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# **A Theoretical Investigation of Radiolytic H<sub>2</sub> Generation from Solids**

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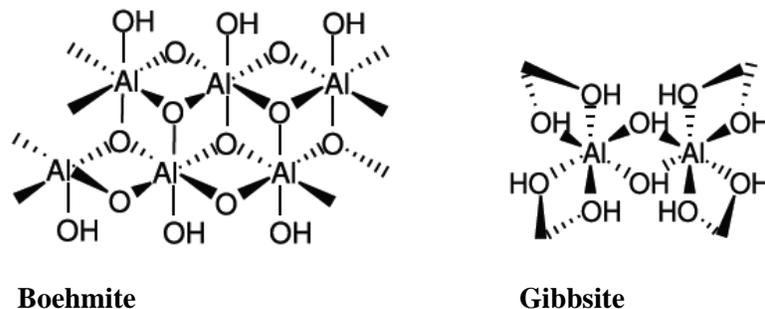
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## 1. EXECUTIVE SUMMARY/INTRODUCTION

Hydrogen generation from materials in nuclear materials storage is of critical interest due to the potential for pressurization and/or flammability issues. Studies have focused on aqueous systems or those with minor amounts of physisorbed water, since conventional knowledge identifies the radiolytic decomposition of water as the source of H<sub>2</sub> gas. Furthermore, the approach to characterize gas generation is typically strictly empirical, relying on determination of G-values from which production in systems is estimated. Interestingly, exploratory work at SRNL<sup>1</sup> on gamma exposure to fully-dried solids with chemically-bound water that are typical of those produced on aluminium-clad nuclear fuel in reactor and post-discharge storage has shown a profound production of hydrogen (as the sole gaseous species) from fully dried boehmite ( $\gamma$ -AlOOH or Al<sub>2</sub>O<sub>3</sub>•H<sub>2</sub>O) powders and no observable hydrogen from gibbsite ( $\gamma$ -Al(OH)<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>•3H<sub>2</sub>O) under gamma irradiation from cobalt-60. This observation is significant in that gibbsite is known to thermally decompose at 80°C whereas boehmite is stable to 400°C.

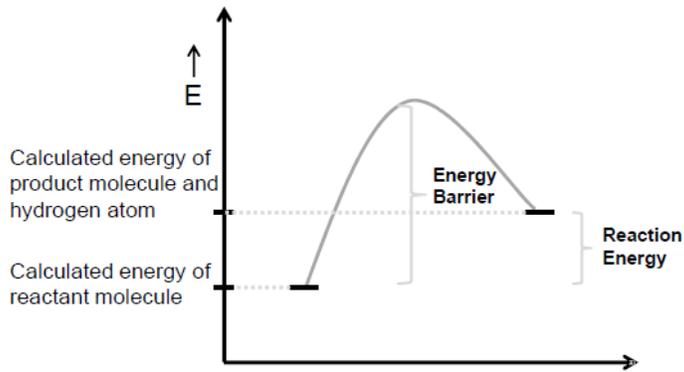
Radiation damage can have various effects on solids, including heating, bond breaking, and rearrangements in the bonding structure. For example, a molecule can be ionized resulting in the generation of free electrons which can, in turn, ionize another molecule. Alternately, reactive radical species such as •OH or cation species may be formed, which can go on to change bonding structures.



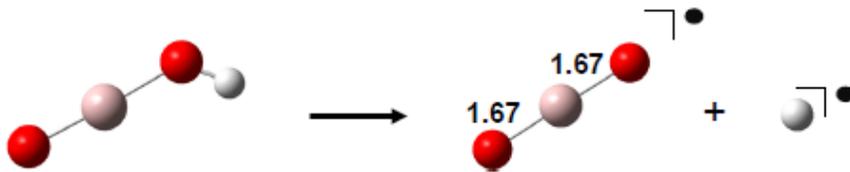
**Fig 1. Boehmite and gibbsite crystal bonding patterns, representing the crystalline orthorhombic dipyradmal and dioctahedral solids, respectively.**

## 1.1. GAS PHASE CALCULATIONS

Preliminary gas phase calculations of hydrogen atom removal from single-molecule models of boehmite and gibbsite were completed. Although these results have higher accuracy than solid phase modeling for energetic predictions, they should not be considered definitive, as structures vary from the overall bonding pattern in the extended crystalline solid. In qualitative agreement with the trend in experimental results, calculations indicate that removal of a hydrogen atom is energetically more favorable from boehmite than from gibbsite. The estimated energy barrier for H-atom loss from boehmite is +7.3 eV and for gibbsite +7.9 eV (Fig. 2). The overall reaction energy for H-loss from the boehmite gas phase model is +4.80 eV, compared to +4.98 eV for the gibbsite (Fig. 2) gas phase model. The increased stability for boehmite relative to gibbsite, at least in the gas phase model, may be explained by the ability of the remaining electron to be delocalized over two bonds, whereas in gibbsite it is more likely to be localized on one bond due to a high resonance barrier. These calculations were performed using density functional theory (DFT), specifically with the B3LYP functional which is composed of Becke's three-parameter hybrid exchange functional<sup>2</sup> in conjunction with Lee, Yang and Parr's correlation functional.<sup>3</sup> The correlation-consistent polarized-valence double zeta cc-pVDZ basis set of Dunning and co-workers<sup>4</sup> was also used, as implemented in the commercial software package Gaussian09©.<sup>5</sup>

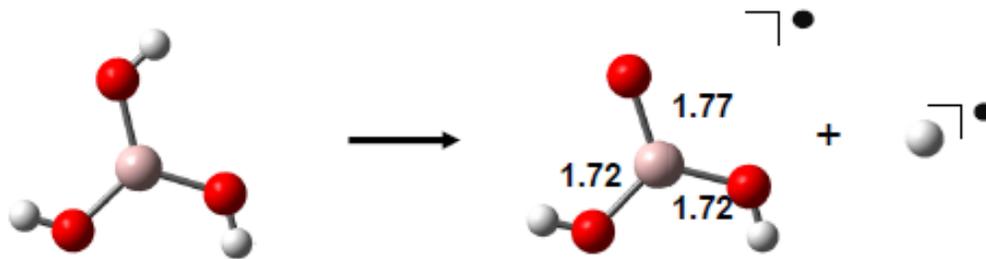


a) Concept of energy barrier and reaction energy for removal of hydrogen from a molecule or extended solid.



c) Boehmite

+7.29 eV reaction barrier  
+4.8 eV reaction energy



c) Gibbsite

+7.92 eV reaction barrier  
+4.98 eV reaction energy

Figure 2. Reaction Barrier diagram and gas phase reactions of removal from hydrogen from single-molecule models of boehmite and gibbsite. Bond lengths given in Angstroms.

## 1.2. SOLID PHASE CALCULATIONS

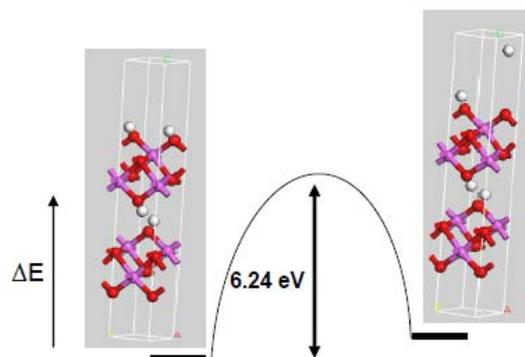
Solid phase crystal structures and energetics were computed using Materials Studio CASTEP.<sup>6</sup> The bulk crystal structure geometries have been optimized using DFT (Fig. 3). The generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof functional (PBE)<sup>7</sup> was used for all computational work at a fine quality integration grid.

The gibbsite structure crystallographic file was obtained from Pearson's Crystal Data,<sup>8</sup> optimized and cleaved on the (001) face. The boehmite structure used was also obtained from Pearson's Crystal Data and cleaved on the (010) face.<sup>9</sup> The boehmite structure is not agreed upon with the confidence as that of gibbsite, however it is generally only the hydrogen bonding pattern between layers that is not well-characterized,<sup>10</sup> and the possible variations are not expected to make a large difference in the relative energies of reactions on the surface.

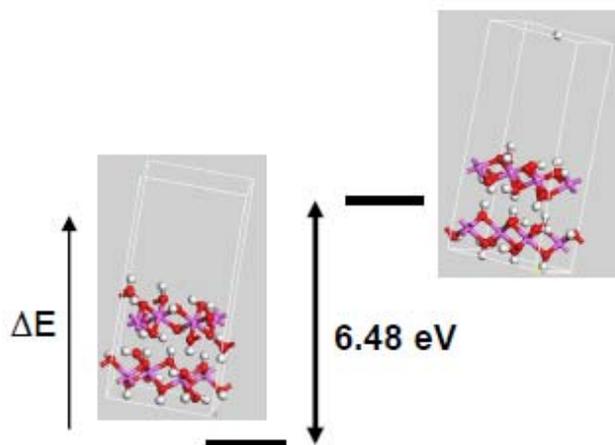
Two model reactions were considered in order to estimate the relative likelihood of hydrogen generation from the two aluminum hydroxide species. In the first, a hydrogen radical is released from the surface (Fig. 3). In the second, a hydrogen free radical is adsorbed onto the surface and an H<sub>2</sub> molecule is subsequently released (Fig. 4). For all reactions considered, the initial and final geometries are optimized to a local energetic minimum structure, followed by a linear synchronous transit (LST) computation to estimate the energy barrier of the reaction. For both types of model reactions, computations indicate hydrogen loss is more favorable for boehmite than for gibbsite. Modifying the model with a larger vacuum slab above the solid crystal may also help to yield accurate overall enthalpies of reaction (although barrier heights are expected to remain the same). That is, in modeling the energy for H-atom removal, the hydrogen is effectively pulled from the cleaved crystal surface, however, it may not reach a stable final energy as a detached species as it is attracted (back to) the crystal surface.

Also, changes to the surface were explored by calculating relaxation energies for the H-deleted boehmite and gibbsite surfaces. This estimates the energy gained by

rearrangement of the geometric structure of the surface after the removal of an H atom. In the cases considered, the boehmite surface showed 1.83 eV relaxation energy, whereas gibbsite was only stabilized by 0.06 eV. Further studies of bonding rearrangements on the two surfaces may be of interest to compare how the remaining radical is stabilized in the two species.

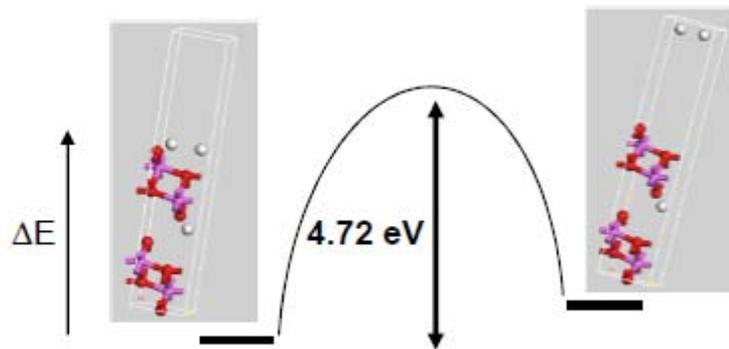


a) Estimated energy for H atom removal from boehmite surface.

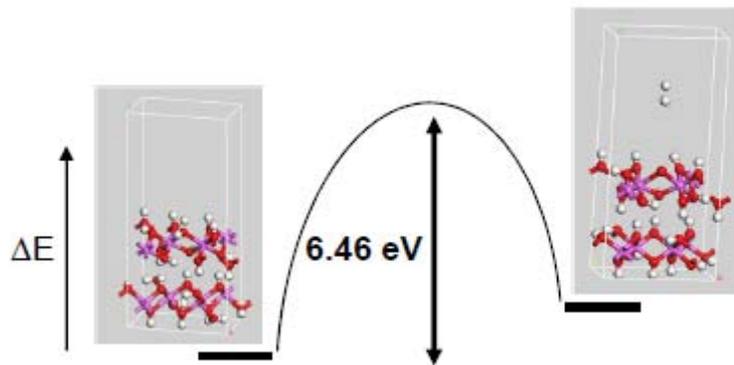


b) Estimated energy for H atom removal from gibbsite surface.

**Figure 3.** Energy barrier diagrams illustrating removal of one hydrogen atom from the boehmite and gibbsite surfaces. For the gibbsite case, no barrier was found in the LST computation.



a) Estimated energy for H<sub>2</sub> removal from boehmite surface.



b) Estimated energy for H<sub>2</sub> removal from gibbsite surface.

**Figure 4. Energy barrier diagrams illustrating removal of a hydrogen (H<sub>2</sub>) molecule from the boehmite and gibbsite surfaces - starting structures were optimized structures with an extra hydrogen atom adsorbed.**

## 2. CONCLUSIONS

An initial investigation of hydrogen bond energies was performed to provide insights to explain the experimental observations of hydrogen generation during gamma irradiation of hydrated oxides of aluminum. The results show qualitative agreement with the experimental findings, that hydrogen generation is more favorable from boehmite than gibbsite. Future extension of this investigation will be planned.

## 3. REFERENCES

1. Fisher, D. L.; Westbrook, M. L.; Sindelar, R. L., Test Results from Gamma Irradiation of Aluminum Oxyhydroxides. *Savannah River National Laboratory* January 2012, *SRNL-STI-2011-00602*.
2. Becke, A. D., DENSITY-FUNCTIONAL THERMOCHEMISTRY .3. THE ROLE OF EXACT EXCHANGE. *Journal of Chemical Physics* 1993, 98 (7), 5648-5652.
3. Lee, C. T.; Yang, W. T.; Parr, R. G., DEVELOPMENT OF THE COLLE-SALVETTI CORRELATION-ENERGY FORMULA INTO A FUNCTIONAL OF THE ELECTRON-DENSITY. *Physical Review B* 1988, 37 (2), 785-789.
4. Woon, D. E.; Dunning, T. H., GAUSSIAN-BASIS SETS FOR USE IN CORRELATED MOLECULAR CALCULATIONS .3. THE ATOMS ALUMINUM THROUGH ARGON. *Journal of Chemical Physics* 1993, 98 (2), 1358-1371.
5. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision A.02. 2009.

6. Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C., First principles methods using CASTEP. *Zeitschrift Fur Kristallographie* 2005, 220 (5-6), 567-570.
7. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Physical Review Letters* 1996, 77 (18), 3865-3868.
8. Saalfeld, H.; Wedde, M., REFINEMENT OF CRYSTAL-STRUCTURE OF GIBBSITE,  $Al(OH)_3$ . *Zeitschrift Fur Kristallographie* 1974, 139 (1-2), 129-135.
9. Bokhimi, X.; Toledo-Antonio, J. A.; Guzman-Castillo, M. L.; Hernandez-Beltran, F., Relationship between crystallite size and bond lengths in boehmite. *Journal of Solid State Chemistry* 2001, 159 (1), 32-40.
10. Demichelis, R.; Noel, Y.; Ugiengo, P.; Zicovich-Wilson, C. M.; Dovesi, R., Physico-Chemical Features of Aluminum Hydroxides As Modeled with the Hybrid B3LYP Functional and Localized Basis Functions. *Journal of Physical Chemistry C* 2011, 115 (27), 13107-13134.