

Effects of γ -radiation on the interfacial chemistry of spheroidal graphite cast iron in contact with Wyoming bentonite slurry

A.G. Muñoz^{a,*}, D. Schild^b, S. Kaufhold^c, D. Dobrev^d, V.F. Viebranz^e, Th. Hassel^e

^a Gesellschaft für Anlagen und Reaktorsicherheit mbH (GRS), Theodor-Heuss-Straße 4, Braunschweig, 38122, Germany

^b Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, 76344, Germany

^c Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, Hannover, 30655, Germany

^d ÚJV Řež, a. s., Hlavní 130, Řež, 250 68 Husinec, Czech Republic

^e Institut für Werkstoffkunde (Materials Science) Leibniz Universität Hannover, An der Universität 2, Garbsen, 30823, Germany

A B S T R A C T

Keywords:

Gamma-radiation
Corrosion enhancement
Iron silicate
Calcium hydroxide
Spheroidal graphite cast iron
Wyoming bentonite

In most concepts for the disposal of high-level radioactive waste, cast-iron canisters containing spent fuels are encapsulated by bentonite that hydrates on contact with inflowing geological waters. This triggers the corrosion of cast iron, which can be turned worse under the exposition to significant levels of γ -radiation in unforeseeable scenarios. Such effects were examined by contrasting the chemistry of the corroded surface of spheroidal graphite cast iron in contact with Wyoming bentonite, fully hydrated with natural aerated Opalinus-Clay water, after 220 days of γ -ray exposition with a dose rate of 130 Gy h⁻¹ at 50 °C and that observed after a similar experiment without radiation. SEM-EDX, XPS, XRD, and ICP-OES were applied. The growth of patches of calcium hydroxide and ferrous hydroxide crystals as well as the presence of iron silicate layers adhered to the cast iron surface as predominant corrosion products are a fingerprint for a strong interfacial alkalization and the creation of a rather reductive milieu by radiation. These chemical transformations reveal an enhanced cathodic electrocatalytic activity of graphite nodules for water reduction under radiation which increases the anodic dissolution of the iron matrix and triggers the formation of a silicate diffusion barrier by dissolution-precipitation reactions. The radiation-induced cathodic activity may constitute an additional, more critical factor than the generation of oxygen for the container integrity, even after having reached the anoxic phase.

1. Introduction

The highly radioactive waste container concept Pollux®, originally designed for the disposal of high-level radioactive waste (HLW) in salt domes [1] is regarded as a reference for claystone and granite repositories [2]. The outer cask, made of spheroidal graphite cast iron (GGG 40/EN-GJS-400–15 C) provides shielding of radiation of the inner spent fuel enabling its use for transportation and storage before disposal. In granite-based repositories, bentonite is used as geotechnical barrier around the canisters. Containers are engineered to stand the adverse mechanical and chemical conditions in deep geological repositories expected for the length of their lifetime estimated in several millennia. Despite the quite low failure probability, it is cautious to ponder the processes triggered by a worst-case scenario, as for instance after a fracture of the container wall caused by radiation- or hydrogen embrittlement or stress corrosion cracking [3–5]. The subsequent

ingress of bentonite soaked with geological water would create a corroding cast iron interface exposed to large radiation doses (>100 Gy h⁻¹) [6]. A comparison of the corrosion rates reported for carbon steels in a series of representative works studying the effects of γ -radiation, let infer that the main predominating factor is the generation of oxygen by radiolysis (see Table A1 in the appendix). The presence of bentonite slurry separating the liquid phase from steel seems to decrease the corrosion rate by hindering the transport of oxygen to the corroding surface. In geological waters with either low content of Cl⁻ (<1 × 10⁻¹ mol dm⁻³) or alkaline conditions, the initial large corrosion rate decreases practically exponentially until attaining values typically < 0.1 μ m y⁻¹ after 50–300 days. Large chloride contents, on the other hand, hinder passivation and the corrosion rate is mainly governed by the diffusion-controlled reduction of radiolytic-generated oxygen. The presence of graphite nodules with a larger cathodic activity [11] plays a decisive role on the corrosion of the iron matrix under a bentonite slurry

* Corresponding author.

E-mail address: andres.munoz@grs.de (A.G. Muñoz).

as a diffusion barrier. Thus, the effects of radiation on their electrocatalytic properties deserves attention.

Liu et al. [10] studied the effects γ -radiation on the corrosion of carbon steel in contact with sodium bentonite hydrated with Beishan water (17 % w/w). They identified the formation of magnetite as main product together with hematite and goethite at the interface without radiation. The exposition to $\sim 3 \text{ kGy h}^{-1}$ radiation for 42 days induced the formation of siderite and magnetite as main products and some amounts of maghemite. This indicates a partial reducing effect, as found by the crystallization of magnetite from suspensions of α - and δ -FeOOH under irradiation [12,13]. The attainment of a reducing milieu after consumption of trapped oxygen was found to favor the formation of magnetite and siderite in long-term corrosion experiments of carbon steel in contact with clay containing 30 wt. % of calcite [14]. Lee et al. [15] have found that nodular cast iron corroded during 12 months in a 5 %w/w aerated slurry of Ca-bentonite under γ -irradiation with a dose rate of 0.1 Gy h^{-1} still shows its bright metallic aspect. This contrasts with the voluminous red-brown deposits of different ferric oxides generated without radiation and points a rather reducing milieu.

The water radiolysis generates the primary products $\bullet e_{aq}$ (0.27) $\bullet OH$ (0.28), $\bullet H$ (0.06), H_2O_2 (0.07), H_2 (0.05), H^+ (0.27), where the number in brackets indicates the yield in $\mu\text{mol J}^{-1}$ [16]. In the presence of Cl^- , radiolysis species $\bullet Cl$, $\bullet Cl_2$ and $\bullet ClOH$ join the complex reaction scheme changing the steady state concentrations of stable products H_2O_2 , H_2 , and O_2 [17]. The irradiation of suspensions of Wyoming bentonite with a dose rate of 540 Gy h^{-1} , was found to increase the amount of structural Fe(II)/Fe_T-ratio from $< 5 \%$ to about 30 % after 12 h [18]. This was explained in terms of a faster reduction of structural Fe(III) by $\bullet e_{aq}$ than the oxidation of Fe(II) by $\bullet OH$.

The electrochemical reduction of radiolytic generated species H_2O_2 and O_2 are generally regarded as the cause of corrosion acceleration observed under irradiation. They are also supposed to oxidize the primary corrosion product $Fe(OH)_2$ to $Fe(III)OOH$, which in turn drives further oxidation by its transformation to Fe_3O_4 [19]. This work pursues the identification of the dominating mechanism for the corrosion enhancement caused by γ -radiation on spheroidal graphite cast iron in contact with aerated Wyoming bentonite slurry. For this, a chemical footprint analysis after a model experiment, regarding the role played by the cathodic electrocatalysis of graphite nodules was carried out.

2. Materials and methods

2.1. Materials and reactor

Fig. 1 shows a schematic of the experimental setup. Four pieces of cast iron GGG40 of 10 mm in diameter and 4 mm in thickness were used for the test. The upper face was polished with grit emery paper and 6 μm to 1 μm diamond suspensions. The samples were sonicated successively in isopropanol, acetone, ethanol, and pure water and dried under argon stream before their mounting in the reactor. The composition of the cast iron is shown in Table 1. The samples were placed on the bottom of a PEEK (polyether-ether-ketone) vessel used as liner of a stainless-steel reactor and covered with a 1:10 (wt/wt) naturally aerated suspension of Wyoming bentonite in Opalinus-Clay water type A [20]. The solution was prepared using analytical grade chemicals and ultrapure water (18.2 M Ω .cm Milli-Q system, Millipore). The chemical composition of the solution (sol.1) and of the bentonite are given in Table 2 and 3, respectively.

The reactor was hermetically closed with a screwed lid and exposed to γ -radiation inside an electric oven at 50°C for 220 days. The selection of these parameters was based for the sake of comparison, on the work of Smart et al. [8]. Accordingly, a reaction time longer than 6 months and doses larger than 10^5 Gy ensures discernable variations of the corrosion rate and a steady state.

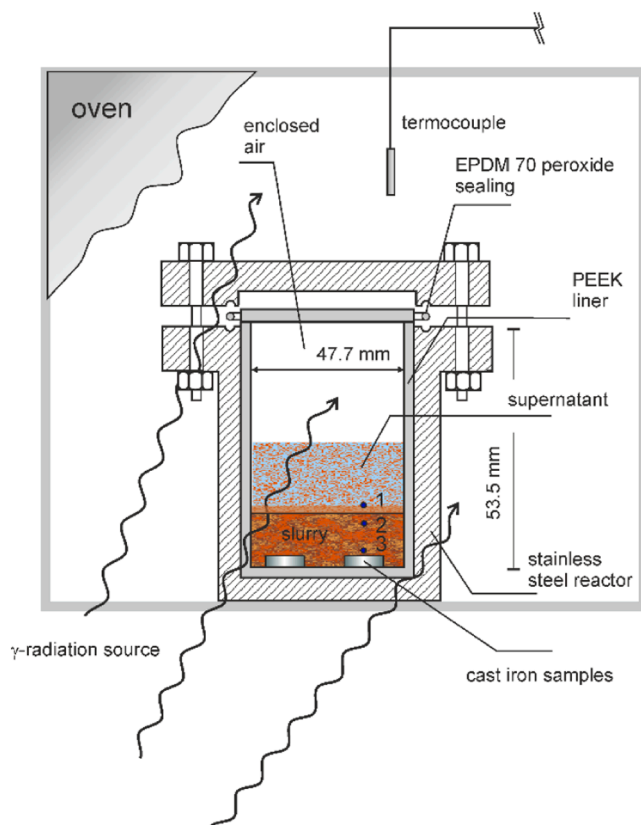


Fig. 1. Schematic of the irradiated cell containing the cast iron samples. Sampling points are also indicated (1, 2 and 3). EPDM: ethylene-propylene-diene-monomer.

Table 1

Nominal chemical composition of GGG40 steel.

Element	%at	Element	%at
C	13.85	Mg	0.10
Si	5.80	Cr	0.039
Mn	0.25	Cu	0.028
P	0.14	Fe	79.86
S	0.004		

2.2. Radiation source

The experiment was performed in the ^{60}Co gamma ray irradiation facility Panoza [21] with a radiation dose of 130 Gy h^{-1} measured in the interior of the reactor before of the experiment by Alanine-ERP Dosimetry ES 200–2106/E2044562 (Bruker Biospin, Germany) according to ISO/ASTM 51,607–2013 (see scheme in Fig. 1). The reactor was opened in a glove box GP concept T2 (Jacomex, France) with Ar atmosphere ($<1 \text{ ppm O}_2$) after 220 days. Non-rinsed cast iron pieces, samples of bentonite taken near and far from the coins and aliquots of the supernatant liquid were kept under anoxic atmosphere for further chemical analysis.

2.3. Solution chemistry

For solution chemistry analysis, ICP-OES (inductively coupled plasma optical emission spectroscopy) Thermo Fischer iCAPTM 7400, ICP-MS Agilent 8900 Triple Quad Spectrometer (inductively coupled plasma mass spectroscopy) and ionic chromatography Metrohm 861 were used. The bentonite particles were separated by centrifuging the sample during 5 min at 3000 rpm. The resulting supernatant was filtered

Table 2

Chemical composition determined by ICP-OES (mol kg⁻¹) of Opalinus-Clay water type A / pH 7.6 before (sol. 1) and after the equilibration with bentonite (sol. 2) and after the corrosion experiment under γ -radiation (sol. 3).

Element	sol. 1	sol. 2	sol. 3	Element	sol. 1	sol. 2	sol. 3
Na	0.24	0.26	0.28	Fe		$< 1.8 \times 10^{-8}$	3.0×10^{-4}
Cl	0.30	0.27	0.31	Si		0.0005	0.0002
K	0.002	0.002	0.025	NO ₃			6.5×10^{-6}
Mg	0.017	0.011	0.015	NO ₂			1.5×10^{-5}
Ca	0.026	0.007	0.021	S (non SO ₄)			0.0036
SO ₄	0.014	0.017	0.014	Sr	0.00065	–	0.00030
HCO ₃	0.0005	–	–	P			1.1×10^{-6}
Al		$< 1.5 \times 10^{-7}$	3.5×10^{-6}	Ti			3.6×10^{-6}

Table 3

Chemical composition of the used Wyoming bentonite before and after the experiment (%w/w) obtained by X-ray fluorescence.

component	reference	point 1	point 2	component	reference	point 1	point 2
SiO ₂	58.0	49.7	46.4	CaO	1.3	1.4	1.6
TiO ₂	0.2	0.1	0.1	Na ₂ O	2.1	4.0	6.0
Al ₂ O ₃	19.0	16.4	15.4	K ₂ O	0.5	0.6	0.6
Fe ₂ O ₃	3.7	8.8	9.8	P ₂ O ₅	0.1	0.06	0.05
MnO	0.01	0.02	0.02	LOI	12.3	15.8	16.7
MgO	2.3	2.3	2.4	Cl	0.005	0.065	0.129

with a syringe filter of 0.45 μ m. According to reference [22], for the solution used here, there is a probability that < 8 % of the total dissolved Si and Al corresponds to detached colloids.

2.4. Surface analysis

For XPS analyses, air sensitive samples were mounted in an Argon glove box (< 10 ppm O₂) on a sample holder. The sample holder was loaded inside the glovebox into a gas-tight transfer vessel (PHI, article no. V5000-K). The closed transfer vessel was removed from the Argon glove box and attached to the intro chamber of the XPS within 10 min. After evacuation of the intro chamber to 10^{-4} Pa, the transfer vessel is opened, and the turbo pump removes the Argon gas from inside of the transfer vessel. The sample holder is moved into the XPS analysis chamber (base pressure 10^{-7}) by a magnetically coupled linear transfer arm.

XPS spectra were recorded with a PHI 5000 VersaProbe II system (ULVAC-PHI Inc.). It was equipped with a scanning microprobe X-ray source (monochromatic Al K α 1486.7 eV) in combination with an electron flood gun and a floating ion gun generating low energy electrons (1 eV) and low energy argon ions (6 eV) for charge compensation of isolating samples (dual beam technique). The base pressure inside the spectrometer was about 2×10^{-7} Pa. The angle between sample surface and analyzer was set to 45°. Survey scans were recorded with pass energy of 187.85 eV of the analyzer and X-ray beam spot sizes 200 μ m of diameter at X-ray source power 30 W. In case of small sample features, scanning X-ray imaging (SXI) with X-ray spot size of 5 μ m was applied to define positions of analysis areas. Survey scans were used to identify the elements and to determine their relative atomic concentrations (except hydrogen) by areas of elemental lines after Shirley background subtraction, elemental sensitivity factors, asymmetry parameters, and transmission function of the analyzer. The relative error of atomic concentrations is expected to be within $\pm (10\text{--}20)$ %. Calibration of the binding energy scale of the spectrometer was performed using well-established binding energies of elemental lines of pure metals (monochromatic Al K α : Cu 2p_{3/2} at 932.62 eV, Au 4f_{7/2} at 83.96 eV) [23]. Narrow scans of elemental lines were recorded at pass energy of 23.5 eV, error of binding energies is estimated to ± 0.2 eV. The line C1s for graphite at 284.6 eV was used as a reference [24].

Subsequently, the coin of cast iron was fixed on a sample stub by double-sided conductive tape and coated with 6 nm of carbon for analysis by a scanning electron microscope (FEI Quanta 650 FEG)

equipped with a silicon drift EDS detector (Thermo Scientific, Noran System 7). X-ray microanalysis of sample surfaces was performed by Pathfinder software ver. 2.11.

2.5. Spectra deconvolution

Core-level photoelectron spectra were deconvoluted using the software UNIFIT 2019. The convolution of Lorentzian and Gaussian functions (Voigt profile) was used for the modeling of the peak shapes. The calculation of the background was included in the fitting procedure using a universal background description for inhomogeneous samples. This includes a polynomial component, $B_p(E) = a + bE + cE^2 + dE^3$, which represents the secondary electron background, a Shirley component: $B_s(E) = eS(E)$ and an improved Tougaard background component using a five-parameter inelastic electron scattering cross section: B, C, C', D and T_0 [25]. The intensity ratio of spin-orbit double peaks and their energy separation were fixed.

2.6. Microstructural characterization

For the metallographic microstructural characterization cross-sections of the corroded coupons were cut by abrasive water jet cutting. First, the specimens were ground and polished (0.06 μ m) employing a VIBROMET 2 (Buehler, Echterding, Germany), followed by etching using a 2 % Nital solution. OM (optical microscopy) of the top view and the cross-section of the GGG40 coupons was carried out using a ZEISS OLYMPUS BX53M (Carl Zeiss AG, Oberkochen, Germany) microscope.

2.7. X-ray diffractograms

XRD powder pattern were recorded using a Malvern Panalytical EMPYREAN X-ray diffractometer (Co-K α radiation generated at 40 kV and 40 mA), equipped with a variable divergence slit (20 mm irradiated length), primary and secondary Soller, diffracted beam monochromator, point detector, and a sample changer (sample diameter 28 mm). The samples were investigated from 2.5° to 80° 2 θ with a step size of 0.03° 2 θ and a measuring time of 3 s per step (total measuring time 2 h 10 min). For specimen preparation the back loading technique was used. The qualitative examination was performed using the software HighScore Plus 4.8 (Malvern Panalytical) in combination with the database PDF-2 (ICDD). Oriented mounts were prepared with a sample density of about

15 mg cm⁻² clay. An aliquot of 1.5 ml of suspension was deposited on a circular (diameter = 2.4 cm) ceramic tile (thickness 3 mm). The suspension was filtered through the tile using a vacuum filter apparatus.

XRD pattern of the oriented mounts were investigated from 2.5° to 40° 2θ with a step size of 0.03° 2θ and a measuring time of 6 s per step (total measuring time 2 h 5 min). Furthermore, the specimens were stored overnight in an ethylene glycol atmosphere at 60 °C. The clay films were measured again as described before after cooling to room temperature, representing ethylen glycolated conditions.

3. Results

3.1. Weight loss

The mean corrosion rate of cast iron was determined by weight loss after having removed residual bentonite and surface oxide by applying the ASTM G3-01 standard [26]. Taking a density of 7.3 g cm⁻³ for GGG40, a mean corrosion rate of 52 μm y⁻¹ can be calculated, assuming a homogeneous corrosion on the whole surface of the sample. Values of 7–11 μm y⁻¹, on the other hand, are reported in similar, non-irradiated weight-loss and electrochemical long-term experiments [27].

3.2. Microstructure

Fig. 2 shows the cast iron microstructure exposed at the top and at the side of a cross section performed on the oxide-free sample. A ferritic matrix with elongated ramified cementite becomes visible. Additionally, spherical graphite precipitates and pearlite can be identified. When the top view is examined, a preferential orientation of the cementite can be detected, caused by anisotropic conditions during solidification. The cross section shows the absence of localized dissolution of the cast iron matrix. A rough surface contour stretching over 100 μm of thickness arises from the unequal dissolution rate of cast iron phases.

3.3. Solution chemistry analysis

The dissolved oxygen in the slurry was lower than 0.03 mg l⁻¹ as measured with an O₂-sensor immediately after opening the reactor. The supernatant solution showed a dispersion of dark-red particles, denoting the formation of ferric oxides. Table 2 shows the chemical analysis by ICP-OES of an aliquot of the supernatant (sol.3: see Fig. 1) after the corrosion experiment compared with that of the Opalinus-Clay water

equilibrated with bentonite in a 1:10 (w/w) ratio without radiation (sol.2). The data indicate a Na-Ca ion-exchange during the equilibration without radiation and some dissolution of phyllosilicates, denoted by the increase of the Si concentration. The analysis after the corrosion experiment (sol.3) shows a marked increase of iron and aluminum contents. Further nitrogen and sulfur (non-sulfate) species denote products of the radiolysis of the solution containing sulfates and nitrogen (air).

3.4. Bentonite characterization

Fig. 3 shows relevant results of the XRD characterization of bentonite sampled at the interface with supernatant solution (point 1) and in the slurry (points 2 and 3 as indicated in the schematic of Fig. 1) and compared with the start material. The utilized bentonite consists mainly of smectite, with a d-spacing of around 12.5 Å, indicating Na⁺ as dominating exchangeable cation, as typical of Wyoming type (Fig. 3a). Admixtures are quartz, plagioclase, cristobalite, gypsum, and some pyrite. The content of calcite was also determined by FTIR spectroscopy [29].

The XRD powder diffractograms of irradiated clay samples (1–3) appear to be significantly different from that of the starting material, particularly for the characteristic basal reflections of clay minerals in the low angle range. The apparent disappearance of the d-(001) reflections of the smectite (samples 1 and 3) is particularly interesting. To

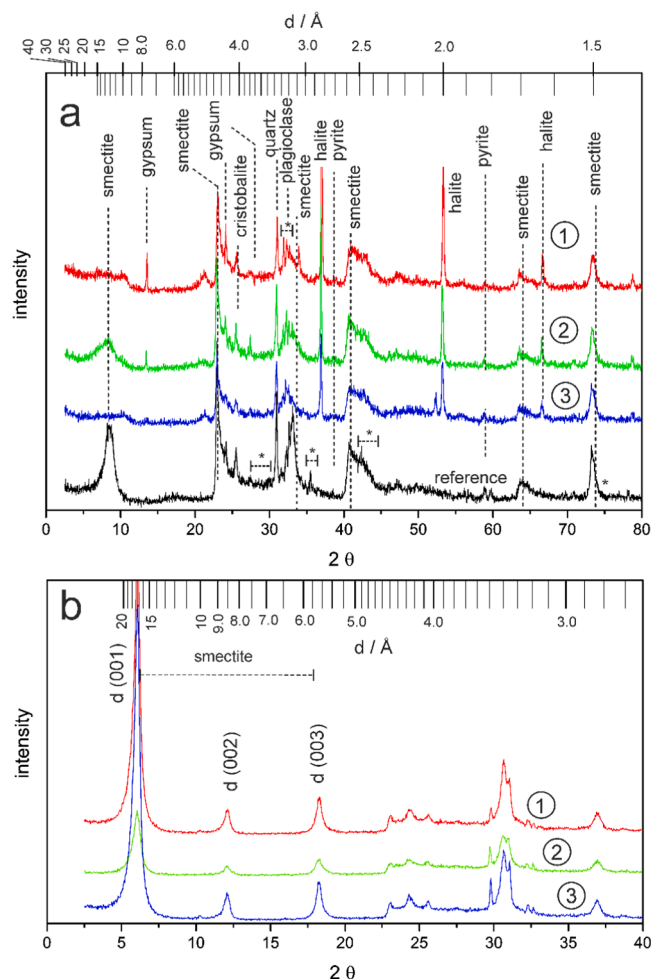


Fig. 3. (a) X-ray diffractograms of bentonite samples taken at point 1, 2 and 3 compared with that of pristine Wyoming bentonite: line assignments correspond to powder X-Ray powder diffractions taken from Ref. [28]; (b) X-rays diffractograms of ethylene-glycolated oriented-aggregate mounts.

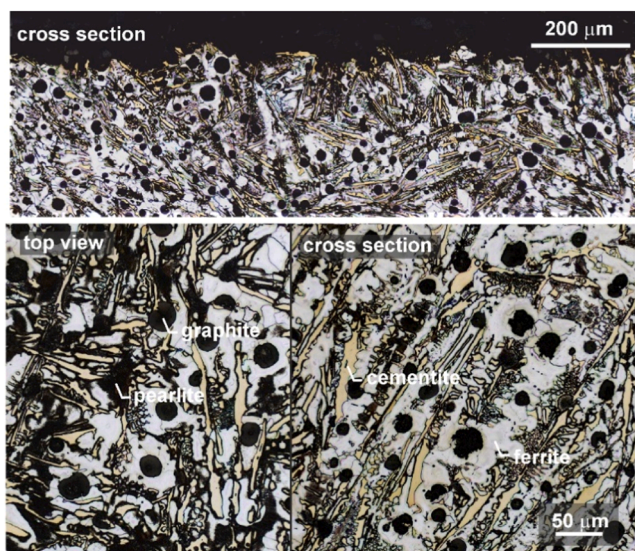


Fig. 2. Cross sectional and top view of the microstructure of a GGG40 sample revealed by etching with 2 % Nital.

investigate possible smectite alteration, air-dried and ethylene-glycolated oriented-aggregate mounts were investigated [30]. The diffractograms of all ethylene-glycolated samples in Fig. 3b show a full expansion of the smectite to 17.0 Å. Thus, the low intensity of the smectite basal reflections in the powder pattern can be ascribed either to a delamination and/or to different hydration states because significant smectite dissolution could be ruled out based on the oriented mounts. Weak intensity was observed at about 10 Å for samples 1 and 3 which indicates that dehydration caused by drying the samples led to a collapse of the interlayer which, based on the oriented mounts, is considered reversible. All powder diffractograms of sampled clays show a strong halite reflection, indicating the precipitation of halite from the remaining saline solution. The appearance of gypsum reflections with intensities proportional to those of halite denotes its precipitation from solution during drying of bentonite. Furthermore, the diffractograms (oriented mounts) of points 1 and 3 show a weak peak at about 10 Å which is indicative of mica. Kaufhold et al. [31] found that Wyoming bentonites can contain large mica particles which may not be reduced in size after grinding. These, in turn, can produce so called “single particle reflexes” which, however, cannot be used to assess their content. Thus, different intensities of the 10 Å reflection, at least of Wyoming bentonites cannot be used to conclude mineral alterations.

The chemical compositions of bentonites sampled at point 1 and 2 were measured by X-ray fluorescence. The results are shown in Table 3, being compared with that of the initial bentonite. It can be seen, that except for a significant increase of the iron and chloride content, there is no major change of composition. The atomic ratio Si:Al remains practically constant at 2.6. The ratio Si:Fe, however, decrease from 15.6 to 5.6 and 4.7 and the Si:Ca from 41, to 32 and 26, at point 1 and 2, respectively.

3.5. SEM-EDX analysis

Fig. 4 shows the general surface aspect of cast iron after a long-term corrosion experiment performed without (a) and under γ -radiation at 50 °C (b). In the former case, the removal of bentonite exhibits an attack pattern visualizing the different anodic reactivity of the cast-iron phases, which correlates with the microstructure of cast iron shown in Fig. 2. The removal of bentonite from the cast iron sample after the experiment under radiation exposes an attack surface characterized by strong adhered corrosion products. No structure-related metal dissolution can be observed in this case. The corroded surface is covered by patches of corrosion products with different morphologies. Figs. 5a-d show SEM-images of different selected areas with indication of the position of chemical SEM-EDX analysis detailed in Table 4. The analysis of the rather granular deposits in points 1 and 2 of Fig. 5a yields Ca:O ratios of $\approx 1:3-4$, which can tentatively be ascribed to hydrated $\text{Ca}(\text{OH})_2$ with minor amounts of smectite and iron (hydroxo)oxides.

The formation of interconnected platelets is also observed. According to the analysis at point 3 and based on their morphology, they can be ascribed to $\text{Fe}(\text{OH})_2$ [32,33]. The analysis on the area free of corrosion products (point 4) reveals a C-rich iron phase covered with some silicates. The chemical composition of the granular deposit indicated as point 5 can be assigned to a $\text{CaCO}_3 + \text{Fe}(\text{OH})_2$. Fig. 5b depicts another area of cast iron surface covered with corrosion products, characterized by geometrical rods covered with polyhedral, leaf-like deposits. Ca and O predominates in the elemental composition of the rods (point 8). This composition and type of morphology was observed for $\text{Ca}(\text{OH})_2$ grown in the presence of SiO_3^{2-} ions [34]. The elemental composition obtained at point 7 suggests that the particles decorating the rods consist of iron silicate. Fig. 5c shows another area of the covering deposits characterized by a network of rectangular platelets. According to the composition at point 9, they can be ascribed to $\text{Fe}(\text{OH})_2$ [33]. Fig. 5d shows some particles inside the covering layer having a shell constituted by ordered radially oriented rectangular lamellae. The elemental composition determined at point 10 and this characteristic structure resembles that

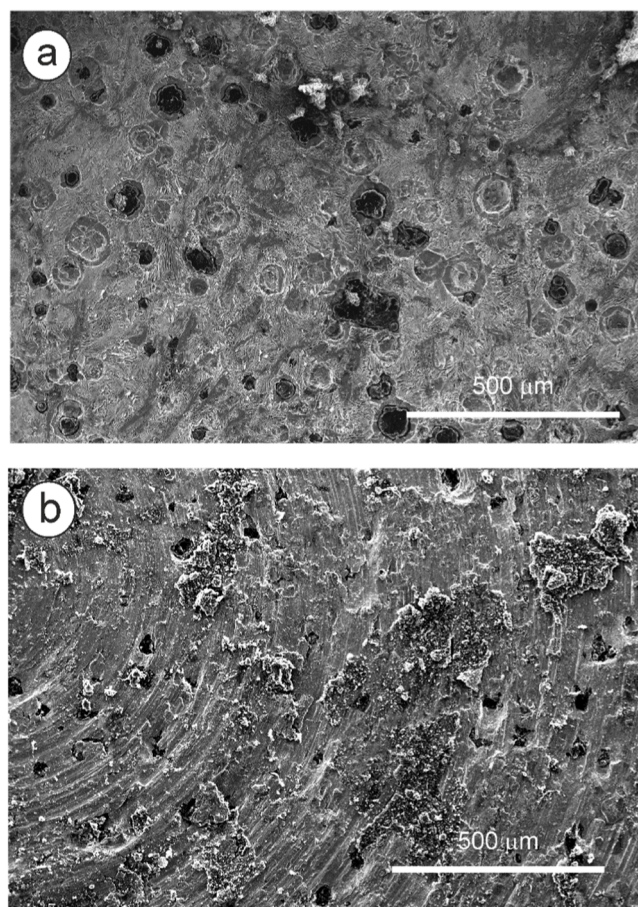


Fig. 4. SEM-micrographs of the cast iron surface partially covered with rests of bentonite (a) after 110 days of corrosion in contact with a 1:10 bentonite slurry without radiation and (b) after 220 days under 130 Gy h⁻¹ gamma radiation.

reported for iron-calcium carbonate after replacement of Fe^{2+} by Ca^{2+} in the siderite formed after corrosion of carbon steel in CO_2 -saturated brines. This reaction causes the growth of a Ca-substituted siderite [35]. The surface of bentonite from a sample taken nearby the cast iron surface is depicted in Fig. 5e and f. The former shows a typical structure constituted of disordered cornflake-like smectite lamellae decorated with bright appearing bunches of particles. The result of EDX-analysis on these particles (point 11, Table 4) can be interpreted as the signal of iron oxide retaining a fraction of the substrate signal (smectite). The morphology and a Fe:O ratio of 0.6 (for %at $\text{O}_{\text{ox}} = \% \text{at O}_{\text{total}} - (\text{O:Si})_{\text{smectite}} \% \text{at Si}$) suggest that these particles corresponds to magnetite. Fig. 7f shows a framboidal pyrite formation embedded in the bentonite layer (with a S:Fe of 2 as determined by EDX). The morphology of the surrounding bentonite resembles stacked flat-lying plates, typical for smectite [36,37]. The composition from the EDX-analysis on this region (21.1 at % Si, 7.7 at % Al, 60 at % O) indicates the formation of a phyllosilicate with an Al:Fe ratio of 4. The morphology of the bentonite side of the interface depicted in Fig. 5g is characterized by stacking of round-shaped flakes. The EDX-analysis (point 12) indicates the formation of a silicate with a large iron content: Si:Fe = 1.3.

In other regions (Fig. 5h) of the interfacial bentonite, bundles of filaments with ratios (at %) Fe:C and Fe:O of 3.4 and 4.7 (point 13), respectively, can be observed. The corrosion products adhering to the bentonite side may correspond to partially oxidized cementite.

3.6. XPS measurements

Fig. 6 shows the Fe 2p, Si 2p and O 1s core level spectra for the cast-

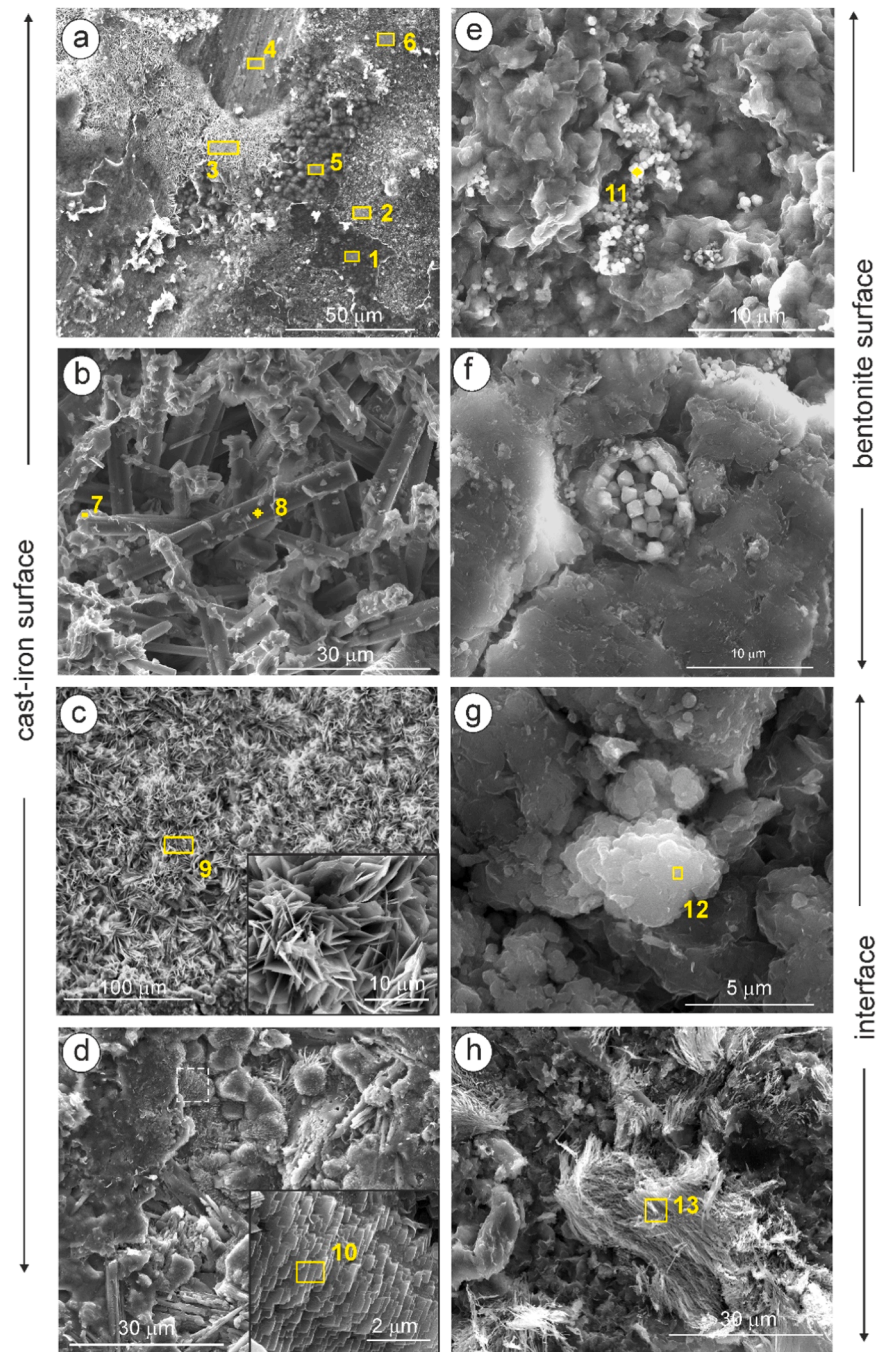


Fig. 5. Secondary electron mode SEM-images of the cast iron surface (a-d), of the bentonite surface from the interface metal-bentonite (e-f) and of a rest of bentonite taken near surface (g-h) after 220 days of corrosion in contact with a 1:10 bentonite slurry under 130 G h⁻¹ gamma irradiation.

Table 4
EDX-determined elemental composition (at %) at selected surface spots indicated in Fig. 5.

Element	Position												
	1	2	3	4	5	6	7	8	9	10	11	12	13
C	3.8	7.8	8.5	20.8	7.9	8.4	7.2	4.2	8.0	12.6	7.4	8.4	17.8
O	69.1	62.9	57.4	12.6	67.5	63.7	62.6	52.1	57.0	67.3	57.5	59.0	12.8
Al	1.1	0.4	1.0	0.2	0.5	0.4	0.4	0.4	1.2		2.9	2.2	1.4
Si	2.8	1.2	2.6	2.9	1.5	1.4	7.1	1.2	2.6		8.2	13.7	3.6
Ca	18.8	22.0	0.3	0.2	7.4	21.9	4.0	42.1		5.6	0.8	1.1	
Fe	3.2	5.0	28.2	63.2	14.7	3.3	17.2		28.4	13.0	19.6	10.1	60.7
Na							0.7		0.6		1.1	0.8	
Cl											1.3	3.3	1.7

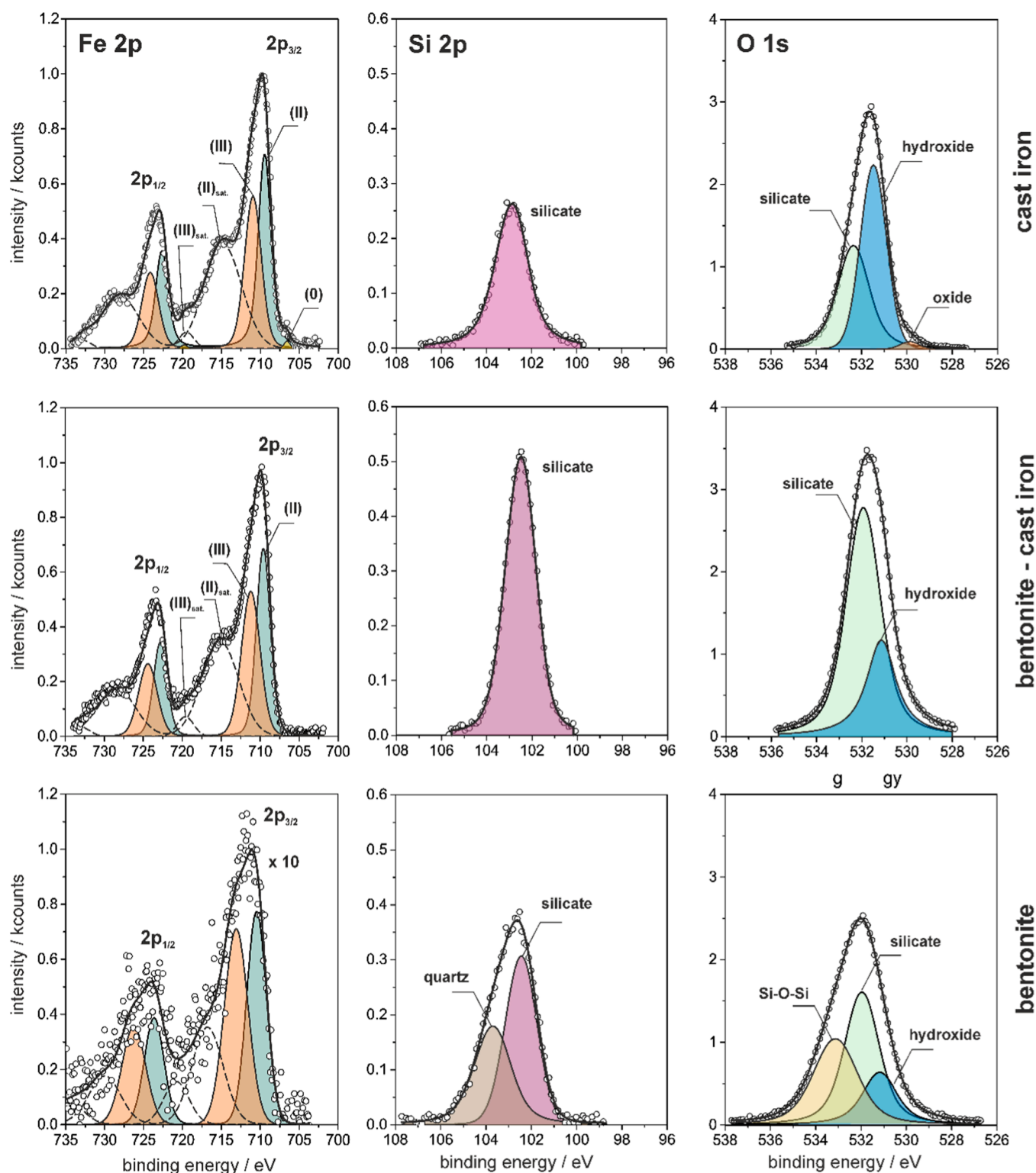


Fig. 6. XPS Fe 2p, Si 2p and O 1s core level XPS-spectra obtained on cast iron (region free of massive corrosion products), on bentonite surface detached from the cast-iron and on bentonite taken near the surface (bulk facing surface of detached bentonite cake).

iron surface, the interfacial bentonite and at the near-surface bulk bentonite. The Fe 2p core level spectra were deconvoluted following the classical way considering the Fe(II) and Fe(III)-lines and their respective satellites. For the cast iron surface, the Fe 2p_{3/2} lines were found at 709.6 eV and 711.2 eV with satellite shifts of +5.6 eV and +8.4 eV respectively and an intensity ratio $I_{\text{Fe(II)}}/I_{\text{Fe(III)}}=1.3$. For the interfacial bentonite, the lines are found at the same binding energies with an intensity ratio I_{Fe}

$I_{\text{Fe(II)}}/I_{\text{Fe(III)}}=1.0$. For the bulk bentonite, an iron signal of about 1/10 of that of the interface was found. Lines appear at 710.5 eV and 713.1 eV with satellite shifts of +6.4 eV and +7.8 eV respectively and an intensity ratio $I_{\text{Fe(II)}}/I_{\text{Fe(III)}}=0.9$.

The Si 2p core level spectra show a line at 102.8 eV for the cast-iron surface and at 102.6 eV for the interfacial and bulk bentonites, which can be ascribed to phyllosilicates [38,39]. The bulk bentonite shows the

appearance of a second line at 103.7 eV, assigned to quartz. The O 1s core level spectra for cast iron and interfacial bentonite are deconvoluted in two lines at 531.5 eV and 532.3 eV, assigned to hydroxide bonds and Si-O-Fe(Al) in phyllosilicates [40,41]. The spectrum for the bulk bentonite includes a third peak at 533.2 eV assigned to Si in quartz.

Fig. 7 contrasts the Fe 2p spectrum of cast iron surface with those of FeO (wüstite) and some ferrous silicates. A clear similarity with the spectra of wüstite and fayalite can be identified. Moreover, the spectrum matches those reported by Elmi et al. [38] for an iron-containing phyllosilicate of the mica-group and those reported for Fe-rich poly-lithionite [39].

For the sake of comparison, the Fe 2p, Si 2p and O 1s core level spectra for cast iron after a similar experiment without radiation are shown in Fig. 8. The iron spectrum shows Fe 2p_{3/2} lines at 709.6 eV and 711.3 eV for Fe(II) and Fe(III) respectively with an intensity ratio $I_{\text{Fe(II)}}/I_{\text{Fe(III)}}=0.76$. The corresponding satellites are shifted by +4.6 eV and +7.0 eV. The presence of a significantly strong line for iron metal at 706.8 eV indicates that the thickness of corrosion product is thinner than the electron inelastic mean free path, estimated by about 2.4 nm for quartz, as representative for silicates for 770 eV of kinetic energy [44]. The Si 2p spectrum can be deconvoluted in two lines attributable to Si in silicates and in quartz. The O 1s signal is characterized by a predominance of the silicate line at 532.2 eV and the appearance of an oxide line at 529.9 eV.

Fig. 9 shows the XPS Fe 3p and Al 2p core level spectra for the cast-iron surface and the interfacial side of bentonite. The absence of Gupta and Sen multiplets [45] and shake-up satellites in the Fe 3p core level signals allows a better quantification of Fe(III) and Fe(II). Thus, intensity ratios $I_{\text{Fe(II)}}:I_{\text{Fe(III)}}$ of 1.5 and 1.1 can be calculated for the cast-iron surface and the interfacial bentonite respectively. The Fe(III)-line of this latter is characterized by a broad signal as typical for disordered bonding structures. An Al 2p line appears at 74.6 eV for both the cast-iron and the interfacial bentonite surface, revealing the preponderancy of an adhered phyllosilicate structure on the cast iron surface. The line intensity is, however, lower than that for bulk bentonite by a factor of 3.

Fig. 10a shows the XPS C 1s core level spectra of different points across the interface cast-iron-bentonite. The spectrum of the surface of

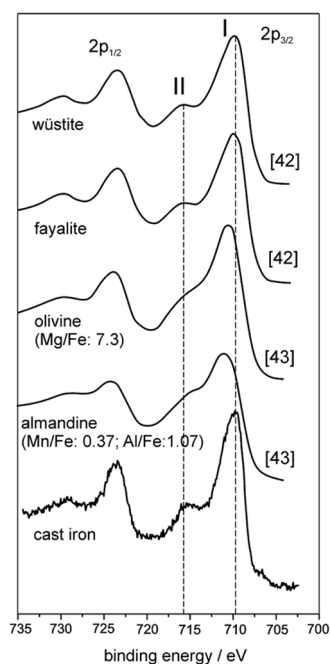


Fig. 7. XPS Fe 2p core level spectra for cast-iron compared with those reported for iron-containing silicates [42,43].

cast iron (1) is characterized by two lines at 284.6 eV and 289.3 eV assigned to graphite and carbonate respectively [46]. The point 2 correspond to a near surface region of bentonite coverage with a grey appearance. The spectrum shows an attenuated graphite signal and a broader carbonate signal with a third, weak line at 285.9 eV attributed to organic contaminations. The interfacial bentonite shows lines corresponding to graphite and organic contaminations. The carbonate signal appears at 289.1 eV. Carbon impurity signals at 285.9 eV and 287.0 eV appear for the bulk bentonite without carbonate, thus suggesting that carbonates are formed near the cast-iron surface.

For the sake of comparison, the XPS C 1s core level spectra of the cast iron surface obtained after the unirradiated experiment is shown in Fig. 10b. It can be observed, that besides the graphite line, wide lines at 285.4 eV and 288.45 eV, corresponding to sp³ bonds C-C and C-H, and oxygen-terminated carbon C=O and O-C=O, respectively [47]. It should be noted that the reduction of these lines in the irradiated sample points the vanishing of amorphous structures as well as of ketone and carboxylic surface sites.

The grey aspect of some parts of the adhered bentonite may be attributed to the presence of calcium products. Fig. 11 shows the deconvolution of the Ca 2p core level spectrum. The 2p_{3/2} lines at 346.9 eV and 348.3 eV can be assigned to CaCO₃ and Ca in phyllosilicates, respectively [46].

The valence band spectra of the cast-iron surface in Fig. 12 shows features at 1.3 eV, 5.2 eV and 10.2 eV that match with those found in a valence band spectrum reported for iron-rich olivine, Mg_{2-x}Fe_x^{II}(SiO₄) [48]. This result strongly supports the formation of a surface silicate.

The elemental composition for the different points of analysis, as determined from the corresponding survey spectra is shown in Table 5.

4. Discussion

One of the main issues of the present investigations, is the growth of a large variety of crystals at the interface of cast iron with hydrated bentonite, predominantly those identified as Fe(OH)₂ and Ca(OH)₂. The total iron concentration measured in the supernatant solution (Table 2) corresponds to that calculated from the K_{ps} of Fe(OH)₂ of 4.87×10^{-17} [49] for pH 7.6, implying an equilibrium with precipitated ferrous hydroxide. Only a tiny fraction of ferric species is expected due to the lower solubility of ferric oxides. The presence of patches with Ca(OH)₂ crystals points pHs > 12.2 regarding the concentration of Ca²⁺ in the Opalinus clay water (Table 2). This suggests a development of a laterally inhomogeneous electrochemical activity, attributed to the generation of cathodic and anodic elements at the graphite nodules and the iron matrix respectively.

The elemental composition calculated from the XPS-survey (see Table 5) at different points across the interface after the radiation experiment indicates an increase of Al and Si contents from the surface towards bulk bentonite, correlated with a decrease of Fe and C contents. According to the C 1s lines (Fig. 10a) the amount of carbonate decreases from 4.0 % at cast iron surface to 1.4 % in the interfacial bentonite. The grey-appearing regions of bentonite contain up to 7.6 % of CaCO₃. The atomic ratio Si/Al remains near 3.3 through the interface, as common for smectite. The gray-aspect part, on the other hand, shows a ratio Si/Al: 4.6, suggesting the formation of iron-rich phyllosilicates. This elemental distribution is compatible with a corrosion scheme, where iron is released under alkaline conditions towards bulk bentonite.

Moreover, the intensity of the line at 531.5 eV in the O 1s core level spectrum, assigned to Fe-OH bonds [50,51] represents 55 % of the signal for the cast iron surface. This value decreases to 29 % in the spectrum of the interfacial bentonite, where the line assigned to phyllosilicate predominates. According to the corresponding elemental analysis (see Table 5), only one half of the amount of oxygen can be assigned to phyllosilicates, with a ratio O/Si of about 2.5, and to carbonates. Thus, it is likely that a large part of oxygen is forming Fe(II)-OH or Fe(III)-OH bonds. The presence of a balanced Fe(II)/Fe(III)-redox system, as

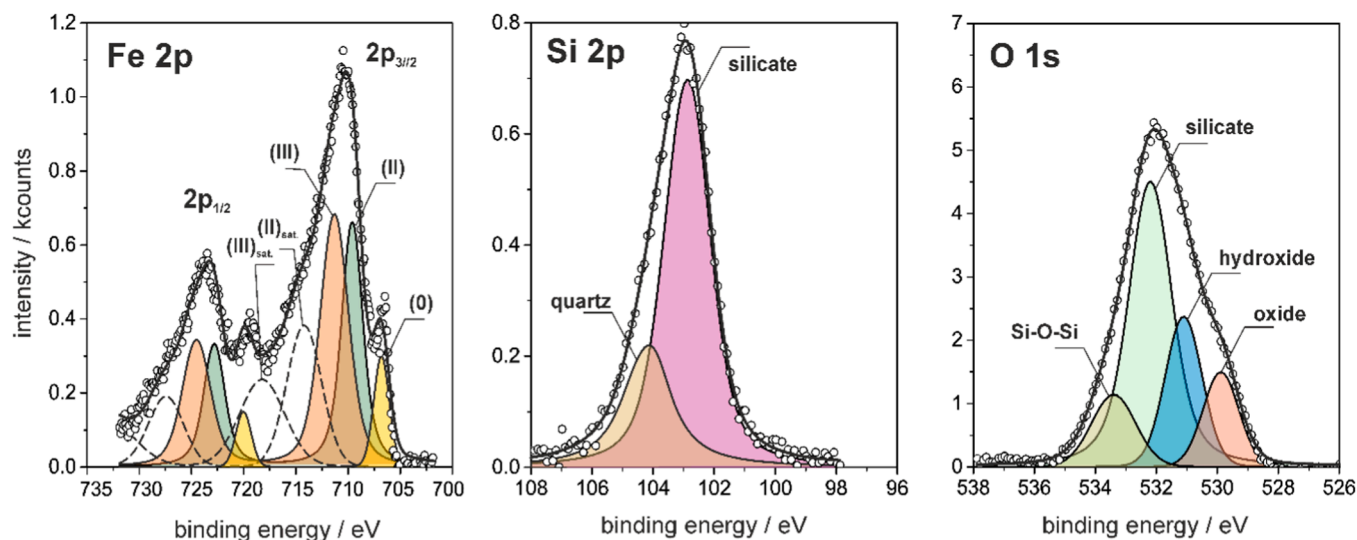


Fig. 8. XPS Fe 2p, Si 2p and O 1s core level XPS-spectra obtained on cast iron after 110 days of corrosion in naturally aerated bentonite slurry at 50 °C.

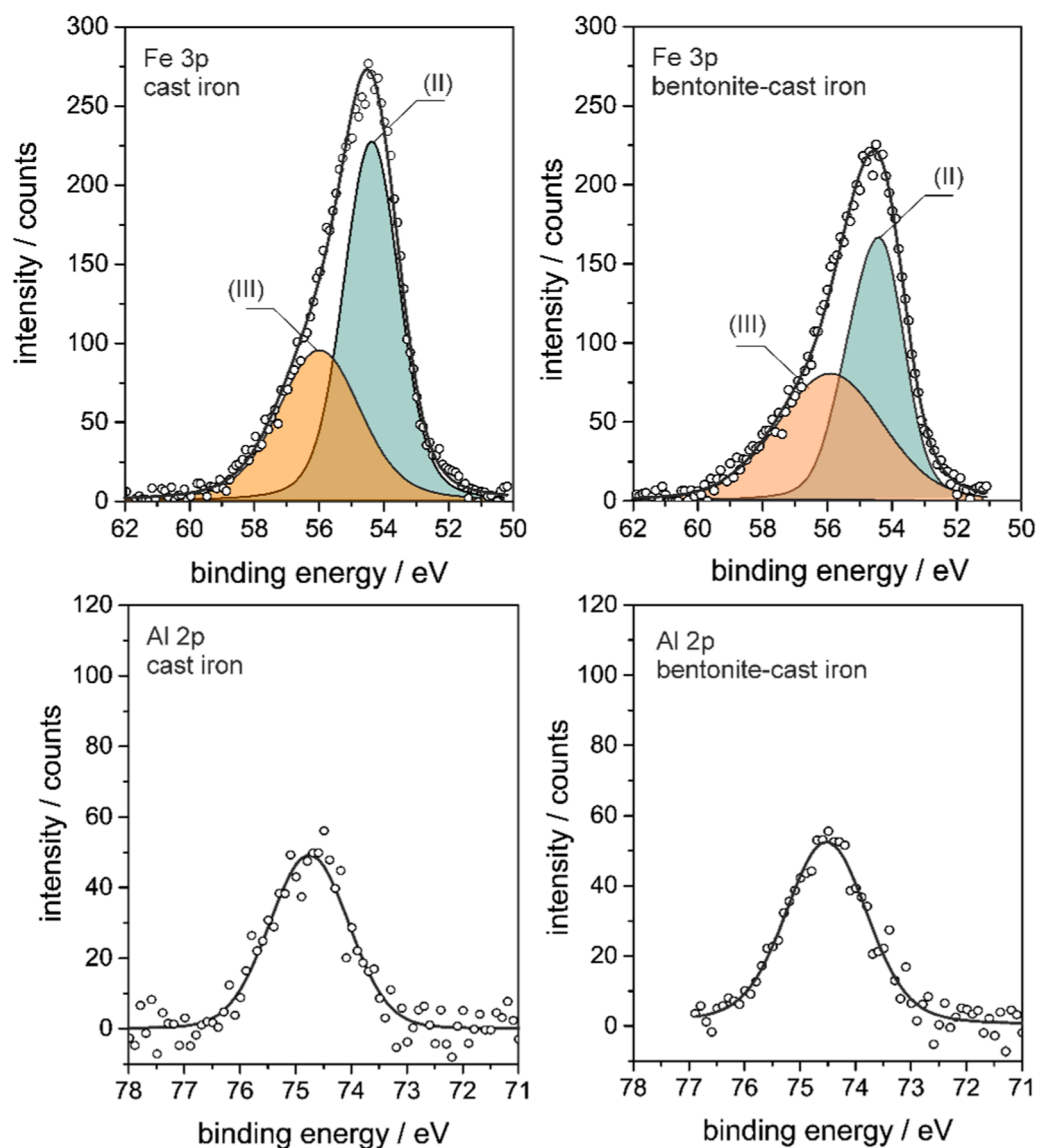


Fig. 9. XPS Fe 3p and Al 2p core level spectra for cast-iron and interfacial bentonite surfaces.

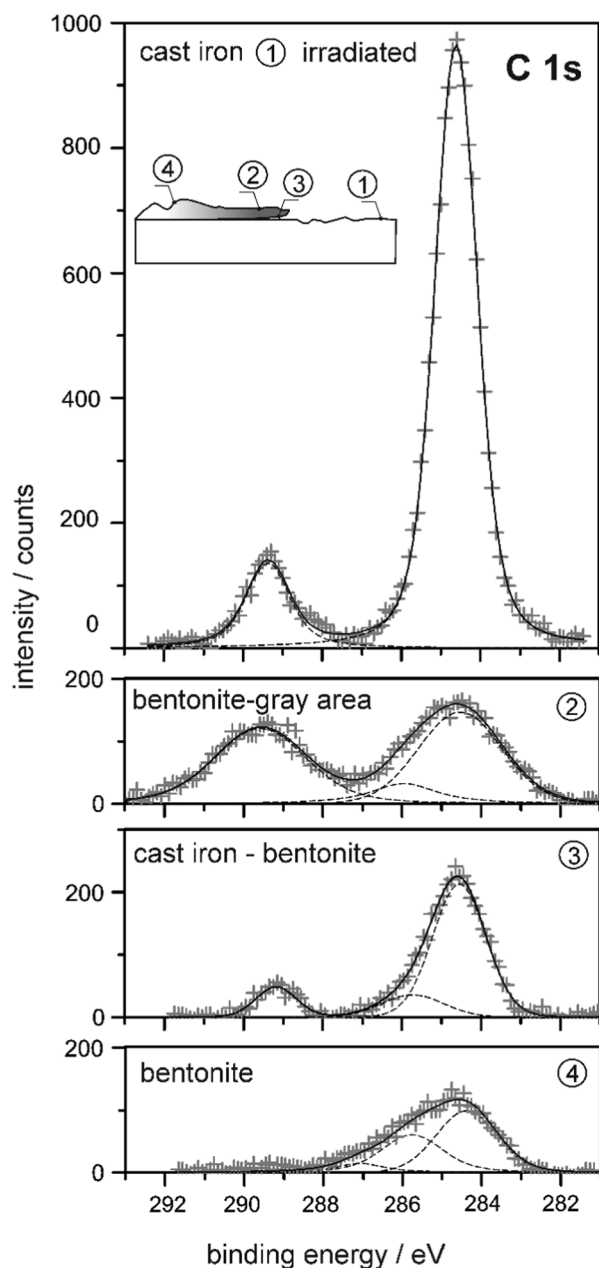


Fig. 10a. XPS C 1s core level spectra of cast-iron, grey appearing interfacial bentonite, interfacial bentonite, and bulk bentonite of an irradiated sample.

indicated by the deconvolution of the Fe 2p core level spectra, is confirmed by the deconvolution of the corresponding Fe 3p signals (see Fig. 9). The similarity of the unresolved spectra with those for fayalite and wüstite (see Fig. 7) suggests that we are dealing with a surface chemistry like that of those ferrous compounds. The absence of the O 1s line with a binding energy characteristic for oxides lets clearly assign this signal to silicates. The nature of the silicate remains however uncertain, because the deconvoluted Fe 2p spectrum resembles that reported for various iron-bearing phyllosilicates.

The intensity ratio $I_{\text{Fe(II)}}/I_{\text{Fe(III)}}$ in the Fe 2p spectra of cast iron surface measured on the irradiated sample is almost twice that measured after the experiment without radiation. This suggests that irradiation develops a rather reducing atmosphere. The larger amount of Fe(III) measured on the non-radiated cast iron surface is linked with an intensity ratio $I_{\text{oxide}}/I_{\text{hydroxide}}=0.61$ in the O 1s core level spectrum (Fig. 8). The large proportion of Fe-OH bonds found after the irradiation

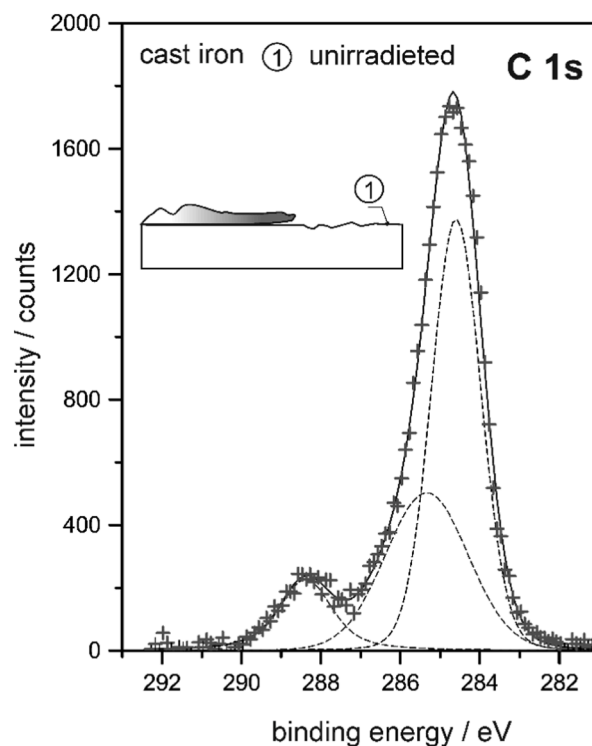


Fig. 10b. XPS C1s core level spectra of cast-iron of an unirradiated sample.

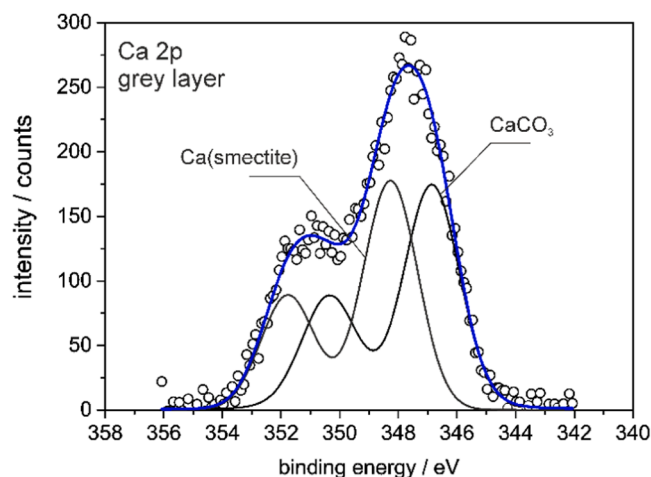


Fig. 11. XPS Ca 2p core level spectrum taken from the grey appearing part of adhered bentonite.

test constitutes another evidence of an interfacial alkalization, which is much stronger than in the absence of radiation. Moreover, the larger amount of generated corrosion products on the radiated sample, as indicated by the SEM-images in Fig. 4 is reflected in the absence of a Fe (0) signal in the Fe 2p spectra.

Daub et al. [52,53] have found that the electrochemical reduction of the radiation-generated H_2O_2 drives the open circuit potential of carbon steel by +0.1 V(SCE) in alkaline borate solutions, thus inducing the formation of a passivating film of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. This contrasts, however, with our system, where a morphologically and chemically inhomogeneous layer with a predominance of Fe(II)-silicates and -hydroxides of distinct crystallographic shapes appears. Preliminary non-irradiated electrochemical polarizations have shown that the anodic dissolution in aerated slurries occurs under an active regime [54]. The covering bentonite slurry hinders the oxygen diffusion and

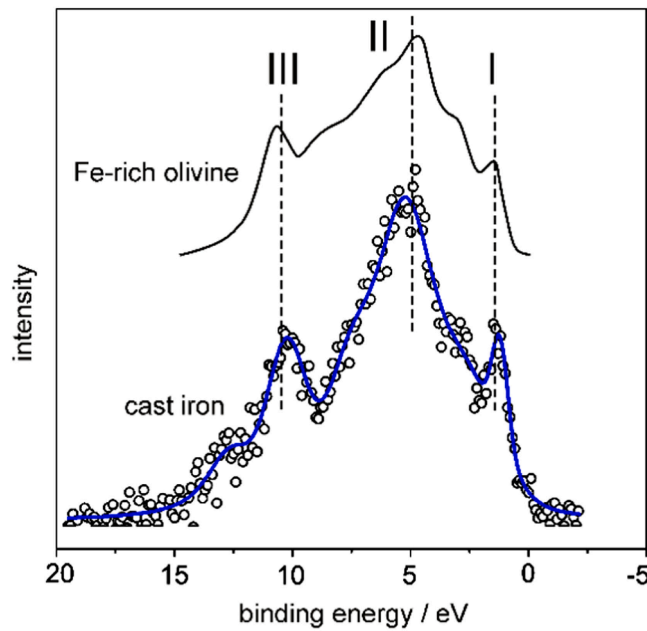


Fig. 12. XPS valence band spectra for the cast-iron surface compared with spectra reported in the literature for iron-rich olivine (Ref. [48]).

Table 5

XPS-determined elemental composition (at %) at selected surface spots.

	C	O	Na	Mg	Al	Si	Cl	Ca	Fe
cast iron surface	31.4	47.0	0.3	0.5	2.0	7.5	1.4	–	10.0
interf. bentonite	10.7	55.9	0.5	0.9	4.2	13.8	1.7	0.6	11.8
bentonite surface	6.2	63.6	1.4	0.9	6.0	19.6	0.4	0.2	1.8
gray-layer on cast iron	17.2	55.3	0.5	0.6	2.4	11.0	1.0	4.2	8.0
cast iron surface w/o rad	27.5	47.0	3.9	1.0	3.3	6.2	2.4	–	6.3

water reduction becomes the main cathodic reaction. The measured corrosion current was $0.815 \mu\text{A cm}^{-2}$, remaining constant for the first 100 days. Weight loss calculations yield 7.48×10^{-3} eq of Fe dissolved from cast iron during the whole experiment. This corresponds to an increase of the mean corrosion current by a factor of 20.6. The enhanced iron dissolution implies a higher partial cathodic current. The increase of the amount of dissolved oxygen by water radiolysis may be a cause. On analyzing the radiolysis of neutral chloride solutions, Morco [55] provided temporal changes of the O_2 and H_2 concentrations which can be described by $r [\text{mol l}^{-1}] = 4.7 \times 10^{-6} [1 - \exp(-4 \times 10^{-5} t [\text{d}])]$ and $r [\text{mol l}^{-1}] = 2.25 \times 10^{-6} [1 - \exp(-5 \times 10^{-5} t [\text{d}])]$, respectively, in a $3 \text{ mol l}^{-1} \text{Cl}^-$ solution under 5 Gy h^{-1} . Because the generation rate depends by a factor one on the chloride concentration and the dose rate, this can be corrected by a factor of 2.6 for 0.3 mol l^{-1} of chloride and 130 Gy h^{-1} . Thus, 1.76×10^{-4} eq of H_2 and 1.36×10^{-4} eq of O_2 can be generated by radiolysis after 220 days. The generation of H_2O_2 , on the other hand, does not seem to be significant during the first 200 days and can be disregarded.

The reduction of NO_3^- generated by radiolysis of the 60 cm^{-3} of air enclosed over the slurry may constitutes another source for the enhanced iron dissolution. Resorting to studies of Morco et al. [56], the formation of 3.76×10^{-6} eq of $\text{HNO}_3(\text{g})$ after 220 days can be estimated for 130 Gy h^{-1} . It is evident that the comparative smaller amounts of equivalents of radiolytic oxidating agents cannot compensate the observed dissolved iron. A very plausible explanation, however, may be given in terms of the electrocatalytic activation of graphite nodules for the water reduction. There is strong evidence, that the treatment of graphite with γ -radiation deoxygenates the surface by elimination of the oxygen-containing surface groups and sp^3 -like defects that enhance its catalytic and electrical properties [57–62]. A modification of the surface

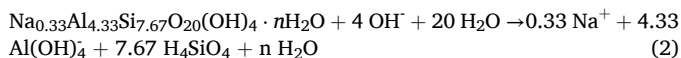
chemistry is indicated by the vanishing of the core level XPS C 1s line corresponding to this type of surface groups after irradiation (see Fig. 10b). This would clarify the formation of $\text{Ca}(\text{OH})_2$ patches at the high localized alkalization at the graphite nodules and $\text{Fe}(\text{OH})_2$ at the matrix surface driven by the driven anodic dissolution of the cast iron matrix. Roughly estimated, graphite nodules cover 10 % of the total surface. Thus, as cathodic spots, they should support a current density of $25 \mu\text{A cm}^{-2}$ considering top and side surfaces of samples. Thus, according to the semi-infinite diffusion equation [63]:

$$[\text{OH}^-]_s(\tau) = [\text{OH}^-]_s(0) + 2j\tau^{1/2} / (F\pi^{1/2}D_{\text{OH}}^{1/2}) \quad (1)$$

where $[\text{OH}^-]_s [\text{mol dm}^{-3}]$ is the surface hydroxyl concentration, $j [\text{A cm}^{-2}]$, is the current density, and F is the Faraday constant. Thus, a diffusion coefficient $D_{\text{OH}} < 8 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$ is necessary for attaining a $\text{pH} > 12.2$ towards the end of the experiment. Diffusion coefficients of this order of magnitude suggest the formation of a diffusion barrier. For instance, calcium hydro-silicates formed by alkaline dissolution of smectite in the presence of $\text{Ca}(\text{OH})_2$ [64].

A large amount of iron and sodium is retained in the bentonite after irradiation as indicated by the X-ray fluorescence results in Table 3. Because no indication of structure changes of smectite are detected (see Fig. 3), it is supposed that $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ -ions coordinates with the silicate sheets by $-\text{OH}$ groups. This in turn brings about a charge imbalance which is compensated by sodium. According to Lantenais et al. [65], dissolved Fe^{2+} -ions may adsorb at the tetrahedral silicate sheets of the smectite inducing the reduction of octahedral structural iron. More Fe^{2+} migrates into the interlayer to compensate for the charge imbalance, dragging more hydration water. Hydration numbers of 3.5 and 9.2 are reported for Na^+ and Fe^{2+} respectively [66]. This, in turn, conducts to a delamination of smectite, as indicated by the vanishing of the

(001)-reflection in the XRD-measurements [65] (Fig. 3). The development of a strong alkaline milieu favors the solubility of smectite according to [67]:



The release of silicic acid is expected to react with the formed $\text{Fe}(\text{OH})_2$ to form silicates. Jullien et al. [68] and Lanson et al. [69] has found the formation of a gel-like phase from clay dissolution acting as a medium for the nucleation of iron silicates as berthierine $((\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_3(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4)$ and cronstedtite $(\text{Fe}_2^{2+}\text{Fe}^{3+}(\text{SiFe}^{3+})\text{O}_5(\text{OH})_4)$. These products are in line with the XPS results, supporting the deposition of iron silicates on the corroding surface.

5. Conclusions

The scheme in Fig. 13 summarizes the mechanism of the enhanced corrosion assisted by γ -irradiation as derived from the experimental evidence. Radiation enhances the catalytic activity of graphite nodules for water reduction, driving a higher anodic dissolution of the cast iron matrix. This leads to a precipitation of $\text{Fe}(\text{OH})_2$ on the matrix, whereas the strong water reduction increases the pH around the cathodic active graphite nodules. The alkalization, in turn, assists the dissolution of contacting smectite generating soluble silicate species that react with $\text{Fe}(\text{OH})_2$ to generate iron gel-like hydro-silicates. These latter reduce the diffusion of OH^- , thus favoring further increase of pH and the precipitation of $\text{Ca}(\text{OH})_2$. Soluble iron species and $\text{Fe}(\text{OH})_2$ diffuses into the overlying bentonite causing its delamination. Dissolved oxygen, on the other hand diffuses towards the metal surface through the bentonite favoring the precipitation of formation of ferric oxides by reaction with the counter diffusing ferrous products.

This demonstrative experiment points out the alteration of the electrocatalytic activity of the corroding surface as the preponderant cause for the corrosion enhancement observed in cast iron. Therefore, a better knowledge of the electrochemical behavior of the galvanic local elements and the related diffusive processes are necessary to be understood for predicting the long-term corrosion behavior under radiation.

Author declaration

We wish to draw the attention of the Editor to the following facts which may be considered as potential conflicts of interest and to significant financial contributions to this work.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

We understand that the Corresponding Author is the sole contact for the Editorial process (including Editorial Manager and direct communications with the office). He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs. We confirm that we have provided a current, correct email address which is accessible by the Corresponding Author.

CRediT authorship contribution statement

A.G. Muñoz: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **D. Schild:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Data curation. **S. Kaufhold:** Writing – review & editing, Investigation, Formal analysis, Data curation. **D. Dobrev:** Writing – review & editing, Investigation, Data curation. **V.F. Viebranz:** Writing – review & editing, Investigation, Data curation. **Th. Hassel:** Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Andres Gabriel Munoz reports financial support was provided by German Federal Ministry for the Environment, Climate Action, Nature Conservation and Nuclear Safety. Thomas Hassel, Stephan Kaufhold,

1. $\text{N}_2, \text{H}_2\text{O}(\text{v}) \xrightarrow{\gamma} \text{HNO}_3$
2. $\text{H}_2\text{O}(\text{l}) \xrightarrow{\gamma} \text{O}_2, \text{H}_2, \text{H}^+$
3. $2\gamma\text{-FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O}$
4. $2\text{Fe}(\text{OH})_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\gamma\text{-FeOOH} + \text{H}_2\text{O}$
5. $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$
6. $\text{H}_4\text{SiO}_4 + \text{Fe}(\text{OH})_2 + \text{Ca}^{2+} \rightarrow \text{hydro-silicate}$
7. $\text{smectite} + x\text{OH}^- \rightarrow \text{Al}(\text{OH})_4^- + \text{H}_4\text{SiO}_4$
8. $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
9. $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$
10. $\text{H}_2\text{O} + \text{H}_{\text{ads}} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$

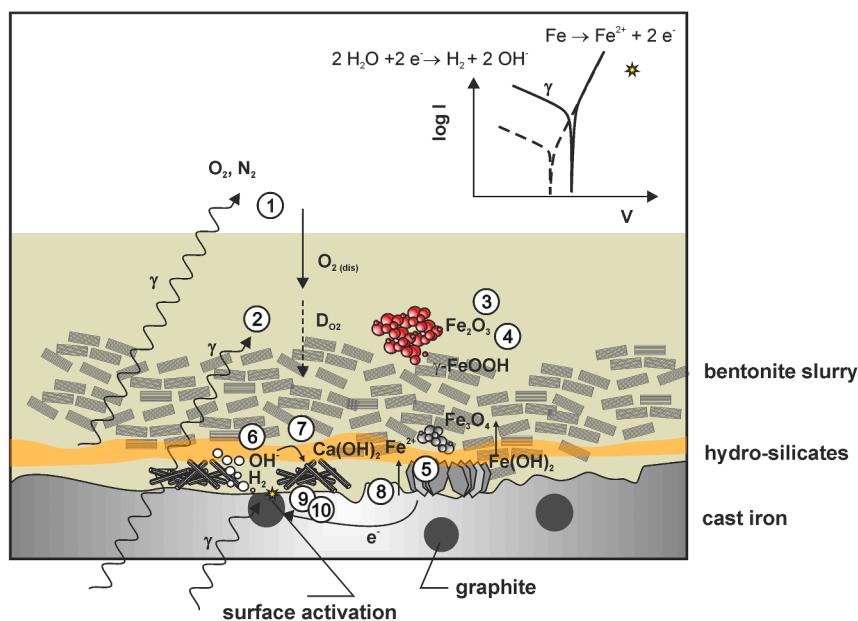


Fig. 13. Schematic showing the interfacial processes occurring at the interface of spheroidal graphite cast iron in contact with a slurry of Wyoming bentonite under γ -irradiation.

Vincent Viebranz reports financial support was provided by German Federal Ministry for the Environment, Clima Action, Nature Conservation and Nuclear Safety. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection (BMUV), under project contract 02 E 11981 and The European Union's Horizon 2020, Agreement 847593, EURAD Programme are expressly acknowledged for the funding of this study.

Appendix

Table A1

Table A1

Compilation of corrosion rates of carbon steels in near neutral and alkaline geological-related milieus with and without γ -irradiation.

material	milieu	Duration days	dose rate Gy h ⁻¹	corr. rate μm y ⁻¹	ref.
forged carbon steel 0.2 % C, 0.08 % Si, 0.6 % Mn, 0.038 % S, 0.01 % P	bentonite / granitic water aerated / 90 °C	473	0	7.7	[7]
	granite / granitic water aerated / 90 °C	169	0	19.2	
	granitic water deaerated / 90 °C	208	0	< 0.1	
	see water deaerated / 90 °C	218	1 × 10 ³	3	
		401	3	11 ^a	
		289	35	50 ^a	
		127	1.0–1.5 × 10 ³	129 ^a	
cold drawn carbon steel wires 0.21 % C, 0.22 % Si, 0.70 % Mn, 0.017 % P, 0.017 % S	Allard water deaerated / 30 °C	12	0	2.1	[8]
	Allard water deaerated / 50 °C	324	0	<0.1 ^b	
	bentonite equilibrated water deaerated / 50 °C	28	11	8.2	
		318	11	<0.4 ^b	
		11	300	5.4	
		361	300	2.6	
		2	0	3.5	
		147	0	<0.1	
		9	300	8.5	
		139	300	<0.3	
		2	0	3.5	
		146	0	<0.1	
		4	300	18	
		260	300	<0.3	
	Carbon steel wires (AISI 1017) 0.17 % C, 0.06 % Si, 0.81 % Mn, 0.01 % P, 0.03 % S, 0.038 % Cr	deaerated cementitious pore water / 80 °C	561	0	
mmol dm ⁻³ / 2.4 SO ₄ ²⁻ , 510 OH ⁻ , 370 K ⁺ , 140 Na ⁺ , pH 13.4 + 100 mg dm ⁻³ Cl ⁻		624	25	2.18	
		22	25	16 ^c	
X65 low carbon steel 0.065 % C, 0.14 % Si, 1.58 % Mn, 0.008 % P, 0.0016 % S, 0.042 % Al, 0.22 % Cr, 0.01 % Ni, 0.02 % Cu, 0.05 % V, 0.015 % Ti, 0.063 % Nb, 0.0025 % Ca	aerated Gaomiaozi Ca-bentonite with 17 wt- % Beishan groundwater / 90 °C	120 161 ^d	0 2.98 × 10 ³	23.7 31.5	[10]

^a steady state values after a linear increase with time

^b steady state values after an exponential decay with time

^c steady state attained after 125 days

^d first 120 days without radiation + 41 days with radiation

Data availability

Data will be made available on request.

References

- [1] H. Spilker, R. Hüggenberg, Description of the German concept of final storage cask, Int. J. Radioac. Mater. Transp. 2 (1991) 67–75, <https://doi.org/10.1179/rmt.1991.2.1-3.67>.
- [2] T. Hassel, A. Köhler, Ö.S. Kurt, Das ENCON-Behälterkonzept: generische Behältermodelle zur Einlagerung radioaktiver Reststoffe für den interdisziplinären Optionsvergleich, ENTRIA-Arbeitsbericht-16, Institut für Werkstoffe, Leibniz-Universität, Hannover, Hannover, Germany, 2019, pp. 2367–3532.
- [3] N. Sandberg, P. Korzhavyi, Theoretical study of irradiation induced hardening and embrittlement in spent nuclear fuel holders, relevant for the Swedish long-term storage, Technical Report SKB R-09-15, Swedish Nuclear Fuel and Waste Management Co, Stockholm, 2009. ISSN 1402-3091.
- [4] P. Sahiluoma, Y. Yagodzinskyy, A. Forsström, H. Hänninen, S. Bossuyt, Hydrogen embrittlement of nodular cast iron, Mater. Corros. 72 (2021) 245–254, <https://doi.org/10.1002/maco.202011682>.
- [5] A. Didot, E. Hermisa, D. Férona, J. Chêneb, D. Crusset, Stress corrosion cracking in the context of deep geological nuclear disposal – investigations on P235 and P265 steels, Corros. Eng. Sci. Technol. 52 (2017) 131–135, <https://doi.org/10.1080/1478422X.2017.1320156>.
- [6] S. Sunder, Calculation of radiation dose rates in a water layer in contact with used CANDU UO₂ fuel, Nucl. Technol. 122 (1998) 211–221, <https://doi.org/10.13182/NT98-A2863>.
- [7] G.P. Marsh, K.J. Taylor, An assessment of carbon steel containers for radioactive waste disposal, Corros. Sci. 28 (1988) 289–320, [https://doi.org/10.1016/0010-938X\(88\)90111-4](https://doi.org/10.1016/0010-938X(88)90111-4).
- [8] N.R. Smart, A.P. Rance, L.O. Werme, The effect of radiation on the anaerobic corrosion of steel, J. Nucl. Mater. 379 (2008) 97–104, <https://doi.org/10.1016/j.jnucmat.2008.06.007>.
- [9] R.J. Winsley, N.R. Smart, A.P. Rance, P.A.H. Fennell, B. Reddy, B. Kursten, Further studies on the effect of irradiation on the corrosion of carbon steel in alkaline media, Corros. Eng. Sci. Technol. 46 (2011) 111–116, <https://doi.org/10.1179/1743278210Y.0000000010>.

- [10] C. Liu, J. Wang, Z. Zhang, E.-H. Han, Studies on corrosion behaviour of low carbon steel canister with and without γ -irradiation in China's HLW disposal repository, *Corr. Eng. Sci. Technol.* 52 (2017) 136–140, <https://doi.org/10.1080/1478422X.2017.1348762>.
- [11] X. Cheng, S. Hu, W. Song, X. Xiong, Improvement in corrosion resistance of a nodular cast iron surface modified by plasma beam treatment, *Appl. Surf. Sci.* 286 (2013) 334–343, <https://doi.org/10.1016/j.apsusc.2013.09.083>.
- [12] I. Marić, M. Gotic, G. Stefanić, A. Pustak, T. Jurkin, γ -irradiation generated ferrous ions affect the formation of magnetite and ferroxhyte, *Rad. Phys. Chem.* 170 (2020) 108648, <https://doi.org/10.1016/j.radphyschem.2019.108648>.
- [13] M. Gotic, T. Jurkin, S. Musić, From iron(III) precursor to magnetite and vice versa, *Mater. Res. Bull.* 44 (2009) 2014–2021, <https://doi.org/10.1016/j.materresbull.2009.06.002>.
- [14] M.L. Schlegel, F. Martin, M. Fenart, C. Blanc, J. Varlet, E. Foy, D. Prêt, N. Trcera, Corrosion at the carbon steel-clay compact interface at 90 °C: insight into short- and long-term corrosion aspects, *Corros. Sci.* 152 (2019) 31–44, <https://doi.org/10.1016/j.corsci.2019.01.027>.
- [15] M. Lee, J. Jang, J.S. Kim, Radiation effect on the corrosion of disposal canister materials, *Nucl. Eng. Technol.* 56 (2024) 941–948, <https://doi.org/10.1016/j.net.2023.11.015>.
- [16] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}$) in aqueous-solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886, <https://doi.org/10.1063/1.555805>.
- [17] S. Sunder, H. Christensen, Gamma radiolysis of water solutions relevant to the nuclear fuel waste management program, *Nucl. Technol.* 104 (1993) 403–417, <https://doi.org/10.13182/NT93-A34900>.
- [18] M. Holmboe, M. Jonsson, S. Wold, Influence of γ -radiation on the reactivity of montmorillonite towards H_2O_2 , *Rad. Phys. Chem.* 81 (2012) 190–194, <https://doi.org/10.1016/j.radphyschem.2011.10.009>.
- [19] J. Vandenborre, F. Crumière, G. Blain, R. Esshehi, B. Humbert, M. Fattahi, Alpha localized radiolysis and corrosion mechanisms at the iron/water interface: role of molecular species, *J. Nucl. Mater.* 433 (2013) 124–131, <https://doi.org/10.1016/j.jnucmat.2012.09.034>.
- [20] F.J. Pearson, D. Arcos, A. Bath, J.Y. Boisson, A.M. Fernández, H.E. Gäbler, E. Gaucher, A. Gautschi, L. Griffault, P. Hernán, H.N. Waber, Mont terri project-geochemistry of water in the Opalinus clay formation at the Mont Terri rock laboratory, *Rep. Fed. Off. Water Geol. (FOWG), Geol. Ser. No. 5, Bern-Ittigen* (2003). ISBN 3-906723-59-3.
- [21] B. Bartonić, M. Đurđić, R. Pejša, V. Plaček, P. Vomačka, S. Vlček, F. Zahálka, PANOZA – gamma irradiator for simulation of harsh environment areas of nuclear power plants, *Nucl. Inst. Meth. Phys. Res. B* 236 (2005) 323–328, <https://doi.org/10.1016/j.nimb.2005.03.270>.
- [22] S. Kaufhold, R. Dohrmann, Detachment of colloidal particles from bentonites in water, *Appl. Clay. Sci.* 39 (2008) 50–59, <https://doi.org/10.1016/j.clay.2007.04.008>.
- [23] M.P. Seah, I.S. Gilmore, G. Beamson, XPS: binding energy calibration of electron spectrometers 5 – Re-evaluation of the reference energies, *Surf. Interface Anal.* 26 (1998) 642–649, [https://doi.org/10.1002/\(SICI\)1096-9918\(199808\)26:9<642::AID-SIA408>3.0.CO;2-3](https://doi.org/10.1002/(SICI)1096-9918(199808)26:9<642::AID-SIA408>3.0.CO;2-3).
- [24] G. Greczynski, L. Hultman, Reliable determination of chemical state in x-ray photoelectron spectroscopy based on sample-work-function referencing to adventitious carbon: resolving the myth of apparent constant binding energy of the C1s peak, *Appl. Surf. Sci.* 451 (2018) 99–103, <https://doi.org/10.1016/j.apsusc.2018.04.226>.
- [25] R. Hesse, M. Weiß, R. Szargan, R. Streubel, R. Denecke, Improved peak-fit procedure for XPS measurements of inhomogeneous samples—development of the advanced Tougaard background method, *J. Electron. Spectrosc. Relat. Phenom.* 205 (2015) 29–51, <https://doi.org/10.1016/j.elspec.2015.06.013>.
- [26] ASTM G1 03 (Reapproved 2011) Standard Practice for preparing, cleaning, and evaluating corrosion test specimens, ASTM International, West Conshohocken, PA 19428-2959. United States. <https://doi.org/10.1520/G0001-03R17E01>.
- [27] N. Smart (ed.), ConCorD Synthesis Report. Deliverable D15.14 of the HORIZON 2020 project EURAD (2024). EC Grant agreement no: 847593. pp.108. <https://www.mineralienatlas.de/>.
- [28] S. Kaufhold, M. Hein, R. Dohrmann, K. Ufer, Quantification of the mineralogical composition of clays using FTIR spectroscopy, *J. Vibr. Spec.* 59 (2012) 29–39, <https://doi.org/10.1016/j.vibspec.2011.12.012>.
- [29] J.I. Drever, The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter-membrane peep technique, *Am. Mineral.* 58 (1973) 553–554 (Print) ISSN: 0003-004X.
- [30] S. Kaufhold, R. Dohrmann, K. Ufer, J. Gröger-Trampe, F. Kober, R. Schneeberger, C. Weber, HotBENT experiment on quality control of bentonites used for granular bentonite material backfilling and block production, *Clay. Mineral.* (2024), <https://doi.org/10.1180/clm.2024.25>.
- [31] Y.G. Shin, D. Guo, N.A. Payne, B.K. Rector, K.G. O'Donnell, G. Whitaker, J. M. Joseph, J.C. Wren, Periodic aggregation patterns of oxide particles on corroding metals: chemical waves due to solution feedback processes, *Phys. Chem. Chem. Phys.* 25 (2023) 2110–2130, <https://doi.org/10.1039/D2CP03470K>.
- [32] K. Rajalakshmi, S. Muthusamy, P. Kannan, K.-B. Lee, J. Xie, Y. Xu, Sprouts-like Fe (OH)₂ hetero-nanostructures assembly on selenium layered nickel foam (NiFe-Se) as an efficient and durable catalyst for electro-oxidation of urea, *Int. J. Hydrogen. Energy* 47 (2022) 31420–31434, <https://doi.org/10.1016/j.ijhydene.2022.07.003>.
- [33] X. Ma, H. Wu, L. Chang, J. Wang, Y. Wang, S. Cui, The influence of calcium hydroxide crystal morphology on the desulfurization of cement kiln flue gas, *J. Mater. Sci.* 57 (2022) 18287–18297, <https://doi.org/10.1007/s10853-022-07801-9>.
- [34] A. Matamoros-Veloza, R. Barker, S. Vargas, A. Neville, Iron calcium carbonate instability: structural modification of siderite corrosion films, *ACS. Appl. Mater. Interfaces.* 12 (2020) 49237–49244, <https://doi.org/10.1021/acsami.0c14513>.
- [35] W.D. Keller, R.C. Reynolds, A. Inoue, Morphology of clay minerals in the smectite-to-illite conversion series by scanning electron microscopy, *Clays. Clay. Mineral.* 34 (1986) 187–197, <https://doi.org/10.1346/CCMN.1986.0340209>.
- [36] F. Bergaya, G. Lagaly, in F. Bergaya, B.K.G. Theng and G. Lagaly (Eds) *Handbook of Clay Science*, vol.1, ch.1, pp.1–18, Elsevier, Amsterdam 2006. ISBN-10: 0080441831.
- [37] C. Elmi, S. Guggenheim, R. Gieré, Surface crystal chemistry of phyllosilicates using X-ray photoelectron spectroscopy: a review, *Clays. Clay. Mineral.* 64 (2016) 537–551, <https://doi.org/10.1346/CCMN.2016.064033>.
- [38] C. Elmi, M.F. Brigatti, S. Guggenheim, L. Pasquali, M. Montecchi, S. Nannarone, Crystal chemistry and surface configurations of two polythionite-1M crystals, *Am. Mineral.* 99 (2014) 2049–2059, <https://doi.org/10.2138/am-2014-4908>.
- [39] C.D. Wagner, D.E. Passoja, H.F. Hillery, T.G. Kinisky, H.A. Six, W.T. Jansen, J. A. Taylor, Auger and photoelectron line energy relationships in aluminium-oxygen and silicon-oxygen compounds, *J. Vac. Sci. Technol.* 21 (1982) 933–944, <https://doi.org/10.1116/1.571870>.
- [40] A. Mekki, D. Holland, C.F. McConville, M. Salim, An XPS study of iron sodium silicate glass surfaces, *J. Non-Cryst. Solids* 208 (1996) 267–276, [https://doi.org/10.1016/S0022-3093\(96\)00523-6](https://doi.org/10.1016/S0022-3093(96)00523-6).
- [41] M. Fondell, M. Gorgoi, M. Boman, A. Lindblad, *J. Electron. Spectrosc. Relat. Phenom.* 224 (2018) 23–26, <https://doi.org/10.1016/j.elspec.2017.09.008>.
- [42] H. Seyama, M. Soma, Fe 2p spectra of silicate minerals, *J. Electron. Spectrosc. Relat. Phenom.* 42 (1987) 97–101, [https://doi.org/10.1016/0368-2048\(87\)85010-7](https://doi.org/10.1016/0368-2048(87)85010-7).
- [43] C.J. Powell, A. Jablonski, NIST standard reference database 82. NIST electron effective-attenuation-length database, Version 1.3, NIST, 2011, Maryland.
- [44] A.P. Grosvenor, B.A. Kobe, M.C. Biesinger, N.S. McIntyre, Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds, *Surf. Interface Anal.* 36 (2004) 1564–1574, <https://doi.org/10.1002/sia.1984>.
- [45] NIST X-ray photoelectron spectroscopy database, NIST Standard Reference Database Number 20, 20099, National Institute of Standards and Technology, Gaithersburg MD, 2000, <https://doi.org/10.18434/T4T88K>.
- [46] X. Chen, X. Wang, D. Fang, A review on C1s XPS-spectra for some kinds of carbon materials, *Fuller. Nanotub. Carbon Nanostruct.* 28 (2020) 1048–1058, <https://doi.org/10.1080/1536383X.2020.1794851>.
- [47] V.P. Zakaznova-Herzog, H.W. Nesbitt, G.M. Bancroft, J.S. Tse, X. Gao, W. Skinner, High-resolution valence-band XPS spectra of the nonconductors quartz and olivine, *Phys. Rev. B* 72 (2005) 205113, <https://doi.org/10.1103/PhysRevB.72.205113>.
- [48] W.M. Haynes (Ed.), *CRC Handbook of Chemistry and Physics*, 97th ed., CRC Press, Boca Raton, 2016. ISBN-13: 978-1-4987-5429-3.
- [49] N.S. McIntyre, D.G. Zetaruk, X-ray photoelectron spectroscopic studies of iron oxides, *Anal. Chem.* 49 (1977) 1521–1529, <https://doi.org/10.1021/ac50019a016>.
- [50] G.C. Allen, M.T. Curtis, A.J. Hooper, P.M. Tucker, X-ray photoelectron spectroscopy of iron-oxygen systems, *J. Chem. Soc., Dalton Trans.* 14 (1974) 1525–1530, <https://doi.org/10.1039/DT9740001525>.
- [51] K. Daub, X. Zhang, J.J. Noël, J.C. Wren, Gamma radiation-induced carbon steel corrosion, *ECS. Trans.* 33 (2011) 15–24, <https://doi.org/10.1149/1.3557748>.
- [52] K. Daub, X. Zhang, J.J. Noël, J.C. Wren, Gamma-radiation-induced corrosion of carbon steel in neutral and mildly basic water at 150 °C, *Corros. Sci.* 53 (2011) 11–16, <https://doi.org/10.1016/j.corsci.2010.09.048>.
- [53] A.G. Muñoz, D. Schild, Corrosion processes at the GGG40 steel-bentonite interface, *SanD 2* (2023) 45–46, <https://doi.org/10.5194/sand-2-45-2023>.
- [54] R.P. Morco, Gamma-radiolysis kinetics and its role in the overall dynamics of materials degradation. <https://ir.lib.uwo.ca/etd/7248>, 2020.
- [55] R.P. Morco, J.M. Joseph, D.S. Hall, C. Medri, D.W. Shoesmith, J.C. Wren, Modeling of radiolytic production of HNO₃ relevant to corrosion of a used fuel container in deep geologic repository environments, *Corros. Eng. Sci. Technol.* 52 (2017) 141–147.
- [56] H. Karimi-Maleh, I.A. Kariper, C. Karaman, S. Korkmaz, O. Karaman, Direct utilization of radioactive irradiated graphite as a high-energy supercapacitor a promising electrode material, *Fuel* 325 (2022) 124843, <https://doi.org/10.1016/j.fuel.2022.124843>.
- [57] B. Li, Y. Feng, K. Ding, G. Qian, X. Zhang, J. Zhang, The effect of gamma ray irradiation on the structure of graphite and multi-walled carbon nanotubes, *Carbon. N. Y.* 60 (2013) 186–192, <https://doi.org/10.1016/j.carbon.2013.04.012>.
- [58] A.T. Nguyen, Y. Lee, P.Q.H. Nguyen, P. Dera, S.-H. Yoon, W. Lee, Enhancing the electrical properties of graphite nanoflake through gamma-ray irradiation, *Sci. Rep.* 14 (2022) 14824, <https://doi.org/10.1038/s41598-022-19232-2>.
- [59] S. Huang, C. Yue, K. Uvdal, Z. Hu, Recent advances in irradiation-mediated synthesis and tailoring of inorganic nanomaterials for photo-/electrocatalysis, *Nanoscale Adv.* 7 (2025) 384–418, <https://doi.org/10.1039/d4na00806e>.
- [60] H. Radinger, A. Ghamlouche, H. Ehrenberg, F. Scheiba, Origin of the catalytic activity at graphite electrodes in vanadium flow batteries, *J. Mater. Chem. A* 9 (2021) 18280, <https://doi.org/10.1039/d1ta04316a>.
- [61] F. Cataldo, Some implications of the radiation-treatment of graphite and carbon black, *Fullerene Sci. Technol.* 9 (2001) 409–424, <https://doi.org/10.1081/FST-100104503>.
- [62] A.J. Bard, L.R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, John Wiley & Sons, New York, 1980.

- [64] H. Maraghechi, F. Rajabipour, C.G. Pantano, W.D. Burgos, Effect of calcium on dissolution and precipitation reactions of amorphous silica at high alkalinity, *Cement Concrete Res.* 87 (2016) 1–13, <https://doi.org/10.1016/j.cemconres.2016.05.004>.
- [65] S. Lantenois, B. Lanson, F. Muller, A. Bauer, M. Jullien, A. Plançon, Experimental study of smectite interaction with metal Fe at low temperature: 1. Smectite destabilization, *Clays. Clay. Mineral.* 53 (2005) 597–612, <https://doi.org/10.1346/CCMN.2005.0530606>.
- [66] Y. Marcus, Thermodynamics of solvation of ions. Part 5. Gibbs free energy of hydration at 298.15 K, *J. Chem. Soc. Faraday Trans.* 87 (1991) 2995–2999, <https://doi.org/10.1039/FT9918702995>.
- [67] Ch.4 J. Cama, J. Ganor, Dissolution kinetics of clay minerals, in: Ch. Tournassat, C. I. Steefel, I.C. Bourg, F. Bergaya (Eds.), *Natural and Engineered Clay Barriers, Developments in Clay Science, Natural and Engineered Clay Barriers, Developments in Clay Science*, 6, Elsevier, Amsterdam, 2015, pp. 101–103. ISBN-13: 978-0081000274.
- [68] M. Jullien, J. Raynal, E. Kohler, O. Bildstein, Physicochemical reactivity in clay-rich materials: tools for safety assessment, *Oil Gas Sci. Technol.* 60 (2005) 107–120, <https://doi.org/10.2516/OGST:2005007>.
- [69] B. Lanson, S. Lantenois, P. van Aken, A. Bauer, A. Plançon, Experimental investigation of smectite interaction with metal iron at 80 °C: structural characterization of newly formed fe-rich phyllosilicates, *Am. Mineral.* 97 (2012) 864–871, <https://doi.org/10.2138/am.2012.4062>.

