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Test Results from Gamma Irradiation of Aluminum Oxyhydroxides

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

Hydrated metal oxides or oxyhydroxides boehmite and gibbsite that can form on spent aluminum-clad nuclear fuel assemblies during in-core and post-discharge wet storage were exposed as granular powders to gamma irradiation in a ^{60}Co irradiator in closed laboratory test vessels with air and with argon as separate cover gases. The results show that boehmite readily evolves hydrogen with exposure up to a dose of 1.8×10^8 rad, the maximum tested, in both a full-dried and moist condition of the powder, whereas only a very small measurable quantity of hydrogen was generated from the granular powder of gibbsite. Specific information on the test setup, sample characteristics, sample preparation, irradiation, and gas analysis are described.

1. INTRODUCTION

Corrosion on aluminium fuel in water-cooled nuclear reactors typically produces two (2) primary aluminum oxyhydroxides. They are boehmite ($Al_2O_3 \bullet H_2O$) and gibbsite ($Al_2O_3 \bullet 3H_2O$). An example of a corroded aluminum fuel assembly with both boehmite and gibbsite is shown in the photograph in Figure 1. Full removal of these corrosion products would be difficult, and therefore transitioning this fuel into dry storage containers requires knowledge of their characteristics and behavior under the conditions of storage.

In a dry storage system, the fuel surfaces, including the attached corrosion products, would be subject to an attendant gamma radiation field from the fuel itself and neighboring fuel in the storage system. This present work explores the response of these compounds to gamma irradiation. A ^{60}Co irradiator was used in this investigation to provide a high dose rate, high-energy gamma field to expose aluminum oxyhydroxides and measure radiolytic gas generation.

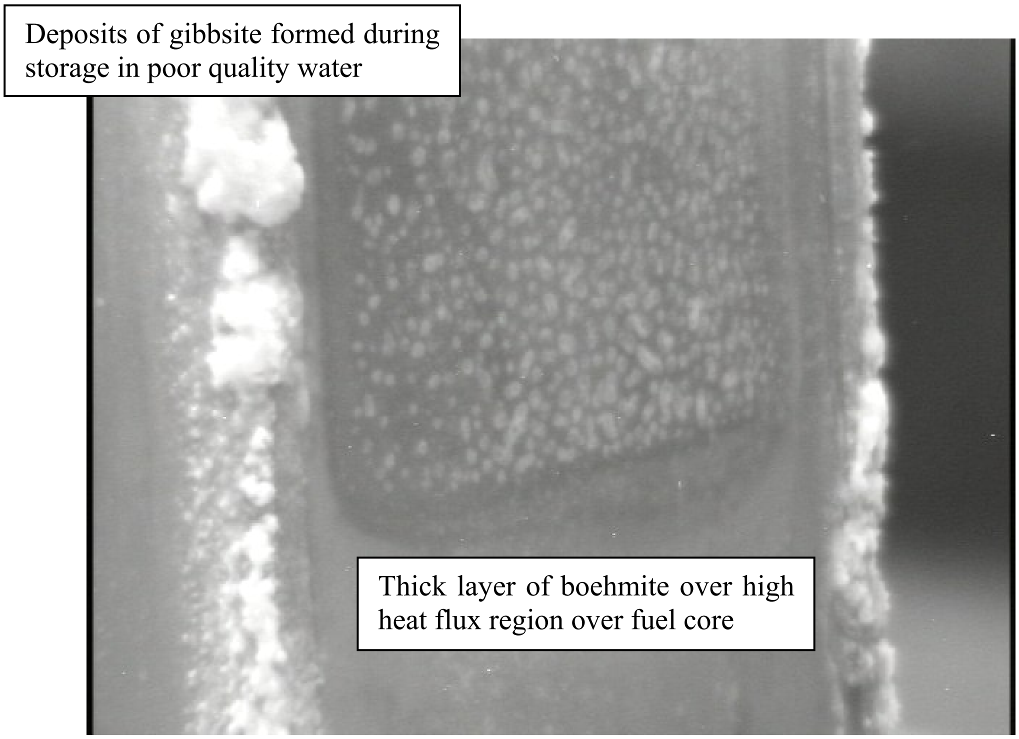

Figure 1 Aluminum-Clad Fuel Assembly Post-Discharge and in Basin Storage

2. EXPERIMENTAL SETUP

The investigation used granular powders of the oxyhydroxides both fully dried of free water, and with absorbed water. The parameters of the experimentation included the type of oxyhyrdroxide, the size of the oxyhydroxide powder, the presence or absence of moisture, air or inert (argon) cover gas, and radiation dose. Details of the investigation were recorded in a laboratory notebook [1].

The gibbsite and boehmite powders were procured from a U.S. chemical manufacturer in powdered form of nominal 100 μm maximum particle size. The powders were sieved at SRNL and batches were of the following size ranges for the second set of tests described below:

boehmite, 45-63 μm particles; 64-75 μm particles

gibbsite, 45-63 μm particles; 64-75 μm particles

The particle size distribution was quantified and X-ray diffraction was used to confirm the identity of the compounds.

Small quantities (~100 grams) from each batch of powders were placed in thin layers in trays for drying in an oven at 60ºC for 24 hours. This heating treatment was assumed to remove water which was not chemically bound to the oxides, leaving the compounds intact.

Initial irradiation tests used stainless steel Parr vessels fitted with valves to form closed sample vessels that interface with the measuring equipment. Powders were loaded into these vessels after treatment from the drying oven, with atmospheric air (either dry or saturated with water vapor) as the cover gas.

Sample treatment and vessel loading and closure for the air-water-saturated test condition took place in a polyethylene bag. The bag contained the oxyhydroxide samples, the vessels, a beaker with 400 mL of demineralized water, and a thermometer. A hold period of 18 hours during which the air and samples were exposed to the saturated air conditions was used prior to sealing in the vessels.

The Parr vessels and their valves were physically large and limited the desired option to place multiple vessels in the gamma cell for the irradiation. One Parr vessel assembly was irradiated at a time in the ^{60}Co irradiator.

Figure 2 shows a typical modified Parr vessel (22 mL volume) assembly used for the initial testing. The Parr vessels are made of stainless steel. A copper gasket was used to seal the lid to the vessel. The lid subassembly included a stainless steel bellows valve. The vessels were cleaned with ethyl alcohol and oven dried.

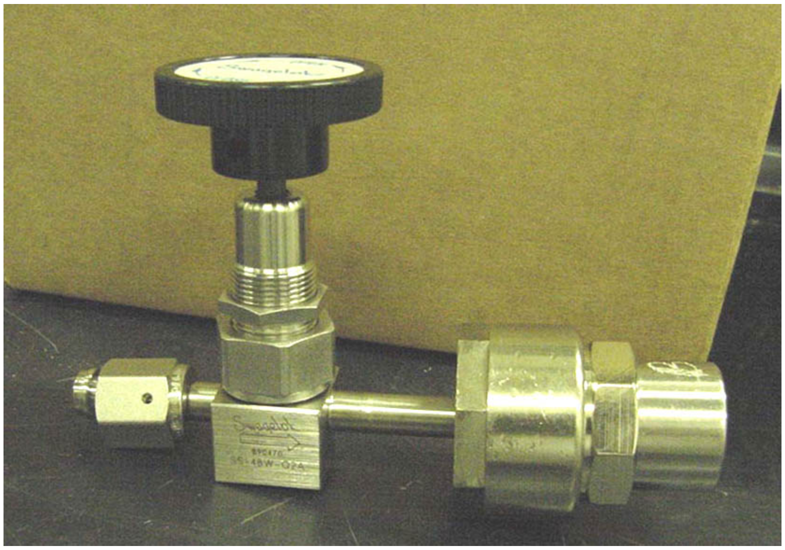

Figure 2 Typical 22 mL Parr Vessel Used for the Initial Set of Irradiation Tests

Six (6) Parr vessels were loaded in room air (at ambient pressure) with 10 g of oxyhydroxide compound, non-sieved (< 100 μm particle size), as follows:

1 with atmospheric air, dried gibbsite

1 with saturated (water vapor @23º C) atmospheric air, gibbsite

1 with atmospheric air, dried boehmite

1 with saturated (water vapor @23º C) atmospheric air, boehmite

1 with 10 g distilled water, remainder of volume atmospheric air

1 with atmospheric air

The samples were placed in a Shepherd 109-08 gamma cell irradiator with a ^{60}Co source at a dose rate of 8.76×10^5 rad/hr[1], and irradiated for 166.6 hours for a dose of 1.41×10^8rad. Following irradiation, all vessels were removed and the gas analyzed with a Pfeiffer GAM400 mass spectrometer. The mass spectrometer was set up for hydrogen detection using calibration gases of 1% and 4.97% hydrogen. The spectrometer was capable of determining oxygen, argon, and water in addition to the hydrogen.

Hydrogen was readily detected from the post-irradiated boehmite samples, and very little hydrogen was detected from the gibbsite samples, none from the water sample, and none from the air sample (see Results section). Subsequent use of the Parr vessels showed inconsistent sealing however, and their size and configuration limited their versatility for this investigation.

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[1] The dose rate for the ^{60}Co γ-radiation irradiator is an estimate only based on the dose rate determined using Fricke dosimetry solutions. That is, no adjustments were made for the specific configuration of the Parr vessel with powder to explicitly calculate the absorbed dose of the powder material including the position-dependency of the dose rate within the irradiation chamber.

In order to irradiate multiple vessels simultaneously, analyze gas during irradiation, and provide consistent sealing with positive indication of leaks, the sample vessel design was changed to a construction of Swagelok® VCR fittings, as shown in Figure 3. The new vessel assembly included a 0.5 micron filter, 3.2 mm tubing, and bellows valve to be placed outside of the gamma cell to connect to the mass spectrometer to allow gas sampling and analysis during the irradiation.

Figure 3 Improved Sample Vessel of Swagelok® VCR fittings

Each of the improved vessels held 2.4 g of oxyhydroxide sample material in a total volume of approximately 8.2 mL. A glove bag loading and closure station shown in Figure 4 was used to prepare the remainder of samples for irradiation. All tests with the new vessel used argon at 1 atm as the cover gas.

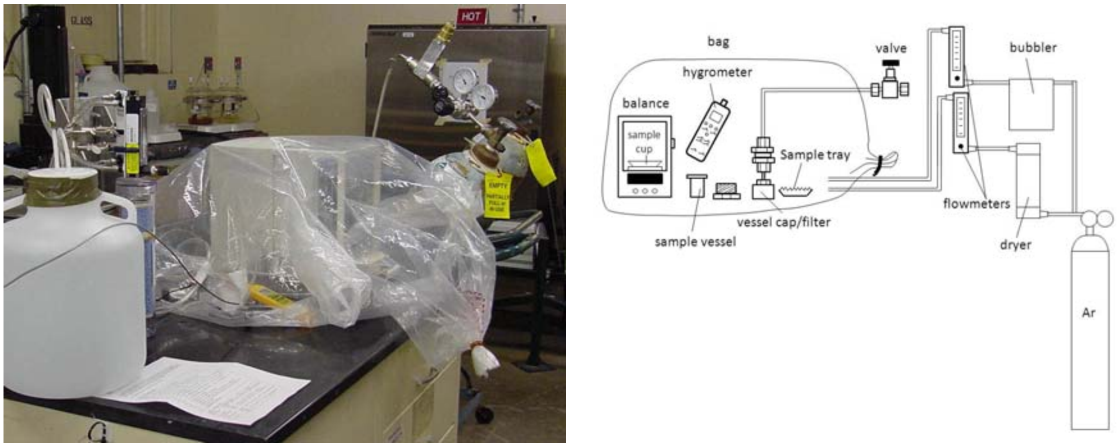

Figure 4 Glovebag for Conditioning Samples and Cover Gas for Vessel Loading. Glovebag contains sample vessels, oxyhydroxides, balance, and hygrometer

A Shepherd 81-22 gamma cell irradiator with ^{60}Co sources was used for testing. The sample vessel's gas tubing could be routed to the mass spectrometer from the irradiation chamber. This was not possible in the other gamma cell. Vessels were placed in the chamber as close to the sources as possible, with their long axis along the radiation path, stacked in rows and columns. Each vessel was thus placed in the same orientation to the beam path, equally exposed. The estimated dose rate for each sample for this configuration at the time of irradiation was 7.5×10^5 rad/hr.

A list of material sample conditions was assembled but only selected sample conditions were completed in the course of the investigation. Ten (10) identical samples of a particular condition were prepared to allow a gas sample to be taken at a dose level. The proposed material sample conditions were:

- dry boehmite, 45-63 micron particles
- dry gibbsite, 45-63 micron particles
- dry boehmite, 64-75 micron particles
- dry gibbsite, 64-75 micron particles
- water-sorbed boehmite, 30% relative humidity @25°C, 45-63 micron particles
- water-sorbed gibbsite, 30% relative humidity @25°C, 45-63 micron particles
- water-sorbed boehmite, 85% relative humidity @25°C, 64-75 micron particles
- water-sorbed gibbsite, 85% relative humidity @25°C, 64-75 micron particles
- argon gas
- water with argon cover gas

The following 3 sets of material sample conditions were chosen from the list, prepared in the lab, and tested in the gamma cell.

10 vessels w/2.4 g of dry boehmite (45-63 micron) covered with dry argon gas

10 vessels w/2.4 g of boehmite (45-63 micron) covered with 85% relative humidity (water vapor) argon gas

10 vessels w/2.4 g of dry gibbsite (45-63 micron) covered with dry argon gas

3. TEST PROCEDURE

Removing gas from a vessel for analysis altered that vessel condition for successive samples by significantly reducing the pressure (i.e., overall quantity of gas) in the vessel. As more gas is taken from a vessel, analysis is made on a reduced sample of gas, artificially indicating a higher proportion of hydrogen in the argon cover gas. Therefore, a series of identical samples were prepared so that a particular compound/environment combination could be irradiated and gas would be drawn from an unaltered vessel at increasing dose increments up to the 10 available vessels prepared at the identical conditions to measure hydrogen production.

The ten (10) vessels loaded with a particular oxyhydroxide compound (45-63 micron particles) and condition (per the list of 3 sets above) covered with argon were bound together and placed in the gamma cell for irradiation at an estimated 7.5×10^5 rad/hr. The attached tubing from the vessel assemblies exited the sample chamber, placing their valves at the mass spectrometer. The VCR® fittings on each valve were connected to the mass spectrometer when the sample was drawn. All tubing, valves from the mass spectrometer (up to the valve seat on the sample valve) were evacuated before the sample valve was opened.

Gas was drawn for analysis from a separate, previously untested, vessel approximately every 24 hours. After a vessel was sampled initially, additional samples were taken from it on 2 succeeding days and the tenth day. The successive samples are not used in the present evaluation, only the first gas sample.

4. RESULTS

The hydrogen generated in the initial irradiated samples (in the Parr vessels) containing aluminum oxyhydroxides is listed below. Each sample received 1.41 x 10^8 rad from ^{60}Co.

dried gibbsite w/dry atmospheric air: 0.8 ppm H_2

dried gibbsite w/saturated (water vapor @25ºC) atmospheric air: 0.4 ppm H_2

dried boehmite w/dry atmospheric air: 42.1 ppm H_2

dried boehmite w/ saturated (water vapor @25ºC) atmospheric air: 9.9 ppm H_2

No hydrogen was detected (< 0.5 ppm) from the vessels that had water or air only.

These initial tests were followed with tests using the 2.4 g sample sets listed in the Experimental Setup section above. No further testing of “wet” gibbsite took place due to the low hydrogen production from the initial tests. The remaining three material conditions were tested, all under argon cover gas rather than air.

The greatest percentage of H_2 produced, consistent with the initial tests, was from dry boehmite, followed by water-sorbed boehmite (Table 1). The lowest hydrogen production from the three sets of samples came from dry gibbsite. These sample sets served to confirm trends from the initial tests and quantify hydrogen production with increasing dose under inert conditions. Spectrographs showed a single sample from each boehmite sample set (of ten samples) contained (atmospheric) gases in addition to argon. These compromised samples and information were discarded. Figure 5 is a graph of hydrogen production with increasing dose. All points are from the first gas sample taken from each vessel.

Table 1. Hydrogen Production from Irradiated Aluminum Oxyhydroxides

	H_2 volume percent 1st sample	H_2 percent subsequent samples	Dose (rad) (1st sample only)	moles H_2 (1st sample only)	grams H_2 (1st sample only)
Dry boehmite	3.6	5.0, 6.5, 28.3	1.80E+07	2.08E-05	4.19E-05
	4	8.8, 15.6, 39.8	3.60E+07	1.65E-05	3.33E-05
	2.5	4.3, 7.6, 19.9	5.40E+07	1.02E-05	2.06E-05
	4.5	7.3, 11.2, 24.5	7.20E+07	1.87E-05	3.77E-05
	6	8.6, 12.0, 22.6	9.00E+07	2.53E-05	5.10E-05
	7	10.4, 14.2, 22.6	1.08E+08	2.98E-05	6.01E-05
	11	14.2, 18.8, 23.3	1.26E+08	4.89E-05	9.86E-05
	9.5	11.9, 15.3	1.44E+08	4.16E-05	8.39E-05
	10.5	13.3	1.62E+08	4.65E-05	9.37E-05
Water-sorbed boehmite	0.2		1.80E+07	7.94E-07	1.60E-06
	1		3.60E+07	4.00E-06	8.06E-06
	1		5.40E+07	4.00E-06	8.06E-06
	3		7.20E+07	1.22E-05	2.46E-05
	3.3		1.08E+08	1.35E-05	2.72E-05
	4.1		1.26E+08	1.69E-05	3.41E-05
	4.4		1.44E+08	1.82E-05	3.67E-05
	6.4		1.62E+08	2.71E-05	5.46E-05
	5.6		1.80E+08	2.35E-05	4.74E-05
Dry gibbsite	0.01		1.80E+07	3.96E-10	7.98E-10
	0.01		3.60E+07	3.96E-10	7.98E-10
	0.02		5.40E+07	7.92E-10	1.60E-09
	0.02		1.08E+08	7.92E-10	1.60E-09
	0.04		1.26E+08	1.58E-09	3.19E-09
	0.06		1.44E+08	2.38E-09	4.80E-09
	0.09		1.62E+08	3.56E-09	7.18E-09
	0.08		2.34E+08	3.17E-07	6.39E-07
	0.09		2.52E+08	3.69E-07	7.43E-07
	0.1		2.70E+08	3.84E-07	7.75E-07

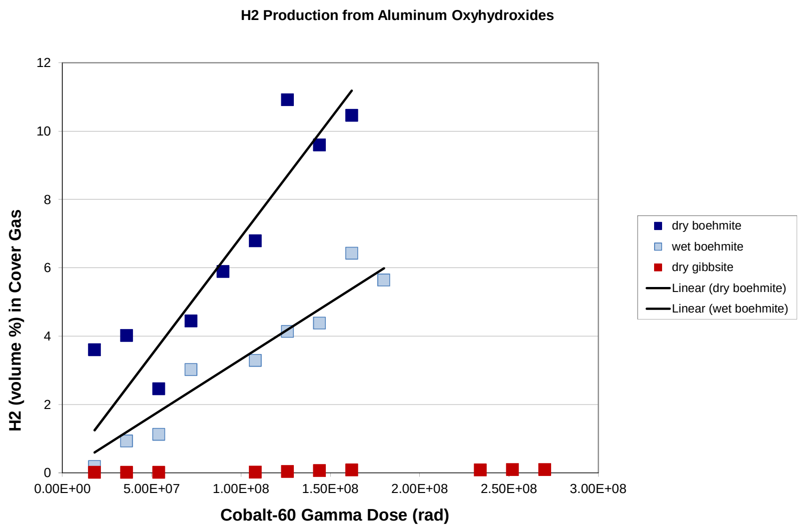

Figure 5. Hydrogen Production with Gamma Dose

The photographs in Figures 6 and 7 show gibbsite and boehmite samples, before and after irradiation. There is no discernible difference between the two conditions, only a slight change in the bulk color (graying).

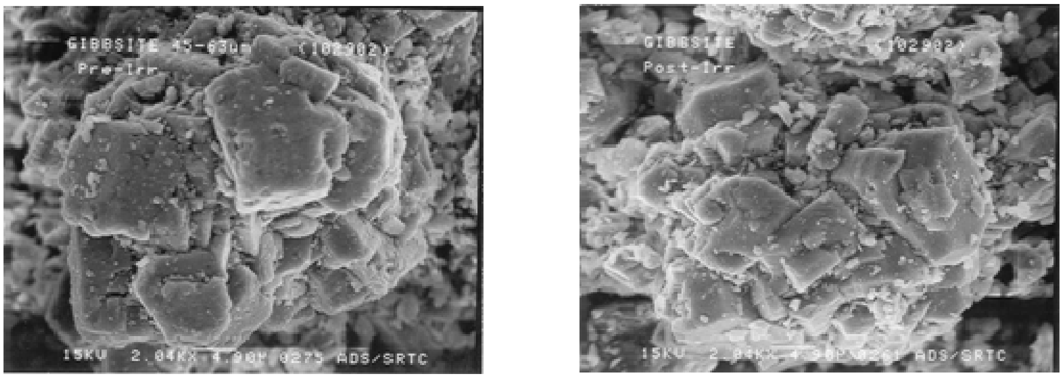

Figure 6. Gibbsite Before and After Irradiation (High Magnification)

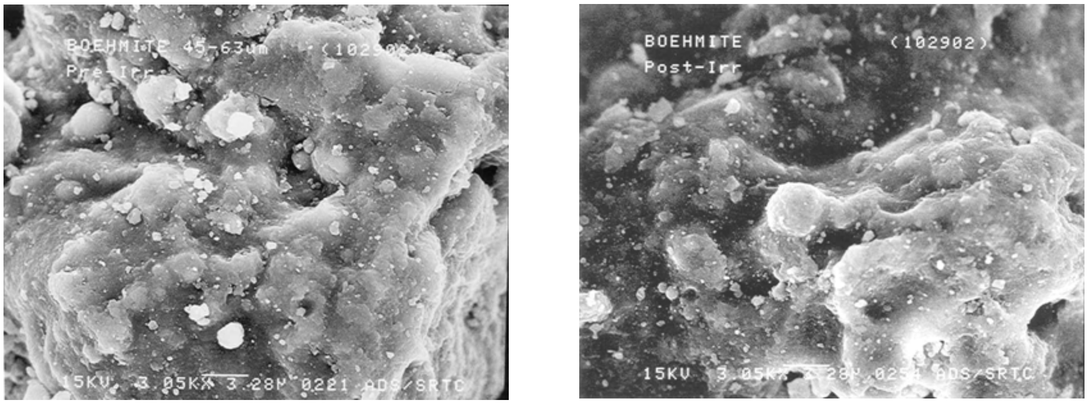

Figure 7. Boehmite Before and After Irradiation (High Magnification)

5. EVALUATION OF HYDROGEN BONDING

The thermal decomposition of gibbsite takes place at 80 ºC and boehmite at 400 ºC. That is, less thermal energy is required to dissociate water molecules from gibbsite. Prior to the testing of the oxyhyrdroxides under gamma radiation, the authors expected that the gibbsite would exhibit greater production of radiolytic products than the boehmite. A mechanistic explanation is sought for this phenomenon.

Radiation damage has 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.

An initial investigation to obtain insights into experimentation results of the boehmite and gibbsite was performed with computational chemistry analysis [2]. Single molecule (“gas phase”) reaction models were first modeled. Although not as accurate as energetic models, they are a way to look for easily identifiable reasons for the results. The estimated energy barrier for H atom loss from a single boehmite molecule is +7.3 eV and from a single gibbsite molecule it is + 7.9 eV.

A structural surface model (solid phase crystalline) was next studied to estimate H atom and H_2 molecule production energies for both substances. The models indicate H atom production from solid gibbsite requires 6.48 eV, and 6.24 eV from solid boehmite. H_2 molecule production from solid gibbsite requires 6.46 eV and solid boehmite requires 4.72 eV.

In all cases the energy required for the net separation of either a hydrogen atom or molecule from boehmite (from a solid surface or single molecule) was less than that of gibbsite. This is in qualitative agreement with the trend observed in the test results. The lack of hydrogen production from gibbsite, and the generation rate of H_2 production from boehmite have not been fully explained by the analysis to date.

Further, the mechanism of energy transfer from the 1.17 MeV and 1.33 MeV energy gamma rays from Co-60 to the cause a displacement of hydrogen from the oxyhydroxide solids is presumed to occur by first creating ballistic electrons in the materials via the Compton effect. Energy transfer from the electron to the H atom would be needed to cause its release from the solid. Additional characterization of this mechanism may provide an insight into the result that no hydrogen was produced from the gibbsite.

6. SUGGESTED FUTURE INVESTIGATION

The phenomenon of hydrogen generated via gamma irradiation of a fully dried granular oxyhydroxide is not reported in the literature to the authors' knowledge.

Additional modeling and confirmatory testing is suggested to enable predictive capability for hydrogen generation from gamma or other incident radiation on aluminum or other metal oxyhydroxide systems. The following outlines areas of suggested modeling and testing activites:

Modeling/Analysis: Activity Area 1 - Evaluate the energy transfer mechanism(s) from the incident gamma radiation to the hydrogen atoms in the oxyhydroxide solids and evaluate the energy barriers to remove the atom.

Modeling/Analysis: Activity Area 2 – Evaluate hydrogen generation in the interior of a solid along with its transportation to the surface, and recombination reactions which may occur. Develop a model to describe the hydrogen production from gamma-irradiated oxyhydroxides.

Testing: Activity 3 – Irradiate oxyhydroxides of other metal systems that would have a range of hydrogen binding energies. Compare the results to the model predictions and to the aluminium oxyhydroxide results.

7. REFERENCES

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2. M. L. Westbrook, *A Theoretical Investigation of Radiolytic H_2 Generation from Solids*, SRNL-STI-2011-00630, January 2012.