Radiolysis of Water in the Presence of Metal Oxide Particles

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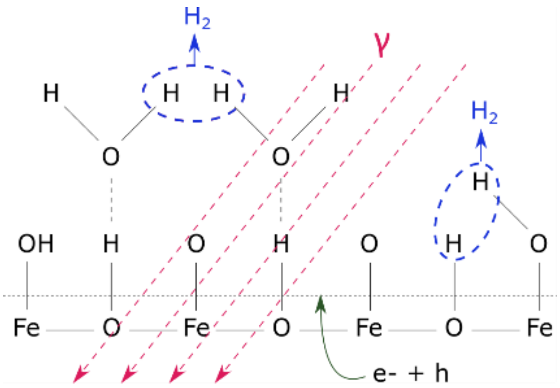
The rate of water decomposition under irradiation in the presence of metal oxides was studied by γ-irradiation followed by measurement of H_2 production, as well as by pulse radiolysis in order to understand the influence of the water/metal oxide interface which is not currently understood.

Keywords: radiolysis, interface, metal oxide, adsorbed water, γ-rays, pulse radiolysis.



Water radiolysis is a well-researched topic due to its applicability to the nuclear industry. However, the rate of water decomposition has been observed to change in the presence of metal oxide surfaces, a phenomenon which is not currently understood. One of the major products of water radiolysis is H_2 and increased rates of H_2 formation can be problematic for the vitrification and storage of radioactive waste, and for the control of water chemistry and material stability in nuclear water circuits. In this work, the production of H_2 at metal oxide surfaces and the nature of the surface chemistry under irradiation was investigated.

Typical surface oxides (Cr_2O_3, Fe_2O_3, Fe_3O_4, $NiFe_2O_4$, ZrO_2) found on plant structural materials were irradiated with γ-rays in pure water under a sealed argon atmosphere. The amount of H_2 generated due to water radiolysis was analysed by gas chromatography connected with thermoconductivity detector, and changes in the rate of H_2 production were observed for the oxides relative to pure water. In order to investigate the mechanisms that drive these changes, the behaviour of H_2O on the oxide surface was analysed by various complementary techniques (Thermal Gravimetric Analysis and Differential Thermal Analysis (TGA/DTA), Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT), X-ray Photoelectron Spectroscopy (XPS)) as it is postulated that adsorbed water is an important variable in H_2 generation under irradiation.

Another important variable to consider is the generation of hydrated electrons from the oxide as it is a precursor of H_2. It is believed to affect H_2 production due to electron/hole pair formation in the bulk oxide and donation of the electrons to solution across the metal/water boundary. It is possible that reaction of the solvated electrons with radiolysis products such as hydrogen radicals leads to changes in H_2 production rates. To investigate this, a pulse radiolysis study with metal oxide/water mixtures was also conducted to elucidate the underlying mechanisms involved in H_2 production.