

TEM Investigations of Green Rust ($\text{GR}_{\text{Na},\text{SO}_4}$) Interacted with Neptunyl (NpO_2^+)

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Green rust (GR) belongs to a family of Fe(II)-Fe(III) layered double hydroxides with anions (e.g. SO_4^{2-}), cations (e.g. Na^+), and water structurally arranged in the interlayers and it crystallizes in thin hexagonal platelets (diameter of typically some 10 nm up to a few micrometers) [1]. It may form in anoxic groundwater and is likely to evolve during corrosion of steel canisters in a nuclear-waste repository. Hence, owing to its redox properties, it is a potential candidate for attenuating the migration of radionuclides in the environment.

^{237}Np is a long-lived actinide (half life of 2.14×10^6 years) present in nuclear waste. When water has access to the waste Np may exist as pentavalent species like the mobile neptunyl-ion Np(V)O_2^+ . B.C. Christiansen and coworkers investigated the interaction of NpO_2^+ with green rust sodium sulphate ($\text{GR}_{\text{Na},\text{SO}_4}$, $\text{NaFe(II)}_6\text{Fe(III)}_3(\text{OH})_{18}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) [2]. They showed that Np(V) is immobilized via reduction and formation of less soluble Np(IV)-species. However, details of the immobilization mechanisms are not yet clear. Notably, there is still a lack of direct evidence concerning the exact location where Np(IV) is immobilized on the GR particles. Hence, the aim of the present work is the localization of Np and transmission electron microscopy (TEM) investigations at high spatial resolution are well suited for this task [3].

Two types of specimens were analyzed: $\text{GR}_{\text{Na},\text{SO}_4}$ alone (synthesis described in [1]) and after reaction with Np(V) (Np-GR). The reaction was performed by adding a NpO_2^+ solution to GR slurry in a proportion corresponding to a Np(V):Fe(II) molar ratio of approximately 7:100. Specimens were prepared for TEM analyses by depositing single droplets of GR suspensions on copper TEM grids covered by holey carbon films. The analyses were conducted using a 200 keV FEI Tecnai G² F20 X-Twin transmission electron microscope located in a radioactive control area at the *Institute for Materials Research (IMF II)* of the *Karlsruhe Institute of Technology*. The microscope allows high-resolution TEM (HRTEM), can be operated in the scanning TEM (STEM) mode, and is equipped with a high-angle annular dark-field (HAADF) detector, and an energy-dispersive x-ray (EDX) spectrometer.

A dark rim (~ 3-5 nm wide) was observed at the edge of the Np-GR platelets by TEM imaging (Fig. 1a), whereas such a rim was not visible for GR alone (Fig. 1b). The rim appeared bright by means of STEM-HAADF (Fig. 2a), suggesting the presence of an element with high atomic number Z. To correlate the high HAADF signal with Np, an EDX linescan was performed across the rim with 16 spectra recorded on a 32 nm path (cf. line in Fig. 2a) by means of an electron probe of about 1-2 nm in diameter (Fig. 2). Two representative spectra are shown in Fig. 2c. A strong Np signal dominates the spectrum recorded at the rim (spectrum 1) whereas Np cannot be detected inside the GR particle (spectrum 2). Hence, Np is clearly localized at the edge of the GR platelets, suggesting that NpO_2^+ did not enter the GR interlayer.

First HRTEM observations indicated that the rim at the edge of the Np-GR platelets is composed of nanocrystallites. Further investigations are in progress to identify the corresponding Np-phase.

References

- [1] B.C. Christiansen et al., *Geochim. Cosmochim. Acta* 73 (2009) 3592.
- [2] B.C. Christiansen et al., *Geochim. Cosmochim. Acta* in preparation.
- [3] E.J. O'Loughlin et al., *Environ. Sci. Technol.* 37 (2003) 721.

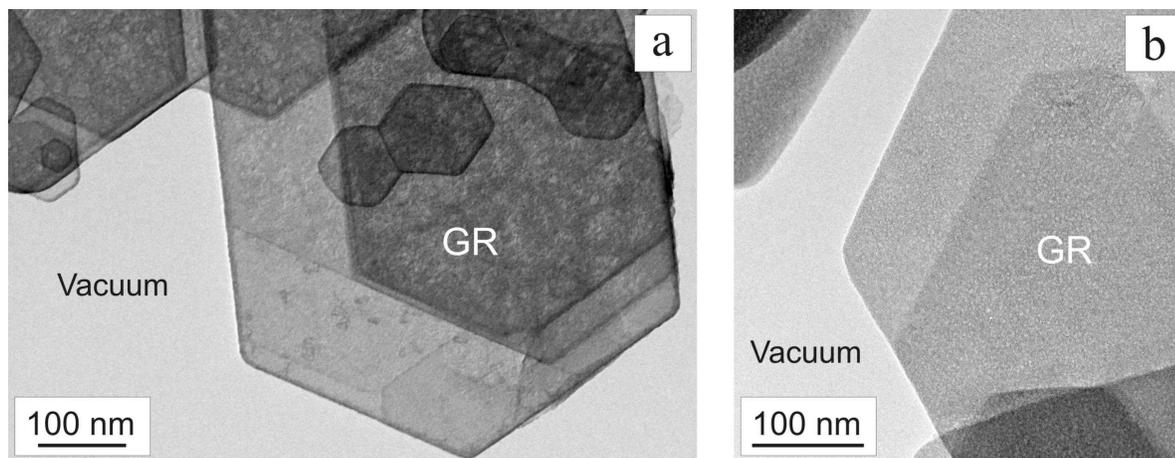


FIG. 1. TEM images of Np-GR (a) and GR alone (b).

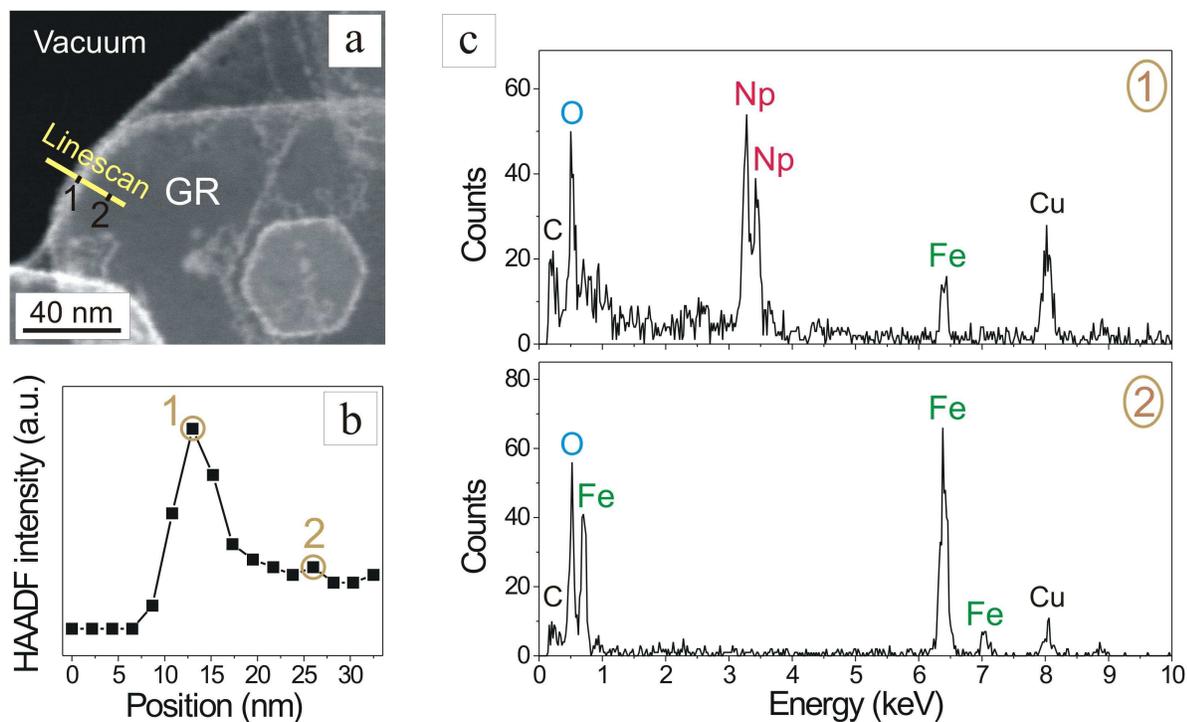


FIG. 2. EDX linescan across the edge of Np-GR. a) STEM-HAADF image, the line marks the path along which spectra were recorded; b) HAADF signal as a function of the position of the electron probe during the linescan; c) representative EDX spectra. The Cu signal results from the TEM grid.