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Radiolysis of water in the vicinity of passive surfaces

S. Moreau [a], M. Fenart [b], J.P. Renault [a,*]

[a] *Laboratoire de Radiolyse, UMR3299 CEA-CNRS SIS2M, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*
[b] *CEA/DEN/DPC/LECA, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*

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ABSTRACT

Porous metals were used to describe the water radiolysis in the vicinity of metal surfaces. The hydroxyl radical production under gamma irradiation was measured by benzoate scavenging in water confined in a 200 nm porous Ni base alloy or in Stainless steel. The presence of the metallic surfaces changed drastically the HO° production level and lifetime. The solvated electron production was measured via glycylglycine scavenging for Stainless steel and was found to be significantly smaller than hydroxyl production. These observations imply that interfacial radiolysis may deeply impact the corrosion behavior of the SS and Ni based alloys.

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1. Introduction

The long term behavior of metallic components exposed to radiation field, in reactors and in storage conditions, is controlled by the impact of radiolysis on corrosion. Indeed, upon irradiation, a water/metal interface is exposed to both reductive and oxidative species that can be formed in aqueous solutions (Eq. (1)) and strongly affect the corrosion kinetics of materials in contact with water [1–3].

$$H_2O \xrightarrow[\text{radiation}]{\text{Ionizing}} OH^\cdot, H^\cdot, e_{aq}^-, H_3O^+, HO_2^\cdot, H_2O_2, H_2 \qquad (1)$$
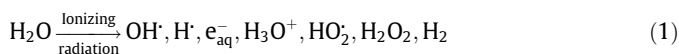
Radiolytic events occur on a short time scale, because most radiolytic species are very reactive. However, these fast events can have an effect for hours, days and even years when a system containing water is submitted to a continuous irradiation field [4,5].

The first well known effect is the accumulation of molecular species such as H_2O_2 and H_2 by recombination of radiolytic radicals [6]. The second one is the presence of a background concentration of reactive species like the hydroxyl radical HO° and the solvated electron e_{aq}^- that are constantly created and destroyed. However, the impact of these species on corrosion is much less understood because it is much more local [7–9]. Previous studies on water radiolysis in porous materials have shown that water/solid interfaces acted both as overproduction and as scavenging sites for radiolytic species [10–12].

In the present contribution, we studied the fate of radiolytic radicals produced by gamma radiolysis in the vicinity of metals of industrial interest like Stainless steel (SS316L) and nickel based alloy (Hastelloy). More specifically, we used porous monoliths of these metals, which present high specific surfaces, to follow the production and surface reaction of HO° and solvated electrons e_{aq}^- via radical scavenging methods.

2. Experimental part

2.1. Chemicals

All chemical used for this study are Sigma Aldrich products (99%), without any further purification, prepared using ultrapure Millipore Milli-Q water with a resistivity of 18.2 MΩ cm and less than 10 ppb organic carbon.

2.2. Porous metal samples

The samples were purchased from Applied porous technologies, Onsala, Sweden. The alloy porosity is created by the interstice between metallic grains. The pore network appears therefore as slits rather than cylindrical pores (Fig. 1). The nominal pore diameter is 200 nm.

The metal compositions given by the producer are, in mass:

- Ni 59.49% ; Mo 16.23% ; Cr 14.75% ; Fe 4.95% ; W 3.62% ; Si 0.67% ; Mn 0.21% ; Co 0.04% ; C 0.02% ; P 0.009% ; S 0.006% ; V 0.003% for Hastelloy.
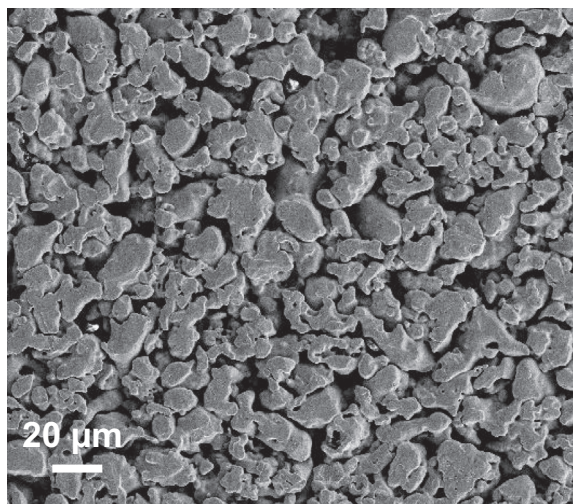
Fig. 1. MEB picture of the porous metals used in the study (here Hastelloy).

- Fe 69.27%; Cr 16.87%; Ni 10.80%; Mo 2.29%; Si 0.66%; Mn 0.05%; C 0.029%; P 0.018%; S 0.007% for SS316L.

The specific pore volumes are

- 44 μl/g for Hasteloy.
- 52 μl/g for SS316L.

2.3. Irradiation and spectrofluorometry

Irradiations were conducted using a ^{137}Cs based GammaCell 3000 Elan irradiator with a dose rate of 5.5 Gy/min as determined using the Fricke dosimeter. Radiolytic yields, unless otherwise stated, were calculated with respect to this dose and to the energy directly deposited in water.

2.4. Hydroxyl radical quantifications

Hydroxyl radical quantifications were conducted through HO° scavenging by benzoate to form fluorescent hydroxybenzoate (Eq. (2)).

Metallic sponges were impregnated with sodium benzoate solutions in deionized water up to 90% pore saturation. Scavenger solutions were added on the top of the metallic monoliths and allowed to impregnate it. All experiments were conducted in aerated conditions. Samples were irradiated with various doses up to 660 Gy. The free solutions of benzoate used for impregnation were irradiated in the same conditions and used as reference to measure bulk water yields.

After irradiation, the products were extracted by adding an excess of water (twenty times the volume of solution initially introduced). After extraction, the supernatant liquid was analyzed by fluorescence spectroscopy for hydroxybenzoate quantification. Fluorescence measurements were taken at room temperature with excitation set at 300 nm and emission intensities measured at 420 nm using a Gemini XPS microplate reader. Under these excitation and extraction conditions, we could check that 2-hydroxybenzoate (2HB) was the only fluorescent product observed: 4HB fluoresces at lower wavelength whereas 3HB is only fluorescent when doubly deprotonated, at basic pH.

Systematic calibrations of the fluorescence intensity were performed by adding a variable amount of hydroxybenzoate (10^{-7}–10^{-3} M) to representative benzoate concentrations

(10^{-3}–1 M) The as prepared solutions were introduced in metallic sponges, extracted and analyzed as described above.

2.5. Solvated electron quantifications

Solvated electron production was quantified through e_{aq}^- scavenging by glycylglycine to form ammonium, the concentration of which was measured using an ion selective electrode (Eq. (6)).

Metallic sponges were impregnated with glycylglycine solutions in deionized water up to 90% pore saturation by adding solutions on top of the metallic monoliths. Samples containing glycylglycine where irradiated up to 25 kGy to achieve sufficient ammonium production. The free solutions glycylglycine used for impregnation were irradiated in the same conditions and used as reference to measure bulk water yields. All irradiations were conducted in anaerobic conditions.

After irradiation, the irradiation products were extracted by adding an excess of water. The quantifications of ammonium were conducted using an Orion 9512 ammonia selective electrode. The pH was raised at the end of the experiments using the appropriate ionic strength adjustor (ISA 951211) following Orion specifications. A calibration of the electrode was performed on a daily basis by adding known amounts of ammonium chloride (10^{-2}–10^{-6} M) to appropriate glycylglycine concentrations (from 10^{-3} to 1 M).

For accurate measurements, we checked whether all scavenging products produced upon irradiation had been extracted from the porous materials. Known concentration of ammonium chloride were inserted in the porous metals in the presence of various glycylglycine concentrations, and extracted following a protocol similar to the one used in irradiation experiments.

2.6. Dose calculations

An accurate dosimetry is a prerequisite to any radiolytic yield measurement. However, standard chemical dosimetry methods cannot be used in nanoporous media, as they all rely on known radiolytic yields that can be modified by confinement. An alternative method is to use Monte Carlo particle transport code like PENELOPE (Penetration and Energy Loss of Positrons and Electrons).

We used the Pencyl part of the PENELOPE code. The porous materials were represented as a stack of alternating water and material disks. Disks have a diameter of 1 cm and a total stack length of 100 μm.

Six types of stacks were defined, with the two different alloys and three different disk thicknesses (10 nm, 100 nm, 1 μm). Therefore, the average density of each system was independent from the elementary disk thickness. The electronic equilibrium at both entrance and exit sides of the material was obtained by adding a 2 mm thick disk of the studied alloy. We checked that a 2 mm thickness was sufficient to ensure the absorption of all secondary electron issued from the disk stacks. For each geometry, 1.5×10^7 particle tracks were simulated and the energy absorption cut-off was set to 100 eV. All interactions were explicitly calculated.

3. Results and discussion

3.1. Systematic hydroxyl radiolytic yields measurements

Even though primary radiolytic species have very limited lifetimes (few μs), they can be quantified by reaction with scavengers [13,14] to form stable products. We have introduced [11] in radiolysis the use of benzoic acid [15] to scavenge HO. radicals and produce fluorescent hydroxylated benzoates (HB, Eq. (2)) In our