copper sulfides and only minor amounts of copper adsorbed on bentonite. In contrast, the sample exposed for 7.1 years with 1.50 g·cm⁻³ dry density shows an equal portion of copper sulfide and copper adsorbed on bentonite close to the contact zone. Far from the contact zone the spectra are only composed of copper adsorbed on bentonite (see Supporting

Information S1: Table S5). Outcomes corroborate that copper sulfides precipitated at the copper-bentonite interface, and that copper ions migrated away from the interface.

4 | Discussion

4.1 | Corrosion Mechanisms in Compacted Bentonite at Elevated Temperature

4.1.1 | Cast Iron With Spheroidal Graphite (EN-GJS-400-15-C)

The corrosion behavior of cast iron with spheroidal graphite was studied by exposure for 1 and 4 months in compacted bentonite saturated with artificial water with chemistry from a crystalline rock in Germany under transient oxic conditions. The observed corrosion products are discussed with regard to the prevailing hydro-geochemical environment, the microstructure of CI and the impact of the compacted bentonite. A schematic illustration of the corrosion mechanism of CI is displayed in Figure 12.

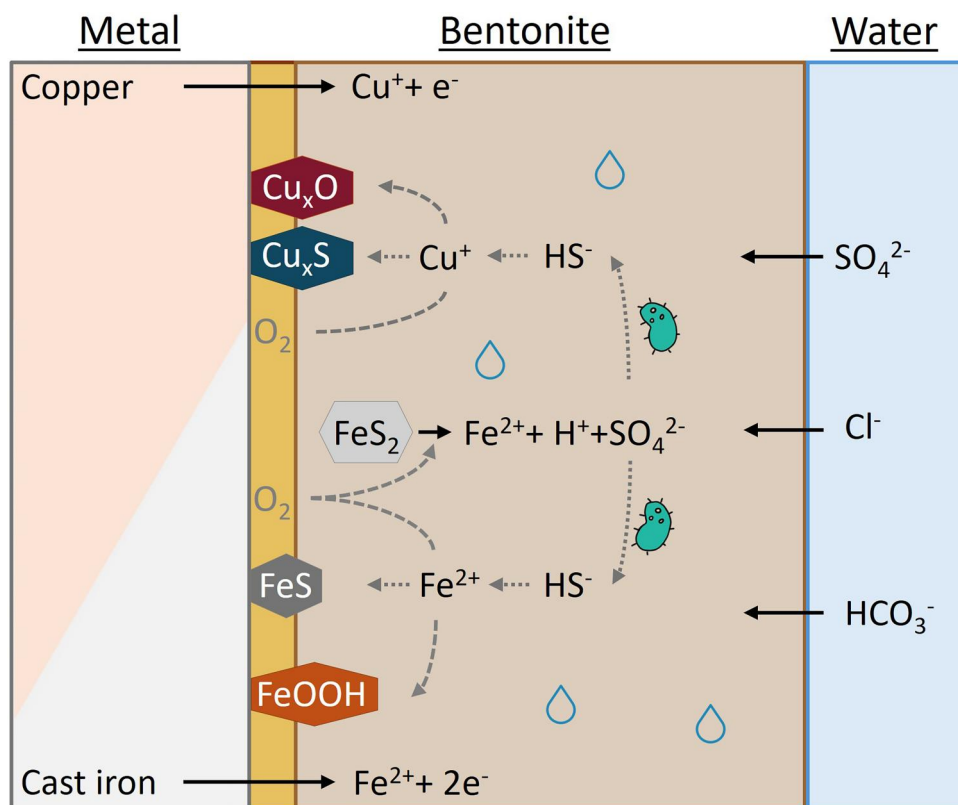
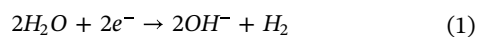


FIGURE 12 | Schematic illustration of the corrosion mechanism of cast iron with spheroidal graphite and copper (pure and phosphorous-doped) in compacted bentonite. The base metal is displayed on the left side in grey (cast iron) and orange (copper). Between canister and bentonite buffer (brown) a chemical-transient layer is illustrated in yellow, which holds for example, initial trapped oxygen. Incoming water from the host rock is shown in blue on the right. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.70250)]

4.1.1.1 | Corrosion Products at Metal Side

Localized brownish/orange color on the metal surface corresponded to iron oxyhydroxides as determined by XRD and μ -Raman spectroscopy. Iron hydroxides are commonly reported to be among the first corrosion products of steel in oxic conditions [15, 37–41]. During the transition from oxic to anoxic conditions, these phases are supposed to recrystallize to more stable phases like α -Fe₂O₃ under still oxic conditions or Fe₃O₄ under anoxic and reducing conditions. In the present study, only minor evidence of Fe₃O₄ and γ -Fe₂O₃ is given by μ -Raman spectroscopy. However, the dark staining on the bentonite surface after exposure might give hints to the presence of Fe₃O₄ [38, 42]. The formation of iron oxides and -hydroxides can be initiated by cathodic water reduction (Equation 1) [43].

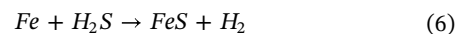


Whereby hydroxide ions may react with Fe to form Fe(OH)₂ (Equation 2) which can act as a precursor for FeOOH, Fe₃O₄ or green rust, as it was identified on the CI coupons in this study.

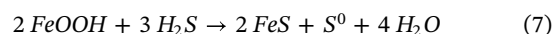


In a sulfide-containing, reducing environment, iron oxyhydroxides can be precursors for the formation of FeS rather than being transformed into stable iron oxides like α -Fe₂O₃ or Fe₃O₄ [44–47]. FeS was observed in the present study after 1 and

4 months of exposure by LOM, SEM-EDS and μ -Raman spectroscopy. The absence of FeS reflections in XRD pattern may be related to the nature of the FeS phase (e.g., poor crystallinity or a thin surface-localized layer). In general, FeS forms upon the following equations (Equations 3–6) which includes anodic dissolution of iron (Equation 3), the acid dissociation equilibrium of H₂S (Equation 4), the cathodic reduction of hydrogen (Equation 5) and the total reaction shown in Equation 6 [48].



If FeOOH acts as a precursor, the following equation (Equation 7) has to be considered [44].



FeS formation is widely reported in the corrosion of oil and gas pipelines and is also relevant in archaeological contexts as well as in high-level radioactive waste repositories [48–52]. The initial formation of FeS, often referred to amorphous or nanocrystalline FeS, is associated with reducing and anoxic conditions as well as the presence of dissolved H₂S. Within the

present study, dissolved H_2S can arise upon two mechanisms. Either sulfide-containing minerals like FeS_2 , as present in the bentonite, are dissolved, or microbial activity where sulfate is reduced to sulfide by SRB. The latter is reported to play a pivotal role for the long-term safety of deep geological repositories [9, 53]. In the present study, the bentonite was compacted to $\sim 1.50 \text{ g cm}^{-3}$ and experiments were carried out at 60°C , both being inhibitors for microbially influenced corrosion (MIC) [13]. A previous study by Necib et al. [54] proposes the formation of initial FeS on carbon steel in compacted bentonite through early-stage oxidation of FeS_2 , during or shortly after emplacement of the corrosion modules. Since the modules used in the present study were assembled outside the glovebox system, initially trapped oxygen, for example, on the metal coupon surface or within the bentonite, cannot be excluded. As depicted in Supporting Information S1: Figure S5 pyrite (FeS_2) can be present directly at the contact zone between bentonite and metal, therefore possibly being a source of Fe^{2+} and SO_4^{2-} . Additionally, a low concentration of sulfate ($5.35 \times 10^{-3} \text{ mol} \times \text{L}^{-1}$) is also present in the artificial water (see Table 1). Further targeted analyses would be necessary to clarify the origin of FeS formation. The transformation of $\text{Fe}^{\text{II}}\text{S}$ to $\text{Fe}^{\text{II}}_{1-3x}\text{Fe}^{\text{III}}_{2x}\text{S}$ implies a change in Fe oxidation state from 1 to 4 months exposure. This might be attributed to sample handling, since FeS is reported to be highly sensitive towards oxygen, transforming into the more stable iron sulfide Fe_3S_4 or FeS_2 [33, 49–51].

4.1.1.2 | Microstructural Impact

Previous studies [16, 17, 22, 55]) report the influence of the microstructure of cast iron with spheroidal graphite on the corrosion behavior. The graphite nodules are expected to act as a cathode and the iron-based matrix as an anode, leading to a subsequent dissolution of iron and the hydrolysis of water. It must be noted, that these studies used a bentonite suspension or pure synthetic water, which, in general, leads to a higher water content at the surface of the metal coupons. Nevertheless, in the present study, a preferred dissolution of the iron around the graphite nodules is observed and is associated with the formation of iron oxides or a calcium-containing phase, probably CaCO_3 (see Figure 3). This observation proceeds from 1 to 4 months of exposure, assuming it to actively driving the corrosion process forward. In contrast, the precipitation of FeS does not seem to be coupled to the graphite nodules. This is in accordance with the study by Tamisier et al. [53], although they did not investigate cast iron with spheroidal graphite exposed in bentonite but in plain sulfide solutions.

4.1.1.3 | Impact of Compacted Bentonite

The observations presented so far suggest an interaction between the metal and bentonite. This is confirmed by a visible change of color from grey to brownish/orange along the metal-bentonite interface. Iron enrichment may occur either by cation exchange and surface complexation on smectite edge sites or by the formation of finely dispersed Fe(III) oxyhydroxide precipitates. Several studies, both in situ and ex situ (laboratory scale), reported the presence of a brownish to black region progressing into the bentonite in contact with carbon steel [18–20, 38, 56, 57]. Mota-Heredia et al. [18, 19] and Kicka et al. [38] suggest that the initial enrichment of iron within the bentonite is linked to the reaction of remaining oxygen from the pore water or

bentonite with Fe^{2+} from the corrosion of the steel to form iron oxyhydroxides. Iron enrichment within the bentonite based on the adsorption of iron (Fe^{2+}) onto the smectite edge sites or at the cation exchange site within the interlayer of the smectite is reported to become more dominant when all oxygen is consumed. In the present study, bulk bentonite was measured by XRD, however no hints on secondary phase formation are given. This can be attributed to a fine distribution of the secondary minerals (e.g., FeOOH or Fe_2O_3) which were not detected by XRD. Generally, Raman spectroscopy is a powerful technique to identify low crystalline phases and small particles which cannot be identified by for example, XRD. However, the high parasitic fluorescence signal originating from bentonite itself makes a precise phase identification difficult. The formation of the brownish halo observed by visual inspection and LOM in this study is in accordance with previous observations, for example, Reddy et al. [20] and may be related to an initial oxidation of Fe^{2+} to Fe^{3+} and a possible electron transfer between surface sorbed Fe^{2+} and structural Fe^{3+} of the montmorillonite.

4.1.2 | Copper (Pure, Phosphorous-doped)

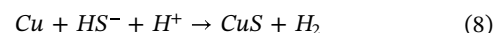
Pure and phosphorus-doped copper were exposed to compacted bentonite for 4 months under oxic transient conditions. A schematic illustration of the corrosion mechanism is displayed in Figure 12. Since no differences were observed between the two copper grades, both are referred to as “copper” in the figure.

4.1.2.1 | Corrosion Products at Metal Side

Under the prevailing conditions, Cu_2O was consistently identified by XRD, μ -Raman spectroscopy and SEM-EDS, indicating that it represents the predominant corrosion product in the studied system. However, as indicated in Figure 3, the Cu_2O layer appears to be very thin, as the grinding marks from the initial surface preparation remain visible. Initial oxygen might be trapped within the system, either located at the metal surface, within the pore space of the bentonite or within the pore water, leading to the formation of Cu_2O [8, 58]. The presence of CuO might be due to its formation before emplacement or to the re-oxidation of Cu_2O after dismantling of the corrosion cells.

Given the rather low chloride concentration present in the artificial water ($7.26 \times 10^{-2} \text{ mol} \times \text{L}^{-1}$), the formation of CuCl is unexpected. However, local physico-chemical differences can explain the precipitation of CuCl . The present study emphasizes the transient state from oxic to anoxic conditions, where heterogeneous interface chemistry is expected and no full saturation is achieved as it is expected in the long-term.

The presence of copper sulfide on the metal surface indicates reducing and anoxic conditions. Under sulfide-rich conditions, CuS or Cu_2S may form at the copper canister surface according to Equations 8 and 9 [8].



The conversion of Cu_2O to Cu_2S under sulfide-rich conditions may initially limit direct attack on the metallic copper by

consuming the pre-existing Cu_2O layer. However, sustained sulfide exposure may become detrimental once the oxide layer is depleted or locally disrupted, allowing sulfide species to interact directly with the underlying base metal [8, 57]. However, in the present study, the co-occurrence of Cu_2O and CuS may point to separate or locally distinct corrosion pathways, rather than providing clear evidence for direct transformation of the oxide layer.

4.1.2.2 | Impact of Compacted Bentonite

The interface between copper and bentonite did not show significant changes after 4 months of exposure. By μ -XRF an enrichment of copper along the interface was detected. However, the interpretation of the μ -XRF mapping results must be treated with caution due to potential matrix effects, which can substantially influence the measured intensities [59]. In addition, the copper signal detected by μ -XRF cannot be unambiguously attributed, as it may also originate from corrosion products adhering to the interface. Therefore, complementary techniques such as μ -XANES are suggested for further investigations, as this method provides element-specific information on the local chemical environment and oxidation state of copper. Overall, the results indicate that copper experiences only minor corrosion under the investigated conditions, with no significant corrosion products or pronounced alterations observed at the copper-bentonite interface during the exposure period.

4.2 | Alteration of the Bentonite From the MaCoTe In Situ Experiment

Long-term in situ tests investigate the corrosion behavior of candidate canister materials and their interaction with bentonite as a buffer material under more realistic conditions. In the present study, bentonite in contact with wrought copper for 4.5 and 7.1 years was investigated, revealing distinct characteristics depending on the exposure time and dry density (Figures 5–8). Except for one sample (7.1 years, $1.25 \text{ g}\cdot\text{cm}^{-3}$), SEM-EDS observations revealed a thin and continuous layer enriched in copper and sulfur along the metal-bentonite interface on the bentonite side. The enrichment of copper along the interface was confirmed for all samples by subsequent sy- μ -XRF mapping (see Figures 7–10). The apparent thickness of the copper sulfide layer may vary, as parts of the bentonite and associated corrosion products may be removed during dismantling of the bentonite from the metal surface after exposure.

4.2.1 | Copper Distribution and Speciation Along the Copper-Bentonite Interface

Despite the enrichment of copper (and sulfur) along the interface, all samples show distinct hotspots or areas of local precipitation of copper and sulfur within the bentonite, either determined by SEM-EDS or sy- μ -XRF. This highlights the local dependency of the chemical milieu along the metal-bentonite interface. As indicated in Section 3.3-2, μ -XANES spectra indicate the presence of copper sulfides and copper adsorbed on bentonite. The greenish-grey discoloration in the bentonites with a dry density of $1.25 \text{ g}\cdot\text{cm}^{-3}$ cannot be unambiguously

explained, as characterization results conducted by WD-XRF, SEM-EDS, sy- μ -XRF, and μ -XANES do not render information on a different phase composition compared to the samples with $1.50 \text{ g}\cdot\text{cm}^{-3}$ dry density. However, variations in dry density may affect the extent to which copper ions can migrate into the surrounding bentonite matrix and locally precipitate, for example as solid copper sulfides.

Previous results of MaCoTe experiment with shorter exposure time (1 year) were reported by Reddy et al. [20]. There, an enrichment of copper and sulfur was observed along the interface but no formation of secondary phases at the bentonite interface were detected, as well as no documentation of differences between the dry densities.

As discussed in Section 4.1.2, copper sulfides are the main corrosion products expected for copper under anoxic conditions (Equations 8 + 9) [4, 58]. The formation of copper sulfides is controlled by several factors, including pH/Eh, temperature conditions, and sulfide flux. Local variations in these parameters across the coupon may therefore account for the occurrence of different copper sulfide phases [60]. Furthermore, Salehi Alaei et al. [61] highlight the importance of the initially formed cuprous oxide layer for the subsequent formation of a copper sulfide film. The presence of Cu_9S_5 as determined by LCF of the μ -XANES measurements may indicate oxidation of Cu_2S by for example, residual oxygen.

Several studies (e.g., Pedersen et al. [62] or Keech et al. [4]) proposed the formation of SRB-related sulfide at the bentonite-groundwater or bentonite-host rock boundary, rather than directly at the bentonite-copper surface. This spatial separation is consistent with the microbial study conducted within MaCoTe, which does not indicate significant microbial activity in the corrosion modules but rather points to sulfide formation in the borehole water [63]. The produced sulfides may subsequently diffuse through the bentonite and react with the copper ions, forming solid copper sulfides.

Schlegel et al. [64] investigated the sorption mechanisms of copper (II) at the clay-water interface. For montmorillonite, which is the main component of bentonite, copper(II) is proposed to adsorb either on the (Al, Mg) octahedra edge site or the (Al, Si) tetrahedra corner site. In both scenarios, copper is co-ordinated to oxygen atoms of the smectite mineral structure. Adsorption of copper on the smectite phase, rather than incorporation of copper into the smectite crystal structure, is in accordance with results from the LOT experiment in the Äspö hard rock laboratory [65].

4.2.2 | Microstructural Effects of Bentonite on Transport and Precipitation

To date, there is no clear evidence of other long-term in situ experiments (e.g., [65]) or modelling approaches reporting local precipitation of copper sulfide within compacted bentonite. One hypothesis might include a heterogeneous swelling behavior during bentonite saturation or the heterogeneous composition of the bentonite arising from the mixture of bentonite powder and pellets used to achieve the target dry density [57, 66]. Smaller particles may create preferential pathways for copper ions

compared to larger pellet fragments, whereas the latter may locally inhibit diffusion and promote precipitation of copper sulfides. Bradbury and Baeyens [67] proposed a conceptual model of the bentonite microstructure in which accessory mineral grains (e.g., quartz, calcite, feldspar) are embedded within the smectite (montmorillonite) matrix. In an idealized structure, smectite layers would be arranged in a parallel orientation, but in natural systems smectite stacks are likely to be randomly oriented, potentially complicating transport pathways [68]. Three main water domains are generally considered in compacted bentonite: free pore water surrounding the accessory minerals (quartz, calcite, feldspar), interlayer water confined within the tetrahedra-octahedra-tetrahedra (TOT) layers of the smectite and electrostatic double layer water located between the mineral surface and free pore water, balancing the charge at the outer surface of the smectite (montmorillonite) [67]. The preferred pathway for ion movement is the free pore water, as it is less restricted by surface charge effects. However, cation mobility can be strongly limited because montmorillonite particles are negatively charged and can therefore readily adsorb cations such as Cu^{2+} . Anions, in contrast, are mainly transported through the free water within the interparticle pore space [67, 69].

Based on this conceptual model, bentonite compacted to a lower dry density (1.25 g cm^{-3}) may allow a higher sulfide flux towards the canister surface, where copper sulfides can subsequently form. It may also provide more diffusion-accessible pore space for dissolved copper species, which may precipitate as copper sulfides when local oversaturation is reached. In contrast, in bentonite compacted to a higher dry density (1.50 g cm^{-3}), sulfide transport is expected to be slower, resulting in lower sulfide availability at the canister surface [70]. Under such conditions, dissolved copper species may preferentially diffuse into the bentonite and adsorb onto montmorillonite edge sites. Also, as recently described by Chowdhury et al. [69], an increasing ionic strength can widen the interparticle pore space containing free

water, which may further influence the observed transport and precipitation behavior.

The depth profiles obtained by sy-XRF (Table 3) indicate no clear relationship with the bentonite dry density and the extent of copper diffusion. Except the sample exposed for 4.5 years at 1.25 g cm^{-3} , all depth profiles indicate an enrichment of $\sim 2.5 \text{ mm}$ from the interface. As reported in the previous section, the system tends to be largely heterogeneous and the constrain on one sample has to be carefully considered.

Further investigations, including reactive transport modelling, are required to better constrain the mechanisms governing diffusion, transport and precipitation processes in this system.

Overall, the results suggest that, under the investigated conditions, corrosion of copper in compacted bentonite is largely confined to the metal-bentonite interface, although copper may also occur within the surrounding bentonite as adsorbed species or precipitated copper sulfides.

4.3 | Implication for Nuclear Waste Disposal

In the present study, the performance of materials intended for use in engineered barrier systems including potential canister materials and bentonite (as a buffer material) exposed to groundwater from a crystalline rock in Germany was investigated. All components play a crucial role in ensuring the long-term safety of a deep geological repository.

The present study shows that the transient period before geochemical equilibrium is reached may be of particular importance for the corrosion of the canister material and the stability of the buffer. Furthermore, the results suggest that the interface shows physico-chemical heterogeneities, with local variations

TABLE 3 | Depth of Cu-enrichment (as determined in Figure 11) and dominant phase Cu speciation as result of the μ -XANES analysis of the bentonite in contact with wrought copper from the Material Corrosion Test.

	Cu- enrichment along the interface [μm]	Depth of Cu- enrichment from interface [mm]	Local hotspots [μm]	Dominant phase composition
4.5 years/ 1.25 g cm^{-3}	240 ± 20	≥ 2	440 ± 40	Mainly Cu_xS_y with maximum $32\% \pm 2\%$ adsorbed copper on bentonite
4.5 years/ 1.50 g cm^{-3}	120 ± 20	2.5	—	Mainly Cu_xS_y with increasing amount of adsorbed copper (max. $66\% \pm 4\%$) with higher distance from the contact zone
7.1 years/ 1.25 g cm^{-3}	100 ± 20	2.5	660 ± 40 1100 ± 20	Mainly Cu_xS_y with increasing amount of adsorbed copper (max. $21\% \pm 1\%$) with higher distance from the contact zone
7.1 years/ 1.50 g cm^{-3}	80 ± 20	2.5	—	Predominantly adsorbed copper on bentonite (up to 100%) with higher amounts of Cu_xS_y (max. $71\% \pm 1\%$) at the interface

in redox conditions, sulfide availability, pH, and copper speciation. These heterogeneities may promote the formation of different copper sulfide phases with either positive or negative protective properties and should therefore be considered when evaluating long-term copper corrosion in sulfide-containing anoxic environments [4, 71].

Under the investigated conditions, the copper–bentonite interface was only slightly affected by corrosion, consistent with the generally low corrosion rate of copper. In contrast, the cast iron–bentonite interface showed a wider range of corrosion products, suggesting stronger sensitivity to transient redox conditions. However, in the KBS-3 concept, cast iron corrosion would only become relevant after failure of the outer copper canister.

The bentonite samples from the MaCoTe experiment, exposed for 4.5 and 7.1 years, indicate that local physico-chemical heterogeneities along the interface may persist over longer exposure times. Further evaluation is needed to determine whether local copper sulfide precipitation within the bentonite and copper adsorption onto montmorillonite affect the mineralogical and/or physical properties of the bentonite buffer.

This study highlights the importance of complementary analytics of both, laboratory and in situ studies for the safe disposal of high-level radioactive waste. While laboratory studies help to develop a corrosion model and foster process understanding, in situ studies, like the Material Corrosion Test, are essential to assess the persistence and repository relevance of these processes.

5 | Conclusions

Here, the corrosion behavior of cast iron with spheroidal graphite and pure as well as phosphorus-doped copper as potential canister materials was investigated under repository-relevant conditions in the laboratory. A Wyoming-type bentonite was used at a compacted dry density of 1.50 g cm^{-3} . The experiments lasted 4 months at 60°C , under transient oxic conditions in saturation with a synthetic artificial water from a crystalline rock in Germany. To provide long-term insights of Cu corrosion, MX-80 bentonite in contact with wrought copper from the MaCoTe experiment was investigated. Four bentonite samples at varying exposure times (4.5 and 7.1 years) and different compacted dry densities (1.25 and 1.50 g cm^{-3}) were analyzed. Complementary analytical methods were applied to investigate the material alteration after exposure. The main findings are summarized as follows:

1. Cast iron with spheroidal graphite shows a uniform corrosion behavior over exposure times of 1 to 4 months. Different corrosion products were observed along the metal–bentonite interface, indicating an evolving chemical environment under decreasing oxygen availability. The main corrosion products identified are iron oxyhydroxides and iron sulfides. Along the cast iron–bentonite interface, a brown halo develops, which evolved over longer exposure time.
2. Both copper grades (pure and phosphorous-doped) exhibit a similar corrosion behavior. In general, only a thin layer of corrosion products (Cu_2O , CuCl , Cu_xS) was observed, as the original metal surface prevailed. The copper–bentonite

interface appears largely unaffected by corrosion after 4-month exposure.

3. The MaCoTe bentonite samples show different secondary phases depending on the distance from the metal–bentonite contact zone and on the compacted dry density. Along the copper–bentonite interface, Cu_9S_5 was identified as the predominant phase, whereas at greater distances from the interface, copper adsorbed onto bentonite becomes the dominant copper species.
4. Laboratory studies typically provide short-term observations, whereas large-scale in situ tests offer insights into the long-term evolution of deep geological repositories. The extent to which long-term laboratory experiments yield results comparable to in situ tests remains to be confirmed.
5. The present study provides an experimental approach for laboratory studies to characterize metal–bentonite interactions in a close to application environment. Although an influence of metal corrosion on the bentonite was observed, further evaluation of the long-term stability of the buffer requires integration of these experimental findings into a coupled thermo-hydraulic model.

Author Contributions

Louisa Panjiyar: conceptualization, investigation, data acquisition, analysis, writing – original draft, visualization. **Christiane Stephan-Scherb:** conceptualization, analysis, writing – review and editing. **Martin Ende:** analysis, data acquisition, writing – review and editing. **Nicolas Finck:** analysis, data acquisition, writing – review and editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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