The effect of gamma radiation on corrosion of copper under anoxic conditions in pure water has been studied experimentally. Copper samples submerged in water were exposed to dose rates of 0.37 or 0.77 kGy/h. Reference samples were used throughout. The copper surfaces have been examined using the techniques of SEM-EDS, IRAS, CR spectroscopy and AFM. Dissolution of copper was measured using ICP-OES. The results show that irradiated samples are more corroded than corresponding reference samples. This is also reflected by the increased concentration of copper in water after irradiation. Surface examination also reveals local corrosion features.

Copper is the material considered for encapsulation of spent nuclear fuel in future deep geological repositories for high level nuclear waste. The main motivation for this is that copper is a corrosion resistant metal under the conditions prevailing in anoxic deep granitic groundwaters. Corrosion of copper under these conditions has been debated quite vigorously during the past decade.

Water in contact with the canisters will undergo radiolysis as a consequence of gamma radiation penetrating the canister walls. During radiolysis oxidizing and reducing species are formed, such as \( \text{H}_2\text{O}_2 \), \( \cdot \text{OH}, \text{H}_2, \text{H}^- \) and \( e^-_{aq} \). The radiation chemical yields for these species in pure gamma irradiated water in the pH-range 4–9 are \( \text{G}_{\cdot \text{OH}} = 0.28 \), \( \text{G}_{\text{H}} = 0.062 \) and \( \text{G}_{e^-_{aq}} = 0.047 \text{ mol/J} \). The standard reduction potential vs. SHE of some of these species, e.g. \( \text{E}^\circ (\cdot \text{OH}/\text{H}_2\text{O}) = 2.59 \text{ V} \) and \( \text{E}^\circ (\text{H}_2\text{O}_2/2 \text{ H}_2\text{O}) = 1.77 \text{ V} \), are significantly higher than the standard reduction potentials for copper, \( \text{E}^\circ (\text{Cu}^+/\text{Cu}(s)) = 0.520 \text{ V} \) or \( \text{E}^\circ (\text{Cu}^{2+}/\text{Cu}(s)) = 0.341 \text{ V} \), from which follows that radiation induced species are capable of initiating corrosion of copper.

Despite the fact that the copper canisters will be exposed to ionizing radiation from the spent fuel, very few studies on radiation induced corrosion of copper have been reported. Electrochemical studies of the influence of gamma radiation on copper have been performed in saline solutions with different outcome. In two cases with dose rates of 0.014–0.063 kGy/h (1 Gy = 1 J/kg) and total doses of 1.4 kGy, in temperatures of 30 and 150 °C under anoxic conditions no corrosion effects could be seen. In the third case, with a dose rate of 0.8 kGy/h and a total dose of 13.6 kGy, in room temperature under anodic conditions, a significantly higher corrosion rate was observed in the presence of gamma irradiation than without. Studies of gamma radiation induced corrosion of copper in moist air have also been performed. With dose rates of 0.1–0.7 kGy/h and total doses of 107–510 kGy, relative humidity of 40–100% and temperatures of 90–150 °C, both cuprite (\( \text{Cu}_2\text{O} \)) and tenorite (\( \text{CuO} \)) could be detected on the copper surfaces. Radiation experiments on copper under anodic conditions in water at 42 °C and groundwater at 95 °C with dose rates of 1–6.5 kGy/h and total doses of 720–5 016 kGy resulted in pitting corrosion and corrosion rates 30 times higher than in similar experiments without radiation. It is interesting to note that in the two studies where no corrosion could be detected both dose rates and total doses are lower than in the studies where corrosion was detected. The two former studies were also performed under anoxic conditions and high ionic strength unlike the latter studies. Hence, it is not meaningful to compare these two types of studies.

Given these somewhat contradictory results we decided to study the effect of gamma radiation on copper corrosion under anoxic conditions in pure water at room temperature. The aim of this paper is to perform a phenomenological investigation rather than a study of copper corrosion under the conditions expected in a deep geological repository.

Experimental

Copper cubes (99.992% Cu, major impurities are Ag and P) of the sizes 10 × 10 × 10 mm were polished on all sides (SiC abrasive papers, 800 grit) followed by polishing with 3 μm polycrystalline diamond paste (Stuers) on one side. All polishing steps were made in 99.5% ethanol. Finally, the copper pieces were placed in 95% ethanol in an ultra-sonic bath for five minutes and then dried under \( N_2 \) in a glove box.

The samples were prepared in a \( N_2 \) filled glove box and then sealed before they were placed in the gamma source. All experiments were performed in duplicates with two separate pieces of copper. A reference sample (not irradiated but otherwise treated the exact same way as the irradiated samples) was also included in every experiment.

The copper cubes were placed in 10 mL deaerated Millipore Milli-Q water in glass beakers. One copper cube was placed in each beaker with the polished side up. The pH was approximately 7 and the temperature 20 °C.

Gamma irradiation was performed for 168 hours using a MDS Nordion 1000 Elite Cs-137 gamma source with a dose rate of 0.10 or 0.21 Gy/s depending on the position of the sample. The dose rates were determined using Frické dosimetry.

Surface characterization of the polished sides was performed using four different analytical instruments:

1. A Digilab FTS 40 Pro infrared reflection absorption spectrometer (IRAS) with P-polarized light with an incident angle of 78° using 1024 scans with a resolution of 4 cm\(^{-1}\). As background sample the non-irradiated reference sample was used.

2. A Jeol JSM-6490LV scanning electron microscope (SEM) with a Jeol EX-230 energy dispersive X-ray spectrometer (EDS).

3. An Agilent 5500 atomic force microscope in static mode with a commercial cantilever (AFM). The surface height profile of the scanned area was then obtained using the line scan on the created AFM image.

4. The confocal Raman imaging was performed on a 40 × 40 μm area of the irradiated sample using a WITEC alpha 300 system Confocal Raman Microscope equipped with a 532 nm laser source and a 50 X Nikon objective.

Trace elemental analysis was performed on all solutions using inductively coupled plasma atomic emission spectroscopy (Thermo
Figure 1. Photography of an experimental set of copper cubes. The cube to the left in the photography is the non-irradiated reference sample. The cube in the middle has received a total dose of 62 kGy while the cube to the right has received a total dose of 129 kGy. The irradiated copper cubes are more corroded than their reference sample.

Scientific iCAP 6000 series ICP spectrometer (ICP-OES)). The analysis for copper was performed at the wavelengths of 221.8 and 224.7 nm.

Results and Discussion

Upon visual inspection of the copper samples, Fig. 1, it can be seen that the irradiated samples are more corroded, judging on color, than the corresponding reference. Dark orange colored layers cover the irradiated sample surfaces together with tiny, black markings. The copper samples exposed to the highest dose, 129 kGy, are more corroded than the samples exposed to the lowest dose, 62 kGy.

Analysis of the IRAS spectra of the irradiated samples reveal only one detectable species, Cu$_2$O, with a peak centered at 648 cm$^{-1}$.

Surface examination of the irradiated copper samples by SEM shows crystalline oxide layers and locally occurring and frequently circular shaped corrosion features of different size, form and depth. These features are spread out all over the whole surface and smaller corrosion features can be seen outside the circular ones, Fig. 2b. Based on SEM-EDS analysis the oxygen content in the surface region of these circular shaped corrosion features is higher than in the surrounding surface.

The appearance of the circular centers varies between the different samples; from a smooth, perfect circular surface to a rough crater. No difference in size or depth can be observed between the two absorbed doses.

Analysis of the reference sample shows only a homogenous surface with polishing markings but no sign of corrosion features, Fig. 2a.

Fig. 3 displays the AFM results obtained for irradiated copper. The center part, z, is surrounded by a smooth and almost flat ring, y. As also seen in Fig. 3, the smooth ring around the center of the corrosion feature has similar height as the outer surrounding surface, x, while the center part is approximately 800 nm deeper. Calculations show that the root mean values of the topography for the central circular feature, the surrounding ring and the parts outside the ring are 216 nm, 35 nm and 58 nm, respectively.

In Fig. 4 confocal Raman spectra of a local corrosion feature are shown. The intensity for cuprite is higher in the center, x', and in the area outside of the corrosion feature, z', than in the smooth circular ring in between, y'.

The appearance of the locally occurring corrosion features might be caused by anodic reactions that take place in the circular centers of the corrosion features and cathodic reactions that take place in the surrounding ring shaped areas. To fully understand the mechanisms...
Figure 4. Confocal Raman image and spectra of a local corrosion feature. The intensities of cuprite is higher in the central area, \( z' \), and the outside area, \( x' \), than in the area of the ring in between, \( y' \).

behind the enhanced corrosion rates in presence of gamma radiation, more experimental data is necessary.

The amount of dissolved copper in the anoxic water was analyzed using ICP-OES. Significantly more copper is dissolved when copper is irradiated. With a dose of 62 kGy the concentration of copper in the water solution is 53 \( \mu \)M. With a dose of 129 kGy the concentration is higher, 152 \( \mu \)M, as compared to 5 \( \mu \)M for the reference sample.

Conclusions

Gamma radiation causes significant corrosion of metallic copper in anoxic aqueous solution. In all experiments the reference sample is much less corroded than the irradiated sample.

The corrosion effect appears both as corrosion products, mainly cuprite, and as local circular cavities on the copper surface. Neither size nor distribution of the corrosion features seem to be dependent on the dose received.

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References