



Milestone 1.2.12: The Fate Of Oxygen Radical Species In Corroded Aluminum Alloys Under Irradiation

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ABSTRACT

The U.S. Department of Energy tasked Idaho National Laboratory to evaluate the feasibility of extended dry storage of aluminum-clad spent nuclear fuel (ASNF) in helium-backfilled canisters. A significant research effort has been devoted to determining the amount of radiation-induced molecular hydrogen (H_2) generation from corrosion layers that would be present on the fuel assembly surfaces. However, limited attention has been directed to the oxygen radical species that are concurrently generated in these H_2 producing radiation environments. This report collates and summarizes the available experimental and computational studies on the fate of these reactive oxygen radicals during the irradiation of aluminum oxyhydroxide and hydroxide polymorphs typically formed on ASNF. Based on this review, it is determined that radiation-induced oxygen-centered radicals do not react to give molecular oxygen gas (O_2), but rather remain trapped in the aluminum corrosion layers in their original crystal lattice positions. Overall, O_2 generation will not be a concern for extended storage of ASNF in helium-backfilled canisters. That is, no O_2 contribution to pressurization of sealed dry storage systems or creation of a flammable atmosphere is anticipated.

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ACRONYMS

AA1100	Aluminum alloy 1100
AA6061	Aluminum alloy 6061
$\text{Al}\cdots\text{OH}^\bullet$	Aluminum surface bound hydroxyl radical
$\text{Al}\cdots\text{OH}^-$	Aluminum surface bound hydroxide group
$\text{Al}\cdots\text{OH}_2$	Aluminum surface bound water
$\text{Al}\cdots\text{O}^\bullet$	Aluminum surface bound oxygen atom
$\text{Al}\cdots\text{O}^{\bullet-}$	Aluminum surface bound oxygen radical anion
Al_2O_3	Aluminum oxide
$\text{Al}(\text{OH})_3$	Aluminum hydroxide
AlOOH	Aluminum oxyhydroxide
ASNf	Aluminum-clad spent nuclear fuel
ATR	Advanced Test Reactor
DFT	Density functional theory
DOE	Department of Energy
EPR	Electron paramagnetic resonance
EXAFS	Extended X-ray absorption fine structure
FTIR	Fourier transform infrared spectroscopy
h^+	Electron vacancy hole
H^\bullet	Hydrogen atom
H_2	Molecular hydrogen gas
H_2	Oxygen gas
He	Helium gas
He^{2+}	Helium ion
SNFWG	Spent Nuclear Fuel Working Group
XANES	X-ray absorption near edge structure
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

1. INTRODUCTION

The U.S. Department of Energy (DOE) is developing strategies for the long-term storage of approximately 14 metric tons of aluminum-clad spent nuclear fuel (ASNF), amounting to approximately 19,000 individual fuel assemblies in their current inventory.¹⁻² One option that has shown potential is extended dry storage of the fuel rods in sealed, helium (He)-backfilled DOE Standard Canisters.³⁻⁶ The goal is to store ASNF in these canisters for 50 years or more, pending ultimate disposition.

To ensure safe dry storage, the U.S. DOE Spent Nuclear Fuel Working Group (SNFWG) met in 2017 and identified five key knowledge gaps to be considered.⁵⁻⁶ One of these gaps centered on the determination of how the aluminum hydroxide and oxyhydroxide corrosion layers formed on corroded ASNF behave under irradiation, specifically their impact on the radiation-induced generation of molecular hydrogen (H₂) and oxygen (O₂) gases. Excessive production of these gaseous products in sealed dry storage could lead to canister integrity concerns due to over-pressurization, aluminum alloy embrittlement, and the potential formation of flammable and explosive gas mixtures.⁷⁻¹⁰

To date, this program's irradiation studies have predominantly focused on the generation of H₂ from the irradiation of hydrated corrosion layers on ASNF. The polymorphs of aluminum normally observed in the ASNF systems are hydroxides (bayerite, nordstrandite, and gibbsite = Al(OH)₃) and oxyhydroxide (boehmite = γ -AlOOH) mineral phases.¹¹ The crystallographic structures of these aluminum phases consist of sub-layers of aluminum surrounded by oxygen atoms, bridged via interlayer hydrogen bonding in different configurations. In this research program, radiolytic H₂ generation from corroded surrogate aluminum alloy (AA) coupons, specifically AA1100 and AA6061, has been measured under a variety of temperatures, backfill gas compositions, and relative humidities.^{2, 12-13} In these studies, the aluminum alloy coupons were corroded in high purity water (18.2 M Ω -cm) at ~95 °C for 30 days prior to cobalt-60 gamma irradiation. The corrosion procedure generated a heterogeneous corrosion layer, approximately 4–10 μ m thick, consisting of a mixture of bayerite, nordstrandite, and gibbsite with small amounts of boehmite.¹²⁻¹³ Additional studies were also completed using “non-native” aluminum corrosion plumes, created by corroding AA6061 plates for 350 days at ambient temperature to grow a thick bayerite layer representative of the deposits observed during inspection of Advanced Test Reactor (ATR) ASNF elements in the Idaho National Laboratory CPP-603 Fuel Handling Cave.¹⁴ The generation of H₂ from these corrosion layers was quantified as a function of the absorbed gamma dose up to tens of MGy.¹⁴ Note, in the presence of air, and thus O₂, radiation-induced H₂ generation was inhibited,¹² and thus there is little concern of canister over-pressurization for vented dry storage scenarios.

Several studies have explored H₂ generation from metal oxide materials like those found on corroded aluminum alloys, and a few key mechanisms have been proposed for radiolytic H₂ generation from these systems. Initially, an electron (e⁻) and hole (h⁺) pair is formed in the solid from radiation-induced ionization and excitation.¹⁵ Analogous to liquid water,¹⁶ the hole can take the form of a water cation (H₂O⁺) on the metal oxide surface. This cation can dissociatively recombine with the electron, forming an excited state (Al···H₂O*) that breaks apart to yield H₂ gas, and a surface bound oxygen atom (Al···O*):



Dissociative electron attachment to a water site on the aluminum hydroxide or oxyhydroxide surface may also occur, yielding hydrogen atoms (H*) and bound hydroxide anions (Al···OH⁻):



Alternatively, the absorption of radiation can directly break down the Al···OH⁻ groups connecting the aluminum hydroxide or oxyhydroxide crystal lattices via ionization:¹⁷⁻¹⁸



or homolytic dissociation mechanisms:¹⁷⁻¹⁸



It is thought that this dissociation is increased when a hole is formed at the site of an oxygen atom, as it weakens the O–H bond.¹⁹ The $\text{H}\cdot$ atoms that are generated can combine with themselves, or remove other hydrogen atoms from nearby surface-adsorbed water or hydroxyl groups to give H_2 and more oxygen-centered radical species:^{12-13, 15, 18, 20-21}



These mechanisms provide an explanation for what happens to the hydrogen component of an irradiated ASNF system, but the question not addressed here is: what is the fate of the oxygen-centered radical species in these systems? To this end, we report a thorough literature review describing the fate of the reactive oxygen radical species in irradiated aluminum oxyhydroxide and hydroxide materials analogous to those generated in ASNF systems.

2. RESULTS AND DISCUSSION

2.1 Gaseous Products

There have been several studies of cobalt-60 gamma or electron beam irradiation of boehmite, gibbsite, and bayerite granular powders with different particle sizes, atmospheres, and levels of moisture.²²⁻²⁶ The focus of these studies was primarily on measuring H_2 generation from these powders using gas chromatography. Some studies reported that their gas phase mass spectrometer was capable of detecting O_2 but made no mention of any measured O_2 yields.²² Other studies explicitly stated that no O_2 generation was detected in their systems.^{17, 27-28} Earlier work by this team also found no radiation-induced O_2 generated from corroded aluminum coupons.¹² Based on these results, and given the detection limits of the techniques employed, it seems unlikely that a significant amount of O_2 is generated upon the irradiation of the aluminum hydroxides and oxyhydroxides present in ASNF.

Recent published results have reported measured O_2 yields from electron beam irradiations of boehmite nanosheets under ultrahigh vacuum (5×10^{-10} Torr) conditions as a function of electron flux.²⁹ It is unclear whether the O_2 being driven off the aluminum oxyhydroxide surface is a property of the boehmite nanoplatelet films or the use of an ultrahigh vacuum. Given that the hyper-specific conditions employed here to yield O_2 are far from those envisioned for the extended dry storage of ASNF in He-backfilled canisters, these findings are not considered relevant.

2.2 Structural Characterization

Irradiated boehmite, gibbsite, and bayerite powders have been characterized directly using a variety of analytical techniques.^{24-25, 30} Vibrational spectroscopies, like Fourier transform infrared (FTIR) and Raman spectroscopy, are techniques used to identify materials based on their chemical bonding, as determined by exciting vibrational modes. X-ray diffraction (XRD) is a bulk characterization technique used to identify a phase based on its crystal structure. Electron beam irradiation studies do not report any changes in the aluminum oxyhydroxide or hydroxide structures observed by XRD and FTIR up to absorbed doses of 120 kGy.²⁴ Similarly, no structural changes were seen in these gamma irradiated powders using infrared or

Raman spectroscopy and XRD up to 2 MGy of absorbed dose.^{25, 30} This result is unsurprising given that gamma radiation-induced damage is primarily instigated by secondary electrons that do not have a lot of momentum to displace atoms. Interestingly, the associated vibrational spectra did appear to be slightly lower in intensity post-irradiation, perhaps indicating a loss of hydroxyl groups from the radiation-induced generation of H₂.³⁰ This interpretation is supported by differential scanning calorimetry measurements, in which the total mass loss decreased and the peaks shifted to higher temperature after irradiation, both indicating a loss of hydroxyl groups and surface-adsorbed waters.³⁰

Boehmite or gibbsite powders have also been irradiated with accelerated helium ions (He²⁺)—an alpha particle surrogate—because alpha particles deposit a larger amount of energy per unit volume traversed than gamma radiation, and can cause more significant defects through ballistic displacement.²⁵ Again, Raman spectroscopy and XRD observed no changes in the boehmite or gibbsite powder crystal structure up to 175 MGy of absorbed He²⁺ ion dose.²⁵

These irradiated gibbsite and boehmite powder surfaces were further examined using X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS).²⁵ XPS is used to determine changes in the electronic state of atoms on the surface post-irradiation.³¹ The XPS O 1s spectra of non-irradiated gibbsite exhibits peaks for surface absorbed water molecules (H–O–H) and hydroxyl groups within the crystal structure (Al–O–H).²⁵ Boehmite exhibits the same two peaks, plus one additional peak for oxygen within the crystal structure (Al–O–Al).²⁵ Both XPS spectra showed little change upon gamma irradiation.²⁵ However, after He²⁺ ion irradiation up to 175 MGy, the absorbed water peaks disappeared, indicating that the surface-adsorbed waters had been completely removed.²⁵ In the gibbsite powder sample, an additional peak for oxygen in the crystal structure (Al–O–Al) also appeared, indicating the sample had undergone structural changes at the surface to more closely resemble aluminum oxide (Al₂O₃) or boehmite.²⁵ It seems reasonable that such a change ought to occur if sufficient hydrogen content has left the system as H₂, and the aluminum and oxygen are left behind. This is also consistent with observations from a similar study on the irradiation of aluminum oxide in which the atomic composition and concentration was not changed by either gamma or He²⁺ ion irradiation.³¹ XANES was used to gain further insight on the local electronic structure of the species that remained in the gibbsite and boehmite powders post-irradiation. Following gamma irradiation, a shoulder was seen on one of the peaks in the XANES spectrum that was assigned to an oxygen-centered defect at the surface (Al···O[•]), an expected product from **Reactions 1–7**.²⁵ EXAFS, which is used to determine the oxidation state and nearest neighbors of an absorbing species, saw no structural changes in the gamma irradiated samples in agreement with the results from the other techniques.²⁵

Overall, despite the measurement of radiation-induced H₂ generation, no changes in the aluminum oxyhydroxide or hydroxide crystal structures were observed, which indicates that complementary oxygen species are not displaced. If oxygen was to be lost from the structure alongside the hydrogen, one might expect to see a collapse of the oxyhydroxide or hydroxide layers with sufficient absorbed dose. This is not the case.

2.3 Electron Paramagnetic Resonance

Electron paramagnetic resonance (EPR) is a technique used for the characterization of paramagnetic radiation-induced species, such as free radical species or paramagnetic anions/cations that are bound or trapped in the aluminum corrosion layers. There have been extensive EPR studies on aluminum oxides that report the presence of Al···O[•] upon irradiation,³² but fewer studies have focused on the hydroxide and oxyhydroxide groups typical of corroded aluminum. Boehmite, gibbsite, and bayerite powders have been explored using EPR on samples irradiated using gamma rays,^{23, 30} X-rays,³² and electron beams^{17, 24}. Pre-irradiation, no radicals are found in these powders.^{23, 30, 32} However, H[•] atoms and O-centered radicals (O[•] and O₃[•]) were observed in boehmite powders at room temperature after gamma irradiation, indicating that

a least some of each species were trapped in cavities in the aluminum oxyhydroxide.^{23, 30} Gamma irradiated gibbsite powders contained only oxygen anion radicals ($O^{\bullet-}$).³⁰ Astonishingly, the EPR spectral features of gamma irradiated gibbsite and boehmite powders remained when remeasured 8–10 months later, and after rehydrating the surface, clearly demonstrating that these oxygen-centered radical species are incredibly stable.³⁰ For X-ray-irradiated boehmite powders, no H^{\bullet} atom centers were seen at room temperature, but several types of paramagnetic O-centered radicals were seen.³² The authors state that some of these species are stabilized by the crystal lattice and form bridging $Al\cdots O^{\bullet-}\cdots Al$ groups³² consistent with the reaction mechanism proposed in the introduction (see **Reactions 1–7**). They also report a half-life for the observed paramagnetic centers of 9.43 ± 0.18 days at room temperature.³² If these radicals are seen to decay, this indicates they react in some manner to form additional products, but the study made no suggestion of what these products or reaction pathways might be. After electron beam irradiation, it was found that the yields of $O^{\bullet-}$ in bayerite and boehmite powders were stoichiometric with the measured amount of H_2 generated, further supporting the proposed reaction mechanism (**Reactions 1–7**). In this study, both $O^{\bullet-}$ and ozonide radical ($O_3^{\bullet-}$) species were found in addition to trapped H^{\bullet} atoms, and the results indicated that $O_3^{\bullet-}$ is a product yielded from the self-combination of $O^{\bullet-}$ anion radicals:^{17, 24}



An additional radical species was also observed in irradiated boehmite powders and assigned to trapped superoxide ($O_2^{\bullet-}$),²⁴ further supporting this mechanism. The EPR spectrum in the oxygen-centered radical region can be difficult to interpret as it also overlaps with the signal from trapped electrons. Perhaps this series of interconverting oxygen-centered radical reactions corresponds to the “ $O^{\bullet-}$ decay” seen for the X-ray-irradiated boehmite powder samples.

2.4 Computational Studies

Additional attempts to determine the reaction mechanisms of radiolytic species in aluminum oxyhydroxides have employed density functional theory (DFT) computational methods.^{26, 33-35} One such DFT calculation determined the energetics of the transport of $O^{\bullet-}$ anion radicals and H^{\bullet} atoms across the interface between boehmite and surface-adsorbed water molecules.³³ This work showed that the oxygen-centered radical species would remain trapped at the boehmite particle’s surface.³³ In fact, even when the simulations initiated the formation of $O^{\bullet-}$ anion radicals in the bulk water near a boehmite particle’s surface, the oxygen-centered radical quickly moved to the interface and was exchanged into the particle’s interfacial sites, where it was captured in a shallow trap.³³ Furthermore, calculations indicated that the energy barrier for oxygen-centered radical diffusion is high for both boehmite and gibbsite particles, such that the $O^{\bullet-}$ anion radical does not move easily through their crystal structures.³⁴

3. CONCLUSIONS

All the discussed experimental and computational results indicate that the oxygen-centered radical species arising from the irradiation of aluminum hydroxide and oxyhydroxide polymorphs, will remain in the crystal lattice structure during and after irradiation by gamma rays, electron beams, and/or He^{2+} ions/alpha particles. Despite the formation of several radiation-induced oxygen-centered radical species (e.g., $O^{\bullet-}$, $O_2^{\bullet-}$, and $O_3^{\bullet-}$) in the crystal structures of aluminum hydroxide and oxyhydroxide polymorphs,

these species do not typically combine to form O₂ in a manner analogous to radiolytic H₂ generation. This lack of gaseous O₂ generation is due to a combination of poor oxygen radical diffusion and efficient oxygen radical trapping sites on the crystal surface. The oxygen radical species produced are so tightly held in the hydroxide and oxyhydroxide lattices that they can still be observed several months after irradiation at room temperature. Consequently, reported observations can be taken together to provide additional insights for the continued improvement of predictive computer models of these systems. Overall, it is clear that O₂ generation will not be a concern for the feasibility of extended storage of ASNF in He-backfilled canisters. Specifically, no O₂ contribution to pressurization of sealed dry storage systems or creation of a flammable atmosphere is anticipated.

4. ACKNOWLEDGMENTS

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