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The effect of plutonium dioxide water surface coverage on the generation of hydrogen and oxygen

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Abstract

The conditions for the production of oxygen during radiolysis of water adsorbed onto plutonium dioxide powder are discussed. Studies in the literature investigating the radiolysis of water show that both oxygen and hydrogen can be generated from water adsorbed on high-purity plutonium dioxide powder. These studies indicate that there is a threshold in the amount of water below which oxygen is not generated. The threshold is associated with the number of monolayers of adsorbed water and is shown to occur at approximately two monolayers of molecularly adsorbed water. Material in equilibrium with 50% relative humidity (RH) will be at the threshold for oxygen generation. Using two monolayers of molecularly adsorbed water as the threshold for oxygen production, the total pressure under various conditions is calculated assuming stoichiometric production of hydrogen and oxygen. The specific surface area of the oxide has a strong effect on the final partial pressure. The specific surface areas resulting in the highest pressures within a 3013 container are evaluated. The potential for oxygen generation is mitigated by reduced relative humidity, and hence moisture adsorption, at the oxide surface which occurs if the oxide is warmer than the ambient air. The potential for oxygen generation approaches zero as the temperature difference between the ambient air and the material approaches 6°C.

Introduction

The potential re-adsorption of water by plutonium oxide after stabilization creates the possibility of generation of both hydrogen and oxygen gas in subsequent storage. Plutonium oxide calcined at 650 °C and handled in an atmosphere of 70% RH is expected to have a significantly increased potential for adsorption of water compared to plutonium oxide calcined at 950 °C and handled in atmospheres with much lower RH. The observation of gas generation of both hydrogen and oxygen from high-purity plutonium oxides has been reported by Vladimirova and Kulikov (VK)[1], Duffey and Livingston (DL)[2], and by Berg et al[3]. The lowest amounts of water that resulted in the generation of both hydrogen and oxygen in each study are given in Table 1. The argument has been made that generation of both hydrogen and oxygen only occurs if water is adsorbed in multiple layers.[4] The average number of monolayers (ML) of water on the surface is not measured directly but is determined by measuring the specific surface area (SAA) and the total amount of adsorbed water. The data in Table 1 illustrate that multiple layers of water are present when hydrogen and oxygen are generated and suggest that the number of ML of water needed could be in the 3 to 5 range. The available data also suggest that in addition to a threshold number of ML of water needed before hydrogen and oxygen are generated, there may be an overall mass fraction of water that is required. Chemical and radiolytic reactions that recombine hydrogen and oxygen are expected to occur in this environment.[5] The competition between formation and consumption is presumed to determine whether hydrogen or oxygen is observed in the gas phase. The rate of formation when the temperature, material wattage, and other conditions are held constant is dependent upon the amount of water. If the water content does not reach an amount where the rate of gas formation overcomes the rate(s) of consumption, then hydrogen and/or oxygen will not be seen in the gas phase. The amount of water needed has not been measured for all situations of concern. The lowest observed moisture mass fraction associated with hydrogen and oxygen generation is that of VK at 3 mg per gram of material (0.3 wt%).

In order to define the bounding conditions within which both hydrogen and oxygen may be generated, we examine what is known about how water is adsorbed onto plutonium oxide, how the amount of water depends upon the relative humidity and SSA, and how the SSA varies with processing conditions of which the most important is calcination temperature. The measured SSA values of the material used in the DL[6] and Berg et al studies are shown in Table 1. The SSA of the VK materials is estimated from the reported calcination temperature. The ML of water on the materials were calculated from the SSA and the amount of water using the conversion factor of 0.022 wt% ML^{-1} $(m^2/g)^{-1}$ (derived from the average water monolayer mass per square meter of 0.22 mg m^{-2} for the crystallographic planes of PuO_2).[7] The limiting water content for each of the DL samples was taken as the LOI value at which the linear fit of net oxygen generation rate crossed zero in their Figures 3 and 5.

Table 1. Mimimum amount of water which generated both hydrogen and oxygen in various plutonium oxide materials formed from calcinations of plutonium oxalate precipitation.

Study	Calcination temperature	Material activity	Water content	Specific Surface Area	Monolayers of water	Fill gas
Vladimirova and Kulikov	550 °C	11.6 W kg^{-1}	1.0 wt%	13-45	1.1 – 3.5	vac
Vladimirova and Kulikov	1000-1200 °C	11.6 W kg^{-1}	0.3 wt%	1	14	vac
Duffey and Livingston	450	2.3 W kg^{-1}	2.6 wt%	41	2.9	air
Duffey and Livingston	700	2.3 W kg^{-1}	1.3 wt%	11	5.4	air
Duffey and Livingston	450	3.3 W kg^{-1}	3.0 wt%	39	3.5	air
Duffey and Livingston	700	3.3 W kg^{-1}	1.2 wt%	9.5	5.7	air
Berg, et al.	600	2.1 W kg^{-1}	0.5 – 1.5 wt%	20 - 30	0.8 – 3.4	He

The adsorption of water onto plutonium oxide surfaces

The mechanism of the adsorption of water onto plutonium oxide surfaces is not well understood. A description that is consistent with available information includes a strongly bound first layer with mixed molecular and dissociative adsorption, followed by a layer of molecular adsorbed water with a heat of adsorption slightly more negative than liquid water, and finally molecular adsorbed water with a heat of adsorption equivalent to liquid water. The latter can be many monolayers thick.

The strongly bound first layer can be described by analogy with experimental and modeling results for ThO_2/CeO_2.[8] As water is adsorbed onto the surface of ThO_2 or CeO_2, the heat of adsorption is initially high at over 100 kJ/mol. As the coverage increases, the heat of adsorption decreases and approaches a value similar to the condensation of liquid water which is 44 kJ/mol at just over of one monolayer. The oxygen of the water molecule in this first layer is associated with the metal cation either as a water molecule or as a hydroxyl with one hydrogen donated to an adjacent oxygen forming a second hydroxyl. The ratio of molecular adsorption to dissociative adsorption depends upon the surface energy and the lattice constant. The amount of dissociated water in the first hydration layer can be as large as 50%.

The second molecularly adsorbed layer of water and subsequent layers are described by Brannuer, Emmett, and Teller (BET) theory. In BET theory as applied to the adsorption of water, physical adsorption of water onto a surface occurs with a heat of adsorption in excess of the heat of condensation of the liquid. Subsequent layers adsorb with a heat of adsorption equal to the heat of condensation of liquid water. The form of adsorption isotherms based on BET theory is given in Figure 1. The expression for c used in the construction of Figure 1 is $c=e^{\Delta H/RT}$ where ΔH is the excess heat of adsorption compared to the heat of condensation of the liquid. It must be clarified that this excess heat may represent adsorption onto a surface that is already covered or partially covered by a more tightly bound chemisorbed layer that remains on the surface throughout the BET measurement, i.e. the strongly bound first layer. For an excess heat of adsorption of 5 kJ/mol the value of c is 7. An increase in the excess heat of adsorption from 5 to 10 kJ/mol results in an increase of c to 55. The effect of an increase in c is substantial increase in the amount of adsorption at low values of RH. An important feature of BET type adsorption is the rapid rise in the number of monolayers adsorbed as the RH approaches and exceeds 60%. At 50% RH the amount of adsorption is about 1.7 ML for a c of 7. By 70% RH the amount of adsorption nearly doubles to 3.2 ML.

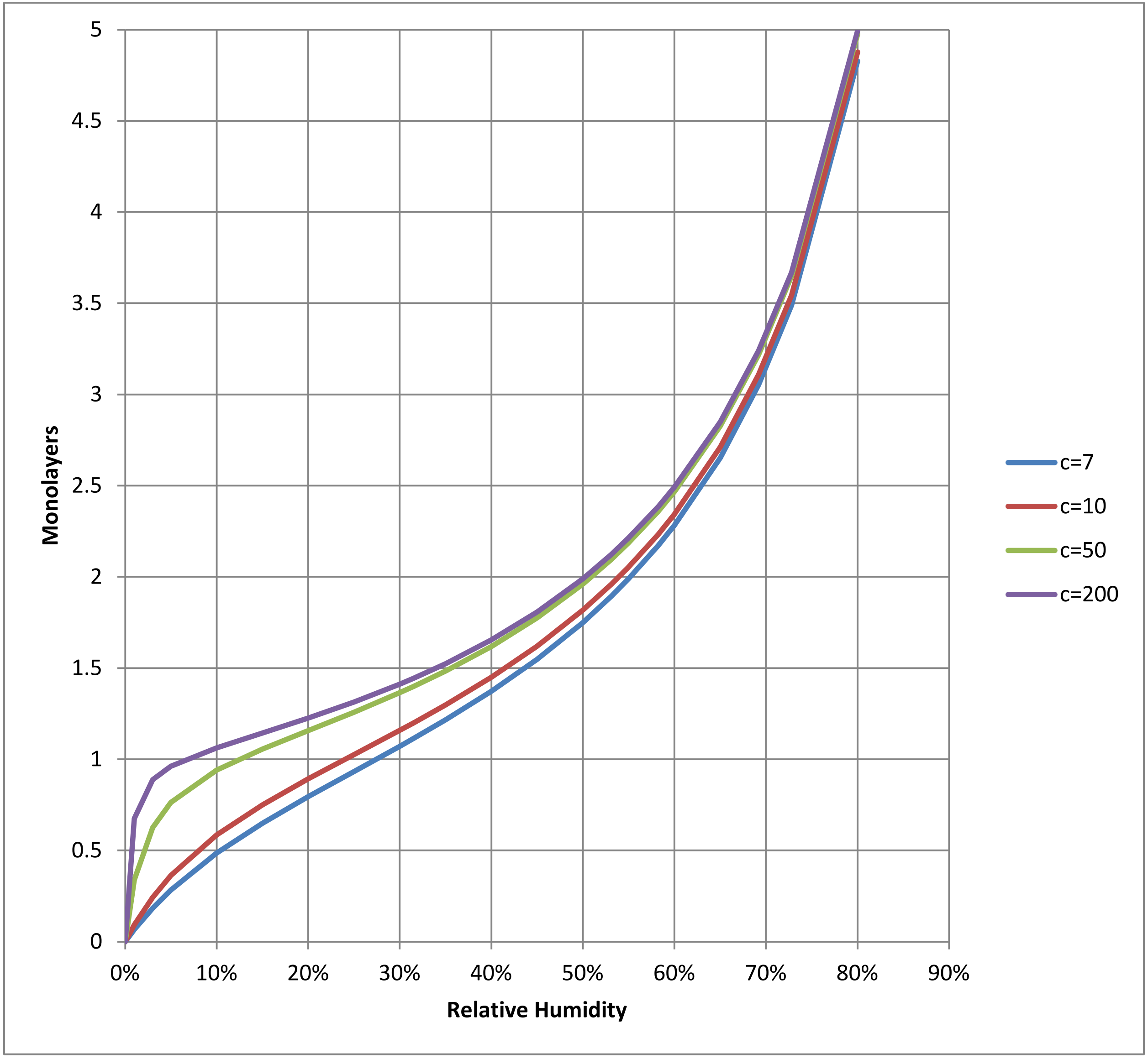


Figure 1. Adsorption isotherms calculated from BET theory.

The experimental evidence for this description of water adsorption onto plutonium dioxide includes the direct observation of the formation of hydroxyls, the empirical observation of water adsorbed onto plutonium dioxide powder varying with RH in a manner consistent with BET theory with c=7, and indirect verification through the observation of water being removed in thermogravimetric analysis.

Surface hydroxyls are observed by x-ray photoelectron spectroscopy (XPS) when plutonium oxide surfaces are exposed to water even for short periods of time.[9] Farr *et al.* estimate that the depth of the hydroxylated layer is 3 nm using attenuation of the XPS signal. However, such a thick layer, approximately 10 ML, is inconsistent with the amount of water bulk plutonium oxide material adsorbs per unit surface area. It is possible that plutonium oxide's very complex particle morphology may have affected the interpretation of the XPS data.

The excess heat of adsorption of physically adsorbed water onto plutonium dioxide powder has been measured to be 4.3 to 6.8 kJ mol^{-1} more negative than the heat of condensation of liquid water using a Branuer-Emmett-Teller (BET) approach.[10] In this study the surface had been previously exposed to water and it is assumed that the strongly bound first layer had been fully formed and was present throughout the study. The plutonium dioxide powder was prepared from oxalate precipitation of nitric acid anion exchange solution calcined to 950°C.

Thermogravimetric analysis (TGA) of high-purity plutonium oxide powders typically shows some moisture desorbed by about 200 °C, which is reasonably assigned as physically adsorbed water, and a second fraction interpreted to be chemically adsorbed water that is desorbed over a wide range of temperature, extending as high as 800 °C and above in some cases. This is illustrated in Figure 2 which shows the TGA/MS of plutonium oxide material from oxalate precipitation calcined to 650 °C.

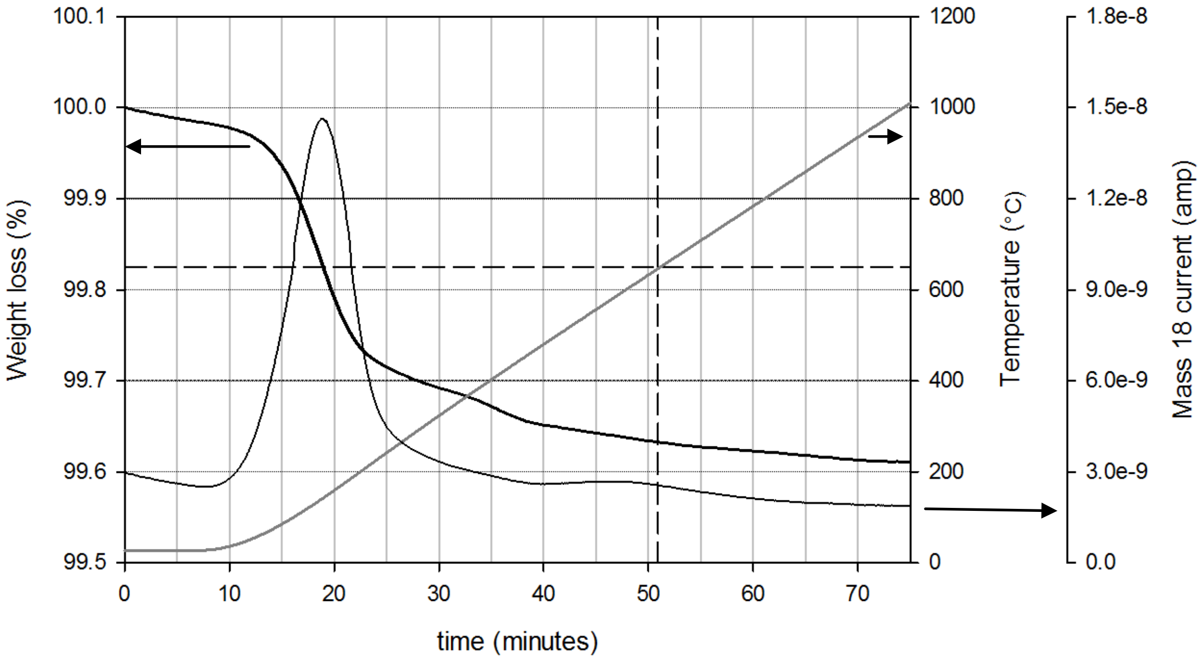


Figure 2. The TGA/MS of plutonium oxide powder showing the mass 18 (water) current. The molecularly adsorbed water is nearly fully desorbed by 200°C. A second much smaller mass 18 peak begins at 40 minutes (~500°C) and continues to 70 minutes (~950°C). The horizontal dashed line is at 650°C and the vertical dashed line shows that mass 18 and weight loss occur above 650°C. The TGA/MS was run within a month of calcination during which the material was protected in a vial within a plastic bag. The material was exposed to air only about 40 minutes total.

In addition to the observation of molecularly adsorbed water and chemically bound water, there are experimental observations that suggest that the physically adsorbed water converts to a more strongly bound form to some extent over time. Water vapor was observed in a LANL full-scale shelf-life study above bulk plutonium oxide that had been exposed to water vapor and gained a mass equivalent to approximately one ML, Figure 3. The water vapor pressure initially was equivalent to approximately 30%

RH suggesting that the added ML is not all in the form of a strongly bound first layer, and therefore that that strongly bound first layer had been all or partially formed prior to the water addition. The water vapor pressure decreased steadily for the first month and persisted for many months.[11] The decrease in water vapor pressure indicates that the most weakly adsorbed molecularly water is gradually becoming more strongly bound. Stated another way, the number of physically adsorbed water monolayers is decreasing with time. The most likely explanation of the loss of molecularly adsorbed water is the slow formation of additional hydroxyls. The slow disappearance of water vapor is reproduced below. The water vapor appeared to continue to decline after almost a year.

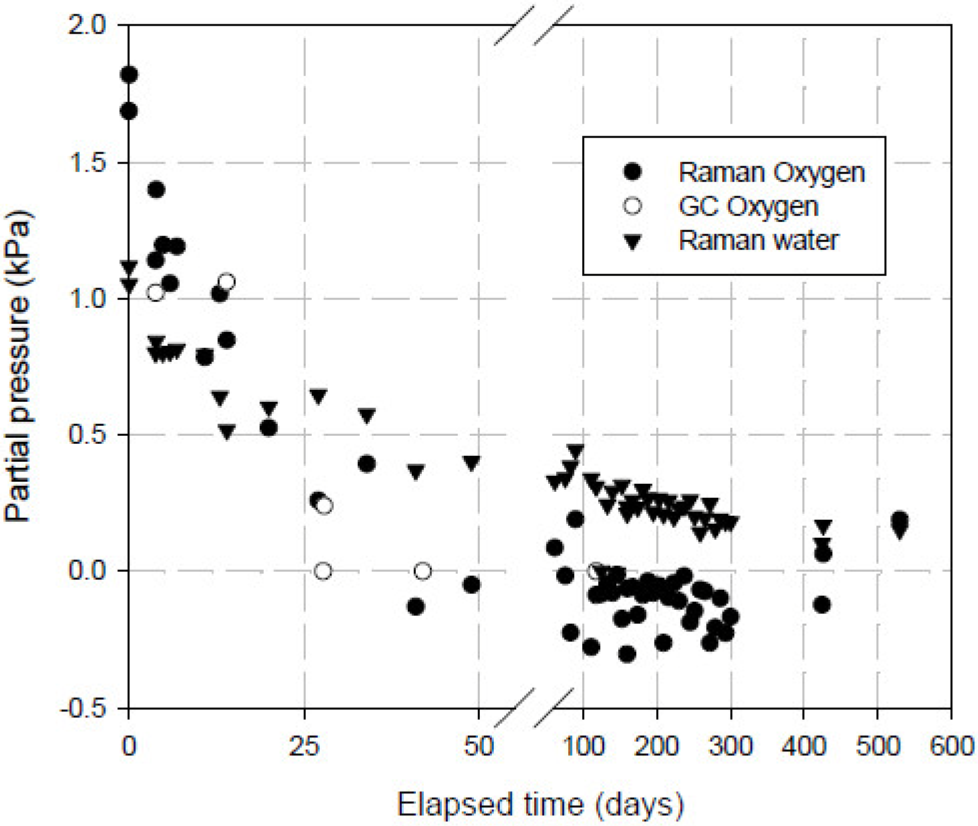
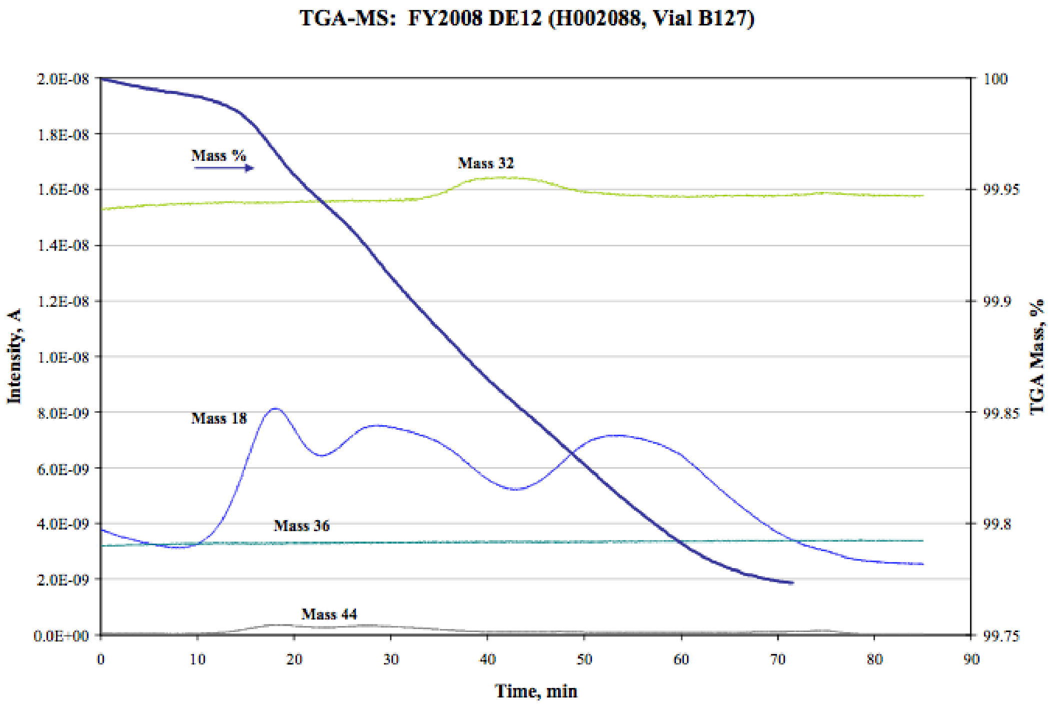


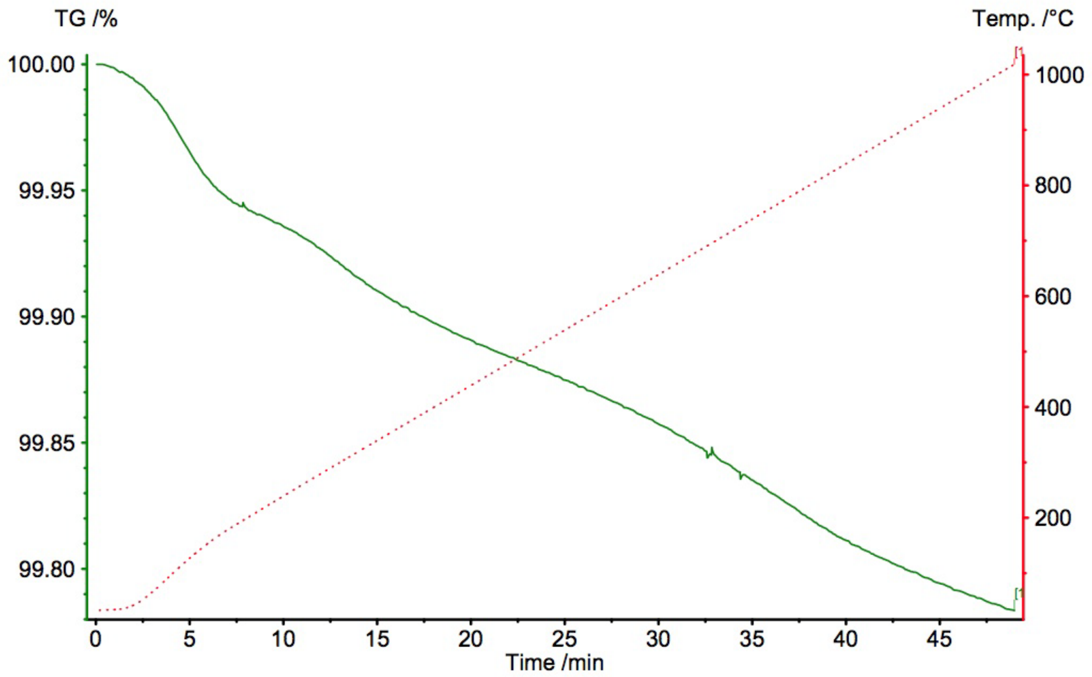
Figure 3. Oxygen and water partial pressures above a high-purity plutonium oxide material calcined to 975 °C with a SSA of 1.09 m^2/g. The material was exposed to water after calcination and picked up approximately 1 ML. The initial gas composition contained oxygen from residual air.

TGA data also suggest that the chemically bound water can increase with time as the molecularly bound water decreases. The 3013 container surveillance program has destructively examined several containers of relatively pure PuO_2 from the storage inventory. A common feature observed in the TGA-MS analysis of moisture on these materials is that a small but clearly observed fraction is volatilized when the material temperature reaches 600 to 1000 °C. To our knowledge this observation has not been documented in a form that can be referenced, so we summarize the primary data here. The information is of potential relevance because such tightly-bound moisture would presumably not be removed by stabilizing at 650 °C.

Two containers of relatively pure oxide packaged at Hanford were opened for DE at SRS in FY08 (FY08DE8 and FY08DE12). Both contained previously stabilized BLO material, as do most of the pure oxide containers with the highest apparent moisture at the time of packaging. One such curve extracted from SRNL-ATS-2008-00065, Rev. 1 for FY08DE12 is shown below. The temperature ramp was 15 C/min and the end of the mass curve is at 1000 C. MS curves extend beyond the temperature ramp.



The TGA-MS replicate measurements on the initial and final samples collected from these two containers are all qualitatively similar in appearance to the one shown. The total mass losses range from 0.21 to 0.24%. The mass decreases at a fairly steady rate until 800 °C then tapers off, though is still decreasing at 1000 °C. The MS signal due to moisture persists throughout the TGA runs and has peak structure that appears to match the mass loss rates. Integration of the MS data by SRNL indicated that FY08DE12 had 0.18% H_20 on the material. Also of note is the similarity of these data to the TGA mass loss of samples collected and analyzed prior to packaging. The packaging data for FY08DE12 is shown below.



The mass losses above 650 °C in these two DE's were 0.065 and 0.07%, or about 1/3 of the total TGA mass loss observed in each case. Both materials had SSA measured at ~2.0 m^2/g so this mass loss corresponds to approximately 1.5 ML of water.

The picture that emerges from these observations is that a clean plutonium oxide surface initially absorbs strongly bound water molecularly and dissociatively, the latter forming hydroxyls. Molecular water adsorbs on top of this strongly bound water, and water can continue to adsorb molecularly for many monolayers as described by BET theory. At vapor pressures of water above 30% RH, molecular multilayers of water can form. As time passes some of the molecularly adsorbed water changes to forms that are more difficult to volatilize presumably by formation of additional hydroxyls, although this reaction is slow. This latter process is presumably assisted by the input of radiation energy. One effect of lowering the calcination temperature from 950 °C is that surface defects such as vacancies, steps, and dislocations become more prevalent. The complexity of surface adsorption increases as the number and type of surface defects increase. Surface defects probably both facilitate the formation of hydroxyls and increase the heat of adsorption of the strongly bound first layer.

Quantifying the amount of water available for H_2 and O_2 generation

The literature cited above that indicates 3 – 5 ML of water are necessary for hydrogen and oxygen generation. The 3 – 5 ML is made up of the strongly bound water and molecularly adsorbed water. The extent of the strongly bound water is not quantified in the studies cited and there is evidence that the amount of strongly bound water varies with time. We assume that the strongly bound water is initially 1 ML. The large-scale observation of PEOF-1, which was freshly calcined and water added by flowing humidified gas for many days, was that no hydrogen or oxygen was generated. The partial pressure of the water vapor that was initially observed corresponds to approximately 30% RH at the material. The 30% RH corresponds to molecularly adsorbed water of between 1 ML to 1.5 ML. The first two molecularly adsorbed water ML are not active to form hydrogen and oxygen. Thus, the water that is active in oxygen gas generation begins with the third molecularly adsorbed layer that occurs at approximately 50% RH. The water activity must be 0.5 or greater for oxygen gas generation to occur.

The extent of the strongly bound layer does not matter as it does not contribute significantly to the water activity.

A qualitative argument for why the water activity must be 0.5 or greater is now given. When surface water is excited by alpha radiation, the excited water intermediate can either transfer its energy to the surface or transition to a stable state by the oxygen beginning to form a bond to the Pu and one hydrogen beginning to form a bond to one of the existing plutonium oxide surface oxygens. This excited complex can transition to form two hydroxyls on the surface, each hydroxyl bonded to a Pu. In order to form hydrogen or oxygen gas the excited water molecule would have to go through the multiple solution reactions that form hydrogen and oxygen gas. In order for water to behave like liquid water, multiple layers of water are needed. The idea is that when multiple water monolayers are present on the surface, the excited water molecule has a path to form gases that involve fewer kinetic barriers and more favorable energetics than if the excited water can re-form a surface-stabilized water molecule or hydroxide.

In order to quantify the mass of water in an adsorbed ML, the SSA is needed. The conversion to weight percent adsorbed water given a number of ML's and an SSA is 0.022 wt% ML^{-1} $(m^2/g)^{-1}$. For a material with 10 m^2/g and 2 ML, the weight percentage of water is 10 m^2/g x 2 ML x 0.022 wt% ML^{-1} $(m^2/g)^{-1}$ = 0.44 wt%. Conversely, for a given wt% of adsorbed water and the SSA, the number of ML can be calculated. The SSA of plutonium oxide materials from oxalate precipitation has been reviewed by Daniel.[12] For each calcination temperature a range of values for the SSA has been observed. A plot of SSA versus calcination temperature was given in his Figure 2-1. The general behavior is that the SSA decreases as the calcination temperature increases. At about 700 °C there is a break in the rate of decrease for the minimum SSAs seen for each temperature. At about 800 °C there is a break in the rate

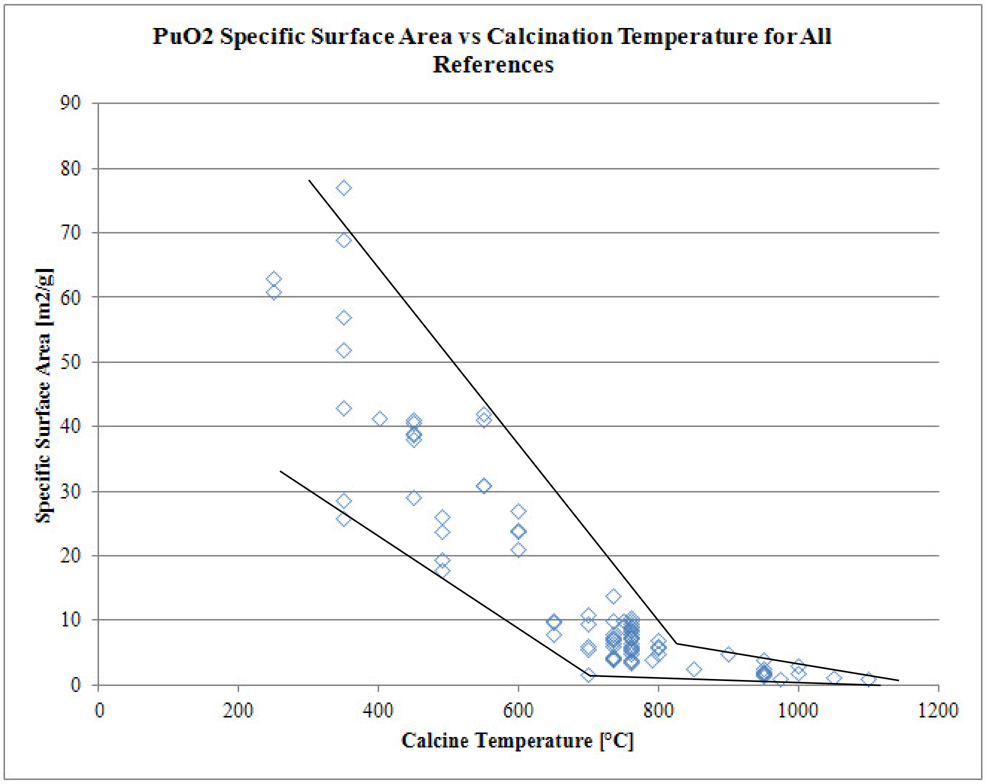


Figure 4. The SSA for high-purity plutonium oxide material from oxalate precipitation as a function of calcination temperature. For each calcination temperature a range of values is possible.

of decrease for the maximum SSAs seen for each temperature. Placing bounding lines on the original plot yields a range of SSA that could be seen at each temperature. This is shown in Figure 4.

Hydrogen and oxygen total pressure

If hydrogen and oxygen can be generated by adsorbed water on plutonium oxide formed from oxalate precipitate calcined to 650°C and subsequently exposed to 70% RH, then it is reasonable to ask what the maximum oxygen partial pressure might be. The most conservative approach to estimating the maximum oxygen partial pressure is to assume all of the water available for radiolysis undergoes radiolysis to form stoichiometric hydrogen and oxygen. As stated above, the expectation is that at only molecularly adsorbed water beyond the first 2 ML are available for hydrogen and oxygen generation. The 3013 packaging requirement that the total moisture be less than 0.5 wt% further constrains the conditions of concern. The amount of strongly adsorbed water is estimated from 0 to 1 ML for this discussion resulting in a minimum total amount of adsorbed water between 2 and 3 ML before generation of both hydrogen and oxygen is observed. Once the amount of water available for radiolysis is estimated, the total pressure in a container can be calculated for different amounts of material if the volume of the container is known. Tables in Appendix 1 show the total pressure from hydrogen and oxygen gas generation for 5000 g of plutonium oxide in a 3013 container using the assumption that all of the water available for oxygen gas generation is converted to hydrogen and oxygen.

The total pressure from radiolysis of available water for 5000 g of plutonium dioxide in equilibrium with humid air at 35°C in a 3013 container is shown in Fig. 5. In this figure it is assumed that the amount of water in the strongly bound layer (SBL) is equivalent to 0.5 ML of water and that the first molecularly bound layer interacts with the surface with an excess heat of ΔH=4.79 kJ/mol corresponding to a value of c=7 at 23°C. Under these conditions, the number of monolayers can be calculated using BET theory. Less than two monolayers of molecularly adsorbed water are present on material in equilibrium with air with 50% or 55% relative humidity. At 60% relative humidity, two monolayers of molecularly adsorbed water is exceeded and the pressure increases linearly with SSA to ~8 $m^2 g^{-1}$ at which point the amount of water is limited by the 0.5wt% constraint. At higher SSA at 60% relative humidity the amount of water available decreases as the SSA increases because a smaller proportion of the 0.5 wt % total water is in

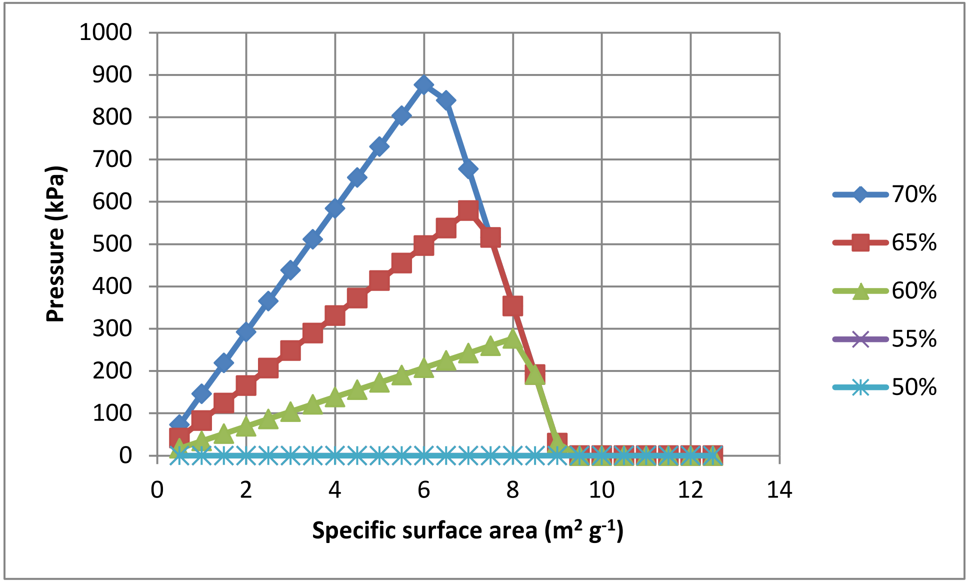


Figure 5. The sum of the hydrogen and oxygen pressure in a 3013 container with 5000 g of material as a function of the material specific surface area for plutonium dioxide in equilibrium with different values of the relative humidity. The data is taken from Table 7 of Appendix 1 for T=35°C, c=7, and SBL=0.5.

the outer layers. Above 9 m^2 g^{-1} all of the water in the SBL and the first two molecularly bound layers sums to 0.5wt% and there is no longer water available for oxygen gas generation. At higher relative humidity the 0.5wt% constraint is reached at lower SSA values, and the total pressure increases. The SSA that results in the maximum total pressure for the different values of the relative humidity varies from 6 to 8 m^2 g^{-1}. Material calcined at 650°C is expected to have SSAs within this range. These general features of the total pressure as a function of RH and SSA are common to material in equilibrium at different temperatures, different values of the extent of the SBL, and for different values of the excess heat of adsorption. The maximum pressure for material in equilibrium with 70% RH for different values of the material temperature, SBL, and c are given in Table 2. The higher temperatures always yield higher pressures, lower values for the SBL always yield the higher pressures, and higher values for c also yield higher pressures. The conditions that result in the highest calculated pressures in Table 2 are SBL = 0, T = 35°C, and c = 200.

Table 2. Comparison of the maximum pressures for two temperatures, two values of c and the three values for the strongly bound layer (SBL) for 3013 containers with 5000 g of material. The specific surface area at which the maximum pressure occurs is indicated.

		SBL 0.0 ML		SBL 0.5 ML		SBL 1.0 ML	
T (^oC)	c	P (kPa)	SSA	P (kPa	SSA	P (kPa)	SSA
23	7	995	7	853	6	776	5.5
23	200	1087	7	963	6	826	5
35	7	1023	7	876	6	803	5.5
35	200	1131	7	1002	6	859	5

Next we consider the effect of the amount of material within a 3013 container on the total pressure. We choose a temperature of 35°C because it is the highest expected ambient air temperature that material may be in equilibrium with. We choose a value of c = 7 because it represents the only measured ΔH. Additional data of the variation of ΔH with calcination temperature is needed. We choose a value of the SBL = 0.5 because freshly calcined material has some SBL water as seen in Figure 2. Additional data on the rate of formation of the SBL is needed. These conditions are not the conditions that will produce the highest pressure in these calculations. However, they represent a more likely condition to be encountered. The results are given in Table 3. The pressure increases as the amount of material increases and decreases as the RH decreases.

Table 14. Maximum pressures in kPa as a function of the mass of material and the RH the material experiences using T = 35^{o}C, c = 7, and SBL = 0.5.

Mass (g)	70%	65%	60%	55%	50%
5000	876	579	277	0	0
4500	770	509	243	0	0
4000	669	442	211	0	0
3500	572	378	181	0	0
3000	480	317	152	0	0
2500	391	258	124	0	0
2000	306	202	97	0	0
1500	225	149	71	0	0
1000	147	97	46	0	0

The calculations described in this section and Appendix 1 assume that all of the available water undergoes radiolysis to form stoichiometric hydrogen and oxygen. This assumption is required because there is a lack of data for the conditions of water adsorbed onto high-purity oxides at known relative humidity. However, there is evidence that the reactions of this type do not proceed to this degree of completion in closed containers. The gas generation of hydrogen is seen to consume a maximum of between 0% and 25% of available water in salt-bearing materials.[13] When hydrogen and oxygen are generated together in salt-bearing materials, it is observed that each gas goes through a maximum pressure and then decreases.[14] The maximum pressure did not exceed approximately 5% of the available water. Gas-phase radiolysis of hydrogen and oxygen to form water is predicted to limit the amount of these gases as their partial pressure increases.[5] In the VK studies the oxygen is observed to plateau at much less than the available oxygen from water and in some cases decreases with time. As the water activity decreases from 70% RH to 50% RH, the ability to form oxygen at partial pressures above that found in ambient air decreases to zero and it is reasonable that not all of the water available between the two ends forms hydrogen and oxygen.

One of the experiments by Duffey and Livingston used weapons grade plutonium oxide prepared by oxalate precipitation and calcined to 700°C. The material was exposed to 70% RH, placed in a sealed container with air as the headspace gas, and the result was a slight loss of oxygen. This suggests that the oxygen generation and consumption reactions were nearly in equilibrium at the ~20kPa partial pressure of oxygen in the initial headspace gas. The material would have generated 20 kPa of oxygen had the oxygen not been there initially. A total pressure increase calculated assuming stoichiometric production of hydrogen and oxygen with 20 kPa of oxygen is 60 kPa. Additional data on the maximum pressure and maximum oxygen partial pressure under different conditions is needed to move away from the assumption that all of the available water undergoes radiolysis.

The effect of the difference in temperature between the material and the glovebox air is very significant in this context. During destructive evaluation of 3013 containers at SRS, the temperatures of the glovebox air and the wall of the convenience container after 12 hours of equilibration have been measured, Table 4. The minimum temperature difference is 1.4°C and the wall temperature is the minimum material temperature. The centerline temperatures are typically 20°C higher than the wall temperature. The material in a container that is not sealed to gas exchange with the air in the surrounding glovebox experiences a relative humidity at the material surface that is lower than that of the glovbox air because it is warmer than the glovebox air. The relative humidity that the material experiences as a function of the temperature difference from the ambient air at 70% RH is given in Table 5. For a temperature difference between the material and the glovebox air of 2°C, the available water for production of oxygen decreases by 50%.

Table 4. Temperature measurements and material properties for 3013 convenience containers measured during destructive evaluation.

Year	DE	Container ID	T center [°C]	T wall [°C]	T GB [°C]	ΔT [°C]	Material Mass [g]	Power [W]
FY09	17	R610806	59.24	34.22	24.20	10.02	4259.0	8.18
FY09	18	H003119	54.33	34.22	25.00	9.22	2429.0	5.53
FY10	1	H004251	46.04	30.00	24.10	5.90	2578.4	3.75
FY10	2	H002496	35.13	25.20	23.80	1.40	1886.5	2.47
FY10	3	H003710	47.78	29.00	24.70	4.30	2498.6	4.46
FY10	4	H003655	48.05	29.58	23.60	5.98	2588.8	4.54

FY10	7	H003900	37.96	28.18	24.30	3.88	2479.9	3.66
FY10	8	H003650	39.09	27.76	23.00	4.76	2483.2	4.62
FY10	10	H002728	51.00	28.94	24.70	4.24	2474.5	4.35
FY10	11	H002786	46.52	27.06	23.00	4.06	2504.8	4.29
FY10	12	H003077	63.51	28.01	23.40	4.61	3332.5	6.86
FY10	13	H003367	37.28	25.83	23.40	2.43	2052.0	2.67
FY10	14	H003704	49.26	30.42	24.40	6.02	2488.7	4.44
FY10	18	S001721	73.44	41.17	23.60	17.57	3971.3	8.32
FY11	1	H003443	42.60	29.42	23.67	5.75	2491.6	4.22
FY11	2	S002129	67.76	36.66	23.60	13.06	4737.1	9.63
FY11	3	H002592	33.60	26.18	23.70	2.48	1374.9	1.82
FY11	4	H003337	42.28	27.33	23.10	4.23	2392.4	3.27
FY11	5	S001105	76.64	37.28	23.40	13.88	4841.4	9.72
FY11	6	H003343	44.69	26.06	23.40	2.66	1921.9	3.65
FY11	7	H003371	41.94	26.11	23.90	2.21	2233.9	3.03
FY11	8	H003526	44.61	28.75	23.00	5.75	2491.9	4.27
FY11	9	H003565	50.94	30.72	23.40	7.32	2466.9	4.62
FY11	11	H003625	48.56	33.56	26.44	7.12	2484.4	4.58

Table 5. The relative humidity that self-heating plutonium oxide material would experience if exposed to 70% RH air at 35°C as a function of the difference in temperature between the material and the air. The effect of the temperature difference on the fraction of water available for producing oxygen is computed from the difference in surface coverage at the various RHs.

ΔT	RH	Fraction of water available
0	70%	100%
1	66%	70%
2	62%	47%
3	59%	33%
4	56%	20%
5	53%	10%
6	50%	0%

Data gaps

There are many data gaps in this analysis. We do not know the amount of water required to generate both hydrogen and oxygen. The high-purity plutonium oxide materials that have been studied in the MIS program have all had at most 1 ML of molecularly adsorbed water so they would not be expected to generate either hydrogen or oxygen. The high-purity plutonium oxide material packaged to date have either been packaged in low RH processing lines or have had very little water due to their low SSA. The region of RH above 50% and high SSA material has not been extensively explored either in the laboratory or during destructive evaluation of 3013 containers at Savannah River Site.

The rate of production of oxygen as a function of relative humidity is not known. The maximum partial pressure of oxygen in a sealed container as a function of relative humidity is not known. The effect of SSA on the maximum partial pressure of oxygen as a function of relative humidity is not known.

The effect of SSA on the number of ML required to generate oxygen has not been explored. As the SSA increases the number of surface defects increases. The amount of surface area internal to particles also increases substantially. The internal surface area can consist of surfaces adjacent to each other on a molecular length scale. This would allow water to form multiple ML locally at lower RH than 50%. The affect of local pockets of water on the formation of gaseous radiolysis products has not been explored. The extent of formation of the strongly bound layer upon initial exposure to water for freshly calcined material is not known. Changes in the excess heat of adsorption with changes in calcination conditions such as temperature or time at temperature are not known.

Conclusion

Experiments show that oxygen is produced from the radiolysis of water adsorbed on high-purity plutonium dioxide powder. There is a threshold in the number of monolayers of adsorbed water below which oxygen is not generated. The threshold occurs at two monolayers of molecularly adsorbed water. Material in equilibrium with between 50% and 55% RH will be at the threshold for oxygen generation. The material specific surface area has a strong effect on the final partial pressure with the highest pressures being generated by material between 5 and 10 $m^2 g^{-1}$. Small temperature differences between material and the glovebox air have a strong effect on the potential for oxygen generation with the potential going to very low values for a temperature difference of 6°C.

Appendix 1. Pressure calculations

The pressure within a 3013 container is calculated for the radiolysis of all the molecularly adsorbed water on plutonium dioxide material above 2 monolayers to form stoichiometric H_2 and O_2. The pressure is calculated for material in equilibrium with atmospheres of 70%, 65%, 60%, 55%, and 50% relative humidity. Material with different specific surface areas is considered. The monolayer coverage is calculated from BET theory using

$$\frac{v}{v_m} = \frac{cx}{(1-x)^2\left(1+\frac{cx}{(1-x)}\right)}$$

where v/vm is the volume of gas adsorbed divided by the volume of gas needed to form a monolayer, i.e. it is the monolayer coverage, $x = P/P_0 = RH/100\%$ and $c = \Delta H/RT$. Two values of c were used; c = 7 corresponding to ΔH = 4.79 kJ/mol at 23^{o}C and c = 200 corresponding to to ΔH = 13.05 kJ/mol at 23^{o}C. Two temperatures, T = 23^{o}C and T = 35^{o}C ,were considered and c was recalculated at the temperature using ΔH and T. Pressures were calculated for specific surface areas (SSAs) from 0.5 to 12.5 $m^2\ g^{-1}$. First, the monolayer coverage was calculated at the RH of interest and a value for the strongly bound layer of 0, 0.5, or 1.0 was added. The monolayer coverage plus strongly bound layer was converted to wt% water at each SSA. If the wt% water exceeded 0.5wt% then the water content was limited to 0.5wt% and the monolayer coverage recalculated from the 0.5wt%. The monolayer coverage was converted to available monolayers for producing oxygen and hydrogen by subtracting 2 and the value of the strongly bound layer. If the result was less than 0, then the value was set to 0. The resulting available water was converted to moles by the product of the number of monolayers, the SSA, 0.022wt%, and the mass of material in grams. The result is multiplied by 1.5 for the stoichiometric production of hydrogen and oxygen. The available gas volume was calculated by

$$V = 2248\ \mathrm{cm}^3 - \frac{M}{11.46\ \mathrm{g\ cm^{-3}}}$$

Where 2248 $cm^3$is the volume of the outer container minus the volumes of the inner and convenience containers from Table B-2 of the 3013 Standard, M is the mass of the oxide in g, and 11.46 g cm^{-3} is the pycnometer density of the oxide. The pressure is calculated using the ideal gas equation.

Table 1. T = 23^{o}C, c = 7, strongly bound water = 0 ML, and 5000 g of material. Pressure in kPa.

SSA m^2 g^{-1}	70%	65%	60%	55%	50%
0.5	71	41	18	0	0
1	142	81	35	0	0
1.5	213	122	53	0	0
2	284	163	70	0	0
2.5	355	203	88	0	0
3	426	244	106	0	0
3.5	498	285	123	0	0
4	569	325	141	0	0
4.5	640	366	158	0	0
5	711	407	176	0	0
5.5	782	447	194	0	0
6	853	488	211	0	0
6.5	924	529	229	0	0
7	995	570	246	0	0
7.5	963	610	264	0	0
8	838	651	282	0	0
8.5	714	692	299	0	0
9	589	589	317	0	0
9.5	464	464	334	0	0
10	340	340	340	0	0
10.5	215	215	215	0	0
11	91	91	91	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 2. T = 23^{o}C, c = 200, strongly bound water = 0 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2\ g^{-1}$	70%	65%	60%	55%	50%
0.5	83	53	31	13	0
1	165	106	61	27	0
1.5	248	159	92	40	0
2	330	212	123	53	0
2.5	413	265	153	66	0
3	496	317	184	80	0
3.5	578	370	214	93	0
4	661	423	245	106	0
4.5	744	476	276	120	0
5	826	529	306	133	0
5.5	909	582	337	146	0
6	991	635	368	159	0
6.5	1074	688	398	173	0
7	1087	741	429	186	0
7.5	963	794	459	199	0
8	838	838	490	212	0
8.5	714	714	521	226	0
9	589	589	551	239	0
9.5	464	464	464	252	0
10	340	340	340	266	0
10.5	215	215	215	215	0
11	91	91	91	91	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 3. T = 35^{o}C, c = 7, strongly bound water = 0 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2 g^{-1}$	70%	65%	60%	55%	50%
0.5	73	41	17	0	0
1	146	83	35	0	0
1.5	219	124	52	0	0
2	292	165	69	0	0
2.5	365	207	87	0	0
3	438	248	104	0	0
3.5	511	290	121	0	0
4	584	331	138	0	0
4.5	657	372	156	0	0
5	730	414	173	0	0
5.5	803	455	190	0	0
6	876	496	208	0	0
6.5	949	538	225	0	0
7	1023	579	242	0	0
7.5	1002	621	260	0	0
8	872	662	277	0	0
8.5	742	703	294	0	0
9	613	613	312	0	0
9.5	483	483	329	0	0
10	354	354	346	0	0
10.5	224	224	224	0	0
11	94	94	94	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 4. T = 35^{o}C, c = 200, strongly bound water = 0 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2 g^{-1}$	70%	65%	60%	55%	50%
0.5	86	55	32	14	0
1	172	110	63	27	0
1.5	258	165	95	41	0
2	343	220	127	55	0
2.5	429	275	159	68	0
3	515	330	190	82	0
3.5	601	385	222	96	0
4	687	440	254	109	0
4.5	773	495	286	123	0
5	859	549	317	137	0
5.5	944	604	349	151	0
6	1030	659	381	164	0
6.5	1116	714	413	178	0
7	1131	769	444	192	0
7.5	1002	824	476	205	0
8	872	872	508	219	0
8.5	742	742	540	233	0
9	613	613	571	246	0
9.5	483	483	483	260	0
10	354	354	354	274	0
10.5	224	224	224	224	0
11	94	94	94	94	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 5. T = 23^oC, c = 7, strongly bound water = 0.5 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2\ g^{-1}$	70%	65%	60%	55%	50%
0.5	71	41	18	0	0
1	142	81	35	0	0
1.5	213	122	53	0	0
2	284	163	70	0	0
2.5	355	203	88	0	0
3	426	244	106	0	0
3.5	498	285	123	0	0
4	569	325	141	0	0
4.5	640	366	158	0	0
5	711	407	176	0	0
5.5	782	447	194	0	0
6	853	488	211	0	0
6.5	807	529	229	0	0
7	651	570	246	0	0
7.5	496	496	264	0	0
8	340	340	282	0	0
8.5	184	184	184	0	0
9	28	28	28	0	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 6. T = 23^{o}C, c = 200, strongly bound water = 0.5 ML, and 5000 g of material. Pressure in kPa.

SSA m^2 g^{-1}	70%	65%	60%	55%	50%
0.5	83	53	31	13	0
1	165	106	61	27	0
1.5	248	159	92	40	0
2	330	212	123	53	0
2.5	413	265	153	66	0
3	496	317	184	80	0
3.5	578	370	214	93	0
4	661	423	245	106	0
4.5	744	476	276	120	0
5	826	529	306	133	0
5.5	909	582	337	146	0
6	963	635	368	159	0
6.5	807	688	398	173	0
7	651	651	429	186	0
7.5	496	496	459	199	0
8	340	340	340	212	0
8.5	184	184	184	184	0
9	28	28	28	28	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 7. T = 35^{o}C, c = 7, strongly bound water = 0.5 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2\ g^{-1}$	70%	65%	60%	55%	50%
0.5	73	41	17	0	0
1	146	83	35	0	0
1.5	219	124	52	0	0
2	292	165	69	0	0
2.5	365	207	87	0	0
3	438	248	104	0	0
3.5	511	290	121	0	0
4	584	331	138	0	0
4.5	657	372	156	0	0
5	730	414	173	0	0
5.5	803	455	190	0	0
6	876	496	208	0	0
6.5	840	538	225	0	0
7	678	579	242	0	0
7.5	516	516	260	0	0
8	354	354	277	0	0
8.5	192	192	192	0	0
9	29	29	29	0	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 8. T = 35^{o}C, c = 200, strongly bound water = 0.5 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2\ g^{-1}$	70%	65%	60%	55%	50%
0.5	86	55	32	14	0
1	172	110	63	27	0
1.5	258	165	95	41	0
2	343	220	127	55	0
2.5	429	275	159	68	0
3	515	330	190	82	0
3.5	601	385	222	96	0
4	687	440	254	109	0
4.5	773	495	286	123	0
5	859	549	317	137	0
5.5	944	604	349	151	0
6	1002	659	381	164	0
6.5	840	714	413	178	0
7	678	678	444	192	0
7.5	516	516	476	205	0
8	354	354	354	219	0
8.5	192	192	192	192	0
9	29	29	29	29	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 9. T = 23^{o}C, c = 7, strongly bound water = 1.0 ML, and 5000 g of material. Pressure in kPa.

SSA m^2 g^{-1}	70%	65%	60%	55%	50%
0.5	71	41	18	0	0
1	142	81	35	0	0
1.5	213	122	53	0	0
2	284	163	70	0	0
2.5	355	203	88	0	0
3	426	244	106	0	0
3.5	498	285	123	0	0
4	569	325	141	0	0
4.5	640	366	158	0	0
5	711	407	176	0	0
5.5	776	447	194	0	0
6	589	488	211	0	0
6.5	402	402	229	0	0
7	215	215	215	0	0
7.5	28	28	28	0	0
8	0	0	0	0	0
8.5	0	0	0	0	0
9	0	0	0	0	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 10. T = 23^{o}C, c = 200, strongly bound water = 1.0 ML, and 5000 g of material. Pressure in kPa.

SSA m^{2} g^{-1}	70%	65%	60%	55%	50%
0.5	83	53	31	13	0
1	165	106	61	27	0
1.5	248	159	92	40	0
2	330	212	123	53	0
2.5	413	265	153	66	0
3	496	317	184	80	0
3.5	578	370	214	93	0
4	661	423	245	106	0
4.5	744	476	276	120	0
5	826	529	306	133	0
5.5	776	582	337	146	0
6	589	589	368	159	0
6.5	402	402	398	173	0
7	215	215	215	186	0
7.5	28	28	28	28	0
8	0	0	0	0	0
8.5	0	0	0	0	0
9	0	0	0	0	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 11. T = 35^{o}C, c = 7, strongly bound water = 1.0 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2\ g^{-1}$	70%	65%	60%	55%	50%
0.5	73	41	17	0	0
1	146	83	35	0	0
1.5	219	124	52	0	0
2	292	165	69	0	0
2.5	365	207	87	0	0
3	438	248	104	0	0
3.5	511	290	121	0	0
4	584	331	138	0	0
4.5	657	372	156	0	0
5	730	414	173	0	0
5.5	803	455	190	0	0
6	613	496	208	0	0
6.5	418	418	225	0	0
7	224	224	224	0	0
7.5	29	29	29	0	0
8	0	0	0	0	0
8.5	0	0	0	0	0
9	0	0	0	0	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

Table 12. T = 35^{o}C, c = 200, strongly bound water = 1.0 ML, and 5000 g of material. Pressure in kPa.

SSA $m^2\ g^{-1}$	70%	65%	60%	55%	50%
0.5	86	55	32	14	0
1	172	110	63	27	0
1.5	258	165	95	41	0
2	343	220	127	55	0
2.5	429	275	159	68	0
3	515	330	190	82	0
3.5	601	385	222	96	0
4	687	440	254	109	0
4.5	773	495	286	123	0
5	859	549	317	137	0
5.5	807	604	349	151	0
6	613	613	381	164	0
6.5	418	418	413	178	0
7	224	224	224	192	0
7.5	29	29	29	29	0
8	0	0	0	0	0
8.5	0	0	0	0	0
9	0	0	0	0	0
9.5	0	0	0	0	0
10	0	0	0	0	0
10.5	0	0	0	0	0
11	0	0	0	0	0
11.5	0	0	0	0	0
12	0	0	0	0	0
12.5	0	0	0	0	0

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