

Literature Review of PuO₂ Calcination Time and Temperature Data for Specific Surface Area

W. E. Daniel

March 6, 2012

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

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EXECUTIVE SUMMARY

The literature has been reviewed in December 2011 for calcination data of plutonium oxide (PuO_2) from plutonium oxalate $\text{Pu}(\text{C}_2\text{O}_4)_2$ precipitation with respect to the PuO_2 specific surface area (SSA). A summary of the literature is presented for what are believed to be the dominant factors influencing SSA, the calcination temperature and time. The PuO_2 from $\text{Pu}(\text{C}_2\text{O}_4)_2$ calcination data from this review has been regressed to better understand the influence of calcination temperature and time on SSA. Based on this literature review data set, calcination temperature has a bigger impact on SSA versus time. However, there is still some variance in this data set that may be reflecting differences in the plutonium oxalate preparation or different calcination techniques.

It is evident from this review that additional calcination temperature and time data for PuO_2 from $\text{Pu}(\text{C}_2\text{O}_4)_2$ needs to be collected and evaluated to better define the relationship. The existing data set has a lot of calcination times that are about 2 hours and therefore may be underestimating the impact of heating time on SSA. SRNL recommends that more calcination temperature and time data for PuO_2 from $\text{Pu}(\text{C}_2\text{O}_4)_2$ be collected and this literature review data set be augmented to better refine the relationship between PuO_2 SSA and its calcination parameters.

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LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
SSA	Specific Surface Area
LANL	Los Alamos National Laboratory
MOX	Mixed Oxide
LTA	Lead Test Assembly
SARP	Safety Analysis Report for Packaging

1.0 Introduction

The literature was reviewed for data concerning the calcination of plutonium(IV) oxalate ($\text{Pu}(\text{C}_2\text{O}_4)_2$) to plutonium oxide (PuO_2) as it relates to the specific surface area (SSA) of the PuO_2 formed. In the following sections, the electronic searches through the SRNL Library website will be explained and then brief descriptions of the various articles will be given. Following the literature summary, all the SSA data found will be identified and then the data most appropriate to correlating to calcination temperature and time will be shown. Finally, some initial correlations to the appropriate SSA data will be given. Note that these initial correlations will be modified or changed as new data is collected or found.

2.0 Literature Review

2.1 SRNL Library Website Electronic Searches

The SRNL Library website electronic search engines were used to look for articles concerning the calcination of plutonium oxalate or like compound as it affects the surface area of the plutonium oxide formed. The key search phrases used in the various search engines were “ PuO_2 surface area,” “Plutonium Oxide surface area,” “Plutonium Surface Area,” and “Plutonium ceramic fuel preparation.” The various search engines used are shown in Table 2-1. Note that the web addresses are not exact but are provided as reference only.

Table 2-1. Search Engines

SRNL Name	Description	Web Name	Web address
Applied Science & Technology	Provides abstracts and indexing of 800 periodicals back to 1983 and full article texts from more than 200 journals back to 1997.	Wilson Web	vnweb.hwwilsonweb.com
Energy Science and Technology	Formerly DOE ENERGY contains worldwide references to scientific/technical research for U.S. Department of Energy from 1976 on.	Dialog Web	www.dialogweb.com
GeoRef	GeoRef is the American Geological Institute's geoscience database containing 2.4 million records of North America since 1785.	OvidSP	ovidsp.tx.ovid.com
IEEE - All Society Periodicals Package	For accessing scientific/technical publications produced by the Institute of Electrical and Electronics Engineers (IEEE) from 1893 on.	IEEE Xplore	ieeexplore.ieee.org
Inspec	Covers over 5,000 journals from 1969 to the present plus 2,500 conference proceedings and books, dissertations, patents and reports.	EBSCO Host	web.ebscohost.com
Intute: Science, Engineering & Technology	Covers the physical sciences, engineering, computing, geography, mathematics and environmental science.	Intute	www.intute.ac.uk
Materials Research Database with Metadex	Contains materials science databases, with specialist content on materials science, metallurgy, ceramics, polymers, and composites used in engineering application.	CSA Illumina	csaweb107v.csa.com
Materials Research Society (MRS) On-line Proceedings Library	Features over 30,000 peer-reviewed papers presented at MRS Meetings.	Cambridge Journals	journals.cambridge.org
National Institute of Standards & Technology Database	Includes scientific, technical, and materials properties data for chemistry, biotechnology, law enforcement, mathematical databases, software, physics and product design.	NIST Data Gateway	srdata.nist.gov
National Technical Reports Library	The National Technical Information Service acquires, indexes, abstracts, and archives U.S. government-sponsored technical reports.	National Technical Reports Library U. S. Dept. of Commerce	ntrl.ntis.gov
Science Citation Index - Web of Science	Provides access to scientific, technical and multidisciplinary information from research journals.	Web of Knowledge-Web of Science	apps.webofknowledge.com
Science Interagency Portal	Includes portals to 17 scientific/technical organizations from 13 federal agencies.	USA.gov for Science	www.science.gov
University of Maryland College Park Technical Reports	Includes abstracts, bibliographies, and full-text technical reports, annual reports, reprints, preprints, etc.	University of Maryland Libraries	www.lib.umd.edu
Worldwide Science	Site with science information from 15 national portals including DOE and the British Library, along with Australia, Brazil, Canada, Denmark, France, Germany, Japan and the Netherlands.	World Wide Science	worldwidescience.org

2.2 Articles Reviewed

The first group of articles reviewed came from Jon Duffey (References 1-17). The next group of articles came from the literature searches discussed in the prior section (References 18-26, 28-30). The last set of articles came from John Berg of LANL (References 27, 31-56). The articles will be cited in the order reviewed rather than order of importance or relevancy.

2.2.1 *Reference 1: Plutonium dioxide particle properties as a function of calcination temperature*

This article¹ contained physical properties of PuO₂ powder with respect to the calcination temperature. The physical properties included microcrystal size, particle morphology, and specific surface area. Plutonium(IV) oxalate was precipitated by adding oxalic acid to a 4 M HNO₃, 8 g/L Pu(IV) solution at 50 °C for one hour. The precipitate was then digested for another hour at 50 °C, cooled, and then filtered without washing. The initial batch of PuO₂ was prepared by firing the Pu oxalate in air at 450 °C for 5 hours and then calcined another 5 hours at the various temperatures (450 °C to 1050 °C). Due to this preparation method the calcination times are treated as a fraction of the initial 5 hours at 450 °C plus the additional 5 hours at the given temperature. The logic chosen for the calcination time t_2 for calcination temperature T_2 is calculated as follows:

$$t_2 = \frac{450}{T_2} \cdot 5 + 5$$

For example, the calcination time for the 650 °C, 7.9 m²/g data point is treated as 8.46 hours. The 450 °C, 12.3 m²/g value was not used in the correlation discussed later since the mean for the other 450 °C data was 39.88 m²/g with a standard deviation of 1.04 giving 3 σ or 99.7% inclusion limits of 37 to 43 m²/g. The 550 °C, 9.1 m²/g value was not used in the model discussed later since the mean for the other 550 °C data was 35.85 m²/g with a standard deviation of 7.42 giving 3 σ or 99.7% inclusion limits of 14 to 58 m²/g data. The Brunauer-Emmett-Teller (BET) method was used for the surface area measurements. The surface area measurements are shown in Figure 4 in the article.

2.2.2 *Reference 2: Adsorption of water on plutonium dioxide*

This reference² contained kinetic and equilibrium data of the water adsorption onto plutonium dioxide in moist air at room temperature. The article discusses how water is adsorbed by a sequence of distinct steps involving five types of adsorbate–oxide interaction and accumulating ten molecular layers of water (approximately 2.1 mg H₂O/m² PuO₂ surface) at 100% relative humidity. Table 1 in this reference contains one specific surface area (by BET) data point of 5.7 m²/g at 700 °C for 12 hours but since this data point originated in reference 3 it will be included with that reference data set.

2.2.3 Reference 3: *PuO₂ Storage: Conditions for Preparation and Handling*

This reference³ contained desorption and adsorption properties of plutonium dioxide based on production-scale experiments that illustrate how to prepare PuO₂ for long-term storage. This article also discusses the conditions for preparing PuO₂ to meet Department of Energy standards for safe storage of plutonium. The plutonium is precipitated as plutonium oxalate before calcining to plutonium oxide. The reference is not clear on what reagent was used during precipitation. The BET specific surface area data of interest are in Table 1 and 4 of this reference. For all the data points the calcination temperature and time are given except for the 350 °C point. For the 350 °C point, the calcination time is assumed to be 2.1 hour based on the other data reviewed. The calcination time for this data point can be adjusted later should other information become available.

2.2.4 Reference 4: *Development of Plutonium Bearing Fuel Materials NUMEC P-80*

This reference⁴ documents early work for the preparation of PuO₂ and PuO₂-UO₂ materials. This document contains precipitation and calcination conditions in its Table 2.1 and specific surface area (as well as bulk and tap density, permeability, particle size, and carbon content) data in its Table 2.2. The plutonium oxalate is precipitated by adding 0.8 M H₂O₂ to a 3 M HNO₃, 100 g/L Pu solution followed by 1 M Oxalic Acid at 35 °C with a hold-up of about 24-25 minutes. The plutonium oxalate cake was washed with deionized water, air dried for 10 minutes, and then calcined in air to plutonium oxide. Both oxalic acid and hydrogen peroxide were used during the precipitation step. All the specific surface area points were used in the empirical regression.

2.2.5 Reference 5: *Development of Plutonium Bearing Fuel Materials NUMEC P-90*

This reference⁵ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. This document contains precipitation and calcination conditions in its Table 2.1 and specific surface area (as well as feed composition, bulk and tap density, permeability, and particle size) data in its Table 2.2. Figure 2.15 in this reference shows for one plutonium oxalate sample the change in SSA with respect to calcination temperature as it is heated continuously in a BET instrument from 100 °C to 500 °C holding 20 minutes at each calcination temperature then dropping by 50 °C and waiting till the SSA stabilized from off-gassing. The reference points out a sudden rise in the surface area at 275 °C in Figure 2.15 and attributes it to a breakdown in the crystallite structure of the plutonium oxalate caused by fissures forming during crystal structure changes and during the escape of decomposition gases. Figure 2.5 through Figure 2.10 in this reference shows that 90% of the equilibrium moisture was adsorbed for the PuO₂ samples at 33-76% relative humidity within 6-12 hours and for 97% relative humidity within 50 hours. This reference also showed that at 97% relative humidity the PuO₂ samples continued to adsorb water for up to 100 hours. This reference stated that at 33-53% relative humidity the plutonium oxalate calcined at 760 °C would only adsorb 0.1-0.15% moisture. Using Figure 2.5 through Figure 2.8, the maximum percent of water adsorbed onto the PuO₂ samples for less than 100 hours was estimated as shown in Table 2-2 and the calcination data came from reference 4 of this review. The data indicates that the higher the calcination temperature and the lower the relative humidity, the lower the adsorbed moisture level. The plutonium oxalate for two samples in this reference is precipitated continuously by adding 0.8 M H₂O₂ to a 3 M HNO₃, 12-20 g/L Pu solution followed by 1 M Oxalic Acid at 35 °C with a hold-up of about 20-23 minutes. The plutonium oxalate for the third sample is precipitated in a batch mode by adding 0.8 M H₂O₂ to a 3 M HNO₃, 10.5 g/L Pu solution followed by 1 M Oxalic Acid at 55 °C. The plutonium oxalate is then dried at 180 °C before calcining to plutonium oxide. All the data points in this reference were used in the later empirical regression of the data from the literature review.

Table 2-2. Estimated Moisture Adsorption for PuO₂ Samples < 100 hours Exposure

Relative Humidity	Calcination Data ⁴			
	Temperature (°C)	350	490	760
	Time (h)	0.58	0.08	0.08
	SSA (m ² /g)	57	53	9.9
33%		0.80 %	0.70 %	0.10 %
53%		1.14 %	1.00 %	0.21 %
76%		1.91 %	1.44 %	0.54 %
97%		3.80 %	2.64 %	1.84 %

2.2.6 Reference 6: Effects of Plutonium Dioxide Moisture Content and Calcination Temperature on the Headspace Gas Composition of Sealed Containers

This reference⁶ documents SRNL efforts to develop a model that predicts the gas generation rate and composition of plutonium dioxide materials during long term storage. This document contains specific surface area data in its Figure 4 which came from references 3, 30, and 58 of this review. Therefore, no new specific surface area data from this reference was used in the empirical correlation.

2.2.7 Reference 7: Plutonium Oxide Polishing for MOX Fuel Fabrication

This reference⁷ contains data from LANL on the polishing of 120 kg of plutonium from surplus nuclear weapons for the European Mixed Oxide (MOX) Lead Test Assembly (LTA). The document indicates that both oxalic acid and peroxide were used during the precipitation step and that the calcination temperature was 650 °C for 4 hours. Figure 5 in this reference shows specific surface area data points for many experiments but does not list any values. SRNL received a table of the values in Figure 5 from Laura Worl of LANL on 02/03/12 which is shown in Table 2-3. Note that all these SSA values are for calcination at 650 °C for 4 hours. This work is also described in greater detail in reference 16 of this literature review. All the specific surface area data in Table 2-3 was used in the calculations even the Sample 10S (4.93 m²/g) and Sample 47 (14.86 m²/g) since the mean of the other 650 °C data was 9.34 m²/g with a standard deviation of 1.51 giving 3σ or 99.7% inclusion limits of 5 to 14 m²/g.

Table 2-3. SSA Data for Figure 5 in Reference 7

Sample	SSA [m ² /g]	Sample	SSA [m ² /g]
Sample10S	4.93	Sample33	11.14
Sample11	10.18	Sample34	8.35
Sample12	9.76	Sample35	8.11
Sample13	10.54	Sample35R	9.82
Sample14	10.86	Sample36	11.20
Sample15	7.89	Sample37	6.85
Sample16	8.47	Sample38	7.45
Sample17	9.29	Sample39	7.70
Sample18	8.64	Sample40	7.82
Sample19	9.08	Sample41	8.11
Sample20	8.30	Sample42	8.22
Sample21	10.31	Sample43	7.87
Sample22	10.23	Sample44	8.75
Sample23	8.91	Sample45	9.01
Sample24	13.56	Sample46	9.89
Sample25	11.50	Sample47	14.86
Sample26	10.37	Sample48	9.07
Sample27	8.04	Sample49	7.77
Sample28	9.07	Sample50	8.19
Sample29	8.90	Sample52	9.07
Sample30	10.54	Sample54	9.37
Sample31	12.04	Sample53	9.26
Sample32	13.51		

2.2.8 Reference 8: Effect of Oxalate Precipitation on PuO₂ Microstructures

This reference⁸ describes how the conditions of plutonium oxalate precipitation can affect the microstructure properties of calcined PuO₂. This document has specific surface area data in its Figure 2 and 3 from Pu(III) and Pu(IV) oxalate from direct and reverse strike of 0.9 M oxalic acid to 0.7-1.1 M HNO₃, 5 g/L Pu solutions at 22 °C to 55 °C during the precipitation step. Figure 2 in this reference contained calcination temperature and time, specific surface area, and crystal size data. Figure 3 in this reference only contained calcination temperature but no time for the specific surface area data. It is believed the specific surface area data shown in Figure 3 of this reference comes from reference 58 and possibly other references in this review and therefore will not be used in the later empirical fits. The specific surface area data in Figure 2 of this reference will be used in the correlations except for the 735 °C, 14 m²/g data point since the mean of the other 735 °C values was 6.17 m²/g with a standard deviation of 1.93 giving 3σ or 99.7% inclusion limits of 0.4 to 12 m²/g.

2.2.9 Reference 9: *A critical examination of the thermodynamics of water adsorption on actinide oxide surfaces*

This reference⁹ discusses the thermodynamics of water adsorption/desorption with respect to PuO_2 and presents a kinetic model for the water adsorption/desorption. The article does indicate that high calcination temperatures lead to lower specific surface area, which in turn leads to less water adsorption. However, no specific surface area data was given in this document that could be used in the modeling.

2.2.10 Reference 10: *Development of Plutonium Bearing Fuel Materials NUMEC P-100*

This reference¹⁰ documents early work for the preparation and characterization of PuO_2 and $\text{PuO}_2\text{-UO}_2$ materials. Table 2.4 lists some specific surface area data but it is for co-precipitated $\text{UO}_2\text{-5 wt \% PuO}_2$ and the document indicates that several calcination steps were used without measuring the intermediate surface area values. No specific surface area data was given in this document that could be used in the calculations.

2.2.11 Reference 11: *Nanoceria – Energetics of Surfaces, Interfaces and Water Adsorption*

This reference¹¹ looks at deriving the relation for surface enthalpy of CeO_2 . There is no specific surface area data for PuO_2 . The article does have in its Table 1 specific surface area data for CeO_2 which will be noted for comparison with PuO_2 . No specific surface area data for PuO_2 was given in this document that could be used for model development.

2.2.12 Reference 12: *Technical Basis for Packaging Glovebox Moisture Content*

This reference¹² describes the thermodynamics of water adsorption onto calcined PuO_2 . There is no specific surface area data for PuO_2 in this document but the article suggests keeping relative humidity low and putting freshly made PuO_2 into sealed containers to limit water adsorption. No specific surface area data for PuO_2 was given in this article that could be used for predictions.

2.2.13 Reference 13: *Gas Generation from Water Adsorbed onto Pure Plutonium Dioxide Powder*

This reference¹³ discusses the generation of H_2 from α -particle radiolysis of water adsorbed onto plutonium dioxide. The article points out that the specific surface area strongly affects the amount of water adsorbed. The article states that if freshly calcined PuO_2 material is put in a hermetically sealed container right after calcination then moisture in the air will be adsorbed as hydroxyl on the surface of the PuO_2 preventing the radiolysis of water in the container to H_2 . Table 1 in the article gives specific surface areas for 600 °C and 975 °C. The article does not reveal the calcination times but SRNL received an email on 02/03/12 from Laura Worl of LANL that stated that the 600 °C calcination was at 6 hours and the 975 °C calcination was at 4 hours

(following an initial 6 hours at 600 °C). The logic chosen for the calcination time t_2 for the temperature 975 °C is calculated as follows:

$$t_2 = \frac{600}{975} \cdot 6 + 4$$

Therefore the calcination time for the 975 °C data point will be treated as 7.69 hours. This calcination data will be used in the calculations.

2.2.14 Reference 14: Gas Generation Testing of Plutonium Dioxide

This reference¹⁴ discusses hydrogen and oxygen gas generation rates for plutonium oxide as a function of several parameters including water content and specific surface area. There is no specific surface area data for PuO₂ in this document but reference 17 of this report does contain the specific surface area data associated with these samples. This reference quantifies H₂ and O₂ generation based on water content for PuO₂ calcined at different temperatures. No specific surface area data for PuO₂ was taken from this article for the calculations.

2.2.15 Reference 15: Effect of Precipitation Conditions on the Specific Surface Area of Neptunium Oxide

This reference¹⁵ discusses the precipitation of neptunium oxalate and its calcination to form NpO₂ under normal and bounding HB-Line flowsheet conditions. The report concludes that the calcination time has a bigger effect on the specific surface area of the NpO₂ than the molarity of the nitric acid solution used for the precipitation. There was no PuO₂ specific surface area data in this article that could be used in the regression.

2.2.16 Reference 16: Plutonium Oxide Polishing for MOX Fuel Production

This reference¹⁶ contains data from LANL on the polishing of 120 kg of plutonium from surplus nuclear weapons for the European Mixed Oxide (MOX) Lead Test Assembly (LTA). The plutonium is precipitated as plutonium oxalate by adding oxalic acid to a 2.5 M HNO₃ Pu solution at 65 °C. The plutonium oxalate precipitate was then filtered and washed with dilute oxalic acid in 2 M HNO₃. The reference indicates that some PuO₂ samples were held at 200 °C for 6 hours then ramped to the calcination temperature at 150 °C per hour. The document lists only an average specific surface area value of 9.77 m²/g for calcining PuO₂ at 650 °C for 4 hours. The detailed data for this reference is actually contained in Reference 7 which has already been included in the model development.

2.2.17 Reference 17: Surface Area (BET) and TGA-MS Analysis of Calcined Neptunium Oxide

This reference¹⁷ discusses gas generation tests and moisture measurements for NpO₂ for the 9975 Safety Analysis Report for Packaging (SARP). This article describes the experimental and analytical testing equipment used to produce NpO₂ following the January 2003 version of the HB-Line Phase II flowsheet. Although this report focuses on the NpO₂, there are some PuO₂ specific surface area data in Table 1 and 9 of this reference. Note that these PuO₂ samples are also discussed in reference 6 and 14 of this literature review concerning gas generation for long term storage. This reference indicates that all the PuO₂ samples were held at 450 °C for 4 hours then heated to their final calcination temperature for 2 hours. For this reason, the calcination times t_2 for calcination temperature T_2 are calculated as follows:

$$t_2 = \frac{450}{T_2} \cdot 4 + 2$$

For example, the calcination time for the 950 °C data is treated as 3.89 hours. All the PuO₂ specific surface area data points from this reference were used in the regression.

2.2.18 Reference 18: Moisture and Surface Area Measurements of Plutonium-Bearing Oxides

This reference¹⁸ discusses the moisture and surface area measurements of plutonium oxide samples prepared at 950 °C for 2 hours. This report has some specific surface area data in its Table 2 but the surface area points were lower than other values seen in this literature review. The article notes that the SSA values are lower than normal and indicates that the presence of chloride salts may be the reason. For this reason and since other data was available at this temperature, no PuO₂ specific surface area data in this article was used for the later empirical fits.

2.2.19 Reference 19: Hydration of Plutonium Oxide and Process Salts NaCl, KCl, CaCl₂, MgCl₂

This reference¹⁹ is a literature review of the data for dehydration and rehydration of PuO₂, NaCl, KCl, CaCl₂, and MgCl₂ and impure oxides containing chloride salts. The pure PuO₂ specific surface area data in this article is the same data already cited in Reference 2 and 3 of this literature review. Therefore there is no new PuO₂ specific surface area data in this article to develop correlations.

2.2.20 Reference 20: Thermodynamics of Water Sorption on PuO₂: Consequences for Oxide Storage and Solubility

This reference²⁰ discusses the thermodynamics of water adsorption/desorption with respect to PuO₂ and derives the Gibbs free energies associated with the adsorption/desorption. The article does not contain any specific surface area for PuO₂ that could be used for our purpose.

2.2.21 Reference 21: Surface chemistry of Pu oxides

This reference²¹ examines the surface chemistry of Pu(IV) compounds including PuO₂ and Pu(OH)₄. The different Pu oxidation states are discussed and the impact of temperature on them. The article did indicate that the PuO₂ surfaces formed hydroxyls when exposed to moisture in the air which persisted to 590 °C. However, the article does not contain any specific surface area for PuO₂ that could be used for calculations.

2.2.22 Reference 22: Thermodynamic Data for Hydrus and Anhydrous PuO_{2+x}(s)

This reference²² discusses the thermodynamic properties of hydrous and anhydrous PuO_{2+x} compounds. However, the article does not contain any specific surface area for PuO₂ that could be regressed.

2.2.23 Reference 23: Calculations of Thermodynamic Properties of PuO₂ by the First-Principles and Lattice Vibration

This reference²³ describes the thermodynamic properties of PuO₂ using first-principles and lattice dynamics calculations. This article does not contain any specific surface area for PuO₂ that could be used to develop a model.

2.2.24 Reference 24: Thermodynamic Modeling of the Plutonium-Oxygen System

This reference²⁴ examines the thermodynamic functions and phase equilibria of the plutonium–oxygen system. The article points out some inconsistencies found for the oxygen chemical potential and vaporization data of Pu₂O₃ + PuO_{2-x} and PuO_{2-x} compounds. However, this article does not contain any specific surface area data or PuO₂ for calculations.

2.2.25 Reference 25: White Paper on Possible Inclusion of Mixed Plutonium-Uranium Oxides in DOE-STD-3013-96

This reference²⁵ describes properties for mixed UO₂-PuO₂ oxide (5-35 wt % Pu) that are calcined under a 6 vol % H₂ and 94 vol % N₂ environment. For this reason the specific surface area data in this article was not used in the later empirical correlations. The article does show that as the Pu wt % increases in the co-precipitated samples that the specific surface area goes down.

2.2.26 Reference 26: Characterization of Representative Materials in Support of Safe, Long Term Storage of Surplus Plutonium in DOE-STD-3013 Containers

This reference²⁶ has some specific surface area data versus different PuO₂ preparation methods at 950 °C in its Figure 5 but gives no details like time or numerical values. For this reason the specific surface area data in this document was not included for calculations.

2.2.27 Reference 27: Characterization of Representative Materials in Support of Safe, Long Term Storage of Surplus Plutonium in DOE-STD-3013 Containers

This reference²⁷ discusses the process (block flow diagrams, equipment flowsheets, stream material balances) for plutonium(IV) oxalate precipitation and PuO₂ calcination for a 100-kg plutonium per day facility. The specific surface area data for PuO₂ in Table 3 of this reference originates from reference 8 of the current report. There was no new specific surface area data in this document to be used in the calculations.

2.2.28 Reference 28: Monthly Report Hanford Atomic Products Operation

This reference²⁸ provides a monthly status for the operations of the Hanford Purex Plant from 1956. The report only mentions that hydrated UO₂ after 1 hour at 480 °C had a specific surface area of 7.38 m²/g. There was no specific surface area data for PuO₂ in this document to be used in the model development.

2.2.29 Reference 29: Savannah River Laboratory Monthly Report, ²³⁸Pu Fuel Form Processes

This reference²⁹ provides a monthly status for the ²³⁸Pu Fuel program at Savannah River Laboratory in 1973. Table 1 in this report lists some specific surface area measurements for ²³⁸PuO₂ calcined at 700 °C. However, there were no calcination times given and the SSA values of 0.73, 1.10, and 1.73 m²/g were significantly lower than the other 700 °C data in this literature review (5.7-10.8 m²/g). Therefore no specific surface area data for PuO₂ in this document was used in the current modeling.

2.2.30 Reference 30: Properties of Plutonium Dioxide

This reference³⁰ discusses the physical and chemical properties of PuO₂ made from different starting materials like Pu(NO₃)₄, Pu(OH)₄, and Pu(C₂O₄)₂. All the starting materials in this document were dried at 120 to 140 °C for 1 hour then heated to the specified calcination temperature at a controlled rate in the muffle furnace that had a stirred bed. The report states that the stirring bed during calcination only seemed to make a difference in the uniformity of the oxides for the less than 400 °C calcination samples. This reference also states that plutonium oxalate does not completely decompose into PuO₂ until reaching temperature greater than 300 °C and the PuO₂ will not approach stoichiometry until the temperature goes above 800 °C. Table 9 of this reference gives a specific surface area for PuO₂ from oxalate of 41.4 m²/g at 400 °C but did not list the calcination time. Based on the other data in this literature review, it is assumed that the calcination time for this 400 °C point is 2.1 hours for the calculations. If other information becomes available then this calcination time can be changed. This reference also presents data on the solubility of PuO₂ in various solvents like 12-16 M HNO₃ with 0.002-0.01 M HF and makes the generalization that the higher the calcination temperature the less soluble the oxide. Table 10 of this reference lists crystal size of PuO₂ from the various starting materials over the various calcination temperatures. This reference also gives the moisture or water gain data for the 60, 20, 10 m²/g PuO₂ from oxalate and indicates that Pu oxalate decomposes to the oxide between 160 and 350 °C.

2.2.31 *Reference 31: Plutonium(III) Oxalate Precipitation and Calcination Process for Plutonium Nitrate To Oxide Conversion*

This reference³¹ discusses the equipment flowsheets and mass balances for plutonium(III) oxalate precipitation and PuO₂ calcination for a 100-kg plutonium per day facility. This report focuses on the precipitation and calcination process and the performance of the PuO₂ manufactured. Three specific surface area data points at 600 °C, 750 °C, and 735 °C calcination temperatures are cited in Table 6 of this reference. The 600 °C data point came from adding 0.8 M oxalic acid at room temperature to a 1.3 M HNO₃, 32 g/L Pu solution (added sulfamic acid to stabilize valence) followed by filtering then washing with a 0.5 M HNO₃, 0.3 M H₂C₂O₄ solution. The plutonium oxalate precipitate for this first data point was air dried at 110 °C for 3 hours, heated 1 hour in N₂ at 150 °C, heated to 600 °C in 1 hour in air, and then held at 600 °C for 3 hours in air. The 750 °C data point came from adding solid oxalic acid at room temperature to 1.84 M HNO₃, 125 g/L Pu solution (added urea to stabilize valence) followed by filtering then washing with water. The plutonium oxalate precipitate for this 750 °C data point was air dried at room temperature for 30 minutes, heated to 750 °C in 2 hours in steam, and then held at 750 °C for 4 hours in steam. The 735 °C data point came from adding 0.9 M oxalic acid at 35 °C to a 1.5 M HNO₃, 4-6 g/L Pu solution (added hydrazine to stabilize valence) followed by filtering then washing with a 0.5 M HNO₃, 0.2 M H₂C₂O₄ solution. The plutonium oxalate precipitate for this third data point was heated immediately (no time given) to 735 °C in air then held at 735 °C for 2 hours in air. The 600 °C and 735 °C specific surface area data points were used in the empirical fits discussed later since the calcination was in air and the 750 °C data point was not used since it was calcined in steam.

2.2.32 *Reference 32: Interim Report on Plutonium Oxalate Precipitation Work*

This reference³² examines how precipitation conditions like oxalate to plutonium molar ratio, ionic strength, residence time, temperature, and agitation affect plutonium oxalate properties like particle growth rates and particle structures. There was no specific surface area data for PuO₂ in this document to be used in the modeling.

2.2.33 *Reference 33: Control of Particle Size and Structure*

This reference³³ presents information on how the precipitation conditions of plutonium oxalate affect the particle size and structural properties of PuO₂. There was no specific surface area data for PuO₂ in this document to be used in the calculations.

2.2.34 *Reference 34: The Thermal Decomposition of Hydrated Plutonium(IV) Oxalates*

This reference³⁴ presents thermal decomposition data for hydrated plutonium(IV) oxalates in air and in nitrogen over the temperature range of 20 to 830 °C. This reference states that in air the plutonium oxalate begins to lose waters of hydration at 45 to 60 °C and between 200 and 290 °C a mixture of PuO₂ and Pu(CO₃)₂ forms. There was no specific surface area data for PuO₂ in this reference to be used in the model development.

2.2.35 Reference 35: Precipitation of Plutonium(III) Oxalate and Calcination to Plutonium Dioxide

This reference³⁵ discusses the precipitation of plutonium(III) oxalate from nitric acid, hydrochloric acid, and sulfamic acid solutions then its calcination. This reference indicates that Pu(III) oxalate decomposes between 300 and 400 °C. The calcination method used in this report was to heat in air from 25 to 125 °C in 1 hour then hold at 1 hour then increase the temperature 3 to 5 °C per minute to the final calcination temperature. The sample would be held for 1 to 2 hours at the final calcination temperature and then allowed to cool to room temperature in an air stream. There was no specific surface area data for PuO₂ in this reference.

2.2.36 Reference 36: Thermal Decomposition of Plutonium (IV) Oxalate and Hydrofluorination of Plutonium (IV) Oxalate and Oxide

This reference³⁶ discusses the decomposition of plutonium(IV) oxalate and the factors affecting the reactivity of the plutonium oxide with hydrogen fluoride. Table 1 in this reference contains PuO₂ particle sizes and surface area per unit volume data for various calcination temperatures but no calcination times. The PuO₂ particle sizes of this reference do not seem to match the newer data (later than 1956) in this literature survey so it is recommended not to use it. Figure 18 of this reference has surface area per unit volume plotted versus calcination temperature but not in the same units as the other area data so it should not be used. No specific surface area data for PuO₂ in this reference was used in the calculations.

2.2.37 Reference 37: Thermal Decomposition of Plutonium Oxalates

This reference³⁷ discusses the various thermal decomposition forms for plutonium oxalate in air for Pu(III) and Pu(IV). There was no specific surface area data for PuO₂ in this reference.

2.2.38 Reference 38: Determination of Plutonium Dioxide Surface Areas from X-Ray Crystallite Sizes

This reference³⁸ describes a relationship between plutonium dioxide surface areas and the X-ray crystallite sizes. This article states that the X-ray average crystal size increases as the surface area decreases across the different starting materials like peroxide, metal, oxalate, hydroxide, etc. Note that the PuO₂ in this article came from calcining plutonium peroxide. There was no specific surface area data for PuO₂ in this reference.

2.2.39 Reference 39: Development of Plutonium-Bearing Fuel Materials, NUMEC-2389-2

This reference³⁹ discusses early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. For this reference 0.8 M peroxide was added to 3 M HNO₃, 26.4-69.6 g/L Pu solutions followed by 1 M oxalic acid with holdup of 30 minutes to form the plutonium oxalate and the precipitate was dried at 100 °C or 180 °C for 16 hours before the calcination. Table 2 of this reference contains PuO₂ specific surface area data for 760 °C calcination with relative short calcination times (0.3-0.5 hours). Since this surface area data matched other data in this literature review, all the data points were used in the regression.

2.2.40 *Reference 40: Development of Plutonium Bearing Fuel Materials, NUMEC-2389-3*

This reference⁴⁰ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials concerning the extrusion of plutonium wire. No specific surface area data was given.

2.2.41 *Reference 41: Development of Plutonium Bearing Fuel Materials, NUMEC-2389-4*

This reference⁴¹ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials concerning mixed oxide sintering studies, preparation of high burn up test specimens, and physical property measurements. This reference focuses on co-precipitated UO₂-PuO₂ materials but there is some PuO₂ specific surface area in Tables 2.3 and 2.4. However, this surface area data is a repeat of the data in Reference 39 of this literature review. Therefore, no new specific surface area data from this reference will be included in the calculations.

2.2.42 *Reference 42: Irradiation Testing of UO₂-PuO₂ Fuels, NUMEC-3432-6*

This reference⁴² documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials concerning the irradiation of instrumented capsules containing UO₂-PuO₂. No specific surface area data was given.

2.2.43 *Reference 43: Development of Plutonium Bearing Fuel Materials, NUMEC-P-20*

This reference⁴³ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials concerning glove-box and equipment setup. This reference had some specific surface area data for thoria. However, no PuO₂ specific surface area data was provided.

2.2.44 *Reference 44: Development of Plutonium Bearing Fuel Materials, NUMEC-P-34*

This reference⁴⁴ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. This reference had some specific surface area data for co-precipitated UO₂-PuO₂ from ammonia. However, no PuO₂ specific surface area data was included.

2.2.45 *Reference 45: Development of Plutonium Bearing Fuel Materials, NUMEC-P-37*

This reference⁴⁵ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. This reference had some specific surface area data for co-precipitated UO₂-PuO₂ from ammonia but no PuO₂ specific surface area data.

2.2.46 *Reference 46: Development of Plutonium Bearing Fuel Materials, NUMEC-P-39*

This reference⁴⁶ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. No PuO₂ specific surface area data was identified.

2.2.47 Reference 47: Development of Plutonium Bearing Fuel Materials, NUMEC-P-40

This reference⁴⁷ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. This reference had some specific surface area data for UO₂ from ammonia but none for PuO₂.

2.2.48 Reference 48: Development of Plutonium Bearing Fuel Materials, NUMEC-P-44

This reference⁴⁸ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials concerning the preparation and characterization of samples for in-pile tests. No PuO₂ specific surface area data was included.

2.2.49 Reference 49: Development of Plutonium-Bearing Fuel Materials, NUMEC-P-60

This reference⁴⁹ discusses early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. For this reference 0.8 M peroxide was added to a 3 M HNO₃, 100 g/L Pu solution followed by 1 M oxalic acid at 55 °C with holdup of 65 minutes to form the plutonium oxalate which was then filtered. The filtered precipitate was then dried 5 hours in air at 80 °C, 5 hours at 130 °C, and then 1 hour at 180 °C before the calcination. Table 2.1 of this reference gives a specific surface area of 28.7 m²/g for the 350 °C calcination. Even though this 350° data point seems low, the mean of the other 350 °C data was 59.46 m²/g with a standard deviation of 13.31 giving 3σ or 99.7% inclusion limits of 20 to 99 m²/g so this data point will be used in the calculations.

2.2.50 Reference 50: Development of Plutonium-Bearing Fuel Materials, NUMEC-P-70

This reference⁵⁰ discusses early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. For this reference 0.25 M peroxide was added to a 3 M HNO₃, 100 g/L Pu solution followed by 1 M oxalic acid at 28 °C with holdup of 20 minutes to form the plutonium oxalate which was then filtered. This reference states that the plutonium oxalate was washed with an unspecified amount of deionized water then air dried for 10 minutes then placed in a forced-convection oven for an unspecified time and temperature to remove excess moisture before calcination. Table 2.1 and 2.2 of this reference give PuO₂ specific surface area data but there are no calcination times listed. Therefore, no PuO₂ specific surface area data in this document will be used in the calculations.

2.2.51 Reference 51: Development of Plutonium Bearing Fuel Materials, NUMEC-P-101

This reference⁵¹ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. In Table 2.4 of this reference are specific surface area data for UO₂. No PuO₂ specific surface area data was listed.

2.2.52 Reference 52: Development of Plutonium Bearing Fuel Materials, NUMEC-P-102

This reference⁵² documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. This reference has specific surface area data for co-precipitated UO₂ with 0.5, 12.5, and 35 wt % PuO₂. Figure 2.2 in this reference shows that the higher weight percent PuO₂ in the co-precipitated oxide and a reducing N₂ calcination environment lowers the specific surface area of the oxides. Table 2.6 in this reference has specific surface area data for PuO₂ from hydroxide. However, no pure PuO₂ from oxalate specific surface area data was given.

2.2.53 Reference 53: Development of Plutonium-Bearing Fuel Materials, NUMEC-P-103

This reference⁵³ discusses early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. For this reference 0.8 M peroxide was added to 3 M HNO₃, 100-200 g/L Pu solutions followed by 1 M oxalic acid at 35 °C with holdup of 30 minutes to form the plutonium oxalate. The plutonium oxalate was then dried at 180 °C for 16 hours. This reference states that the plutonium oxalate was washed with 1 liter of deionized water before calcining at 760 °C for 30 minutes. Table 2.3 of this reference gives PuO₂ specific surface area data which was used in the current calculations.

2.2.54 Reference 54: Development of Plutonium-Bearing Fuel Materials, NUMEC-P-104

This reference⁵⁴ discusses early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials concerning the formation of PuO₂ from peroxide. This reference states that the peroxide precipitation behaved like the oxalate precipitation. However, since the PuO₂ was not formed by oxalate precipitation, the specific surface area data were not used.

2.2.55 Reference 55: Development of Plutonium Bearing Fuel Materials, NUMEC-P-105

This reference⁵⁵ documents early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. For this reference 0.8 M peroxide was added to a 3 M HNO₃, 200 g/L Pu solution followed by 1 M oxalic acid at 35 °C with holdup of 30 minutes to form the plutonium oxalate. The plutonium oxalate precipitate was then dried at 100 °C for 24 hours before calcining at 760 °C for 30 minutes. Table 2.4 of this reference gives a specific surface area of 4.88 m²/g for this PuO₂ sample. This reference has mostly specific surface area data for co-precipitated UO₂ with 0.5, 12.5, 35 and wt % PuO₂. This data point was used in the calculations.

2.2.56 Reference 56: Development of Plutonium-Bearing Fuel Materials, NUMEC-P-103

This reference⁵⁶ discusses early work for the preparation and characterization of PuO₂ and PuO₂-UO₂ materials. For this reference 0.8 M peroxide was added to a 3 M HNO₃, 228.3 g/L Pu solution followed by 1 M oxalic acid at 35 °C with holdup of 30 minutes to form the plutonium oxalate which was then dried for 16 hours at 150 °C before calcination. Table 2.2 of this reference gives PuO₂ specific surface area data that was used in the calculations.

2.2.57 Reference 57: *Ceramic Properties of PuO₂*

This reference⁵⁷ is a literature survey of the physical properties for PuO₂ from NUMEC-P-10 through P-106, NUMEC-2389-1,4,6 reports as well as many other references. This reference contains specific surface area which originates from reference 4 (NUMEC-P-80) and 5 (NUMEC-P-90) of this literature review. Therefore, no new PuO₂ specific surface area data is available from this document.

2.2.58 Reference 58: *Savannah River Laboratory Monthly Report: Pu-238 Fuel Form Process*

This reference⁵⁸ contains some SSA data in its Table 5 for reverse and direct strike of 0.9 M Oxalic acid to a 0.4 M HNO₃, 4 g/L Pu feed solution with hydrazine and ascorbic acid. This reference concludes that the SSA is independent of the particle morphology but dependent on the internal porosity of the PuO₂. This reference also discusses how Pu₂(C₂O₄)₃·10H₂O dehydrates at 55 to 195 °C to form Pu₂(C₂O₄)₃ and loses CO and CO₂ at 300 to 350 °C to form PuO₂. This reference also states that the 10 to 15 m²/g increase in surface area from 250 °C to 350 °C may be due to lattice disruption from gas evolution or a change in crystallite size between the oxide and the oxalate phases. The specific surface area data from this document will be used in the calculations.

2.3 Calcination Temperature, Time, and Specific Surface Area Data from Literature Reviewed

Table 2-4 lists all the calcination temperature, time, and specific surface area data from all the references cited in Section 2.2. An * next to a calcination time means that it is an estimated value based on other times from this data set or how the sample was calcined (see each reference in Section 2.2). Should more correct calcination times be identified then the values can be updated. The SSA values with superscripts are not used in the correlation. The superscripts are ^lmissing time, ^pperoxide precipitation, ^σoutside ±3σ limits, ^hmixed plutonium-uranium oxides calcined in 6 vol% H₂ – 94 vol% N₂, ^aaverage value of Ref 7 values, ^dduplicate reference value, and ^scalcined in steam. More details of these exclusions are in Section 2.2 for each reference. These choices can be modified later as more information becomes available. Figure 2-1 is a plot of the calcination temperature versus the specific surface area data for all the references.

Table 2-4. All Calcination Temperature, Time, and SSA Data

Calcination Temperature [°C]	Calcination Time [h]	SSA [m ² /g]	Reference	Year
250	2.0	61	58	1975
250	2.0	61.7	58	1975
350	0.25	52	5	1961
350	0.50	43	4	1961
350	NA	25.8 ^t	50	1961
350	1.0	28.7	49	1961
350	2.0	68.9	58	1975
350	2.0	76.4	58	1975
350	2.1*	57	3	1995
400	2.1*	41.4	30	1965
450	4	38.88	17	2003
450	4	39.09	17	2003
450	4	40.56	17	2003
450	4	40.97	17	2003
450	10	12.3 ^σ	1	1996
490	NA	17.9 ^t	50	1961
490	0.5	19.5 ^p	54	1963
490	0.5	23.7 ^p	54	1963
490	0.5	26 ^p	54	1963
550	2.0	30.6	58	1975
550	2.0	41.1	58	1975
550	9.09*	9.1 ^σ	1	1996
600	3	27	31	1980
600	6	21	13	2006
600	12	23.9	3	1995
650	1.3	10 ^h	25	1997
650	4	9.77 ^a	16	2005
650	4	4.93	7	2007
650	4	10.18	7	2007
650	4	9.76	7	2007
650	4	10.54	7	2007
650	4	10.86	7	2007
650	4	7.89	7	2007
650	4	8.47	7	2007
650	4	9.29	7	2007
650	4	8.64	7	2007
650	4	9.08	7	2007
650	4	8.30	7	2007
650	4	10.31	7	2007
650	4	10.23	7	2007
650	4	8.91	7	2007
650	4	13.56	7	2007
650	4	11.50	7	2007

Table 2-4. All Calcination Temperature, Time, and SSA Data

Calcination Temperature [°C]	Calcination Time [h]	SSA [m ² /g]	Reference	Year
650	4	10.37	7	2007
650	4	8.04	7	2007
650	4	9.07	7	2007
650	4	8.90	7	2007
650	4	10.54	7	2007
650	4	12.04	7	2007
650	4	13.51	7	2007
650	4	11.14	7	2007
650	4	8.35	7	2007
650	4	8.11	7	2007
650	4	9.82	7	2007
650	4	11.20	7	2007
650	4	6.85	7	2007
650	4	7.45	7	2007
650	4	7.70	7	2007
650	4	7.82	7	2007
650	4	8.11	7	2007
650	4	8.22	7	2007
650	4	7.87	7	2007
650	4	8.75	7	2007
650	4	9.01	7	2007
650	4	9.89	7	2007
650	4	14.86	7	2007
650	4	9.07	7	2007
650	4	7.77	7	2007
650	4	8.19	7	2007
650	4	9.07	7	2007
650	4	9.37	7	2007
650	4	9.26	7	2007
650	8.46*	7.9	1	1996
700	NA	1.73 ^t	29	1973
700	12	5.7 ^d	2	1997
700	12	5.7	3	1995
700	4.57*	9.48	17	2003
700	4.57*	10.83	17	2003
735	2	4.2	8	1976
735	2	4.2	31	1980
735	2	4.5	8	1976
735	2	6.4	8	1976
735	2	7.3	8	1976
735	2	7.5	8	1976
735	2.0	9.1	58	1975
735	2	14 ^σ	8	1976
750	4	10 ^s	31	1980

Table 2-4. All Calcination Temperature, Time, and SSA Data

Calcination Temperature [°C]	Calcination Time [h]	SSA [m ² /g]	Reference	Year
750	8*	2	1	1996
760	0.08	10.5	3	1995
760	0.28	7.5	3	1995
760	0.28	7.5	4	1961
760	0.28	9.11	39	1964
760	0.28	9.55	39	1964
760	0.28	9.94	39	1964
760	0.5	3.4	3	1995
760	0.5	3.4	4	1961
760	0.5	3.69	56	1963
760	0.5	3.99	56	1963
760	0.5	4.88	55	1963
760	0.5	5.4	4	1961
760	0.5	5.49	53	1962
760	0.5	5.83	53	1962
760	0.5	6.58	39	1964
760	0.5	7.15	5	1961
760	0.5	7.89	53	1962
760	0.5	8.3	5	1961
760	0.5	8.66	56	1963
760	NA	9 ^t	50	1961
760	1.00	6.1	5	1961
800	2.0	5.5	58	1975
800	2.0	5.7	58	1975
800	10	5.8	3	1995
850	7.65*	2.6	1	1996
900	1.3	5 ^h	25	1997
950	2	2.7	3	1995
950	3.89*	1.54	17	2003
950	3.89*	1.65	17	2003
950	3.89*	1.87	17	2003
950	3.89*	1.88	17	2003
950	7.37*	2.1	1	1996
975	7.69*	1.09	13	2006
1050	7.14*	1.2	1	1996
1100	2.0	<1	58	1975
1100	2.0	<1	58	1975

*estimated time value

^tmissing time, ^pperoxide precipitation, ^σoutside ±3σ limits, ^hmixed plutonium-uranium oxides calcined in 6 vol% H₂ – 94 vol% N₂, ^aaverage value of Ref 7 values, ^dduplicate ref. value, ^scalcined in steam so not used in correlation

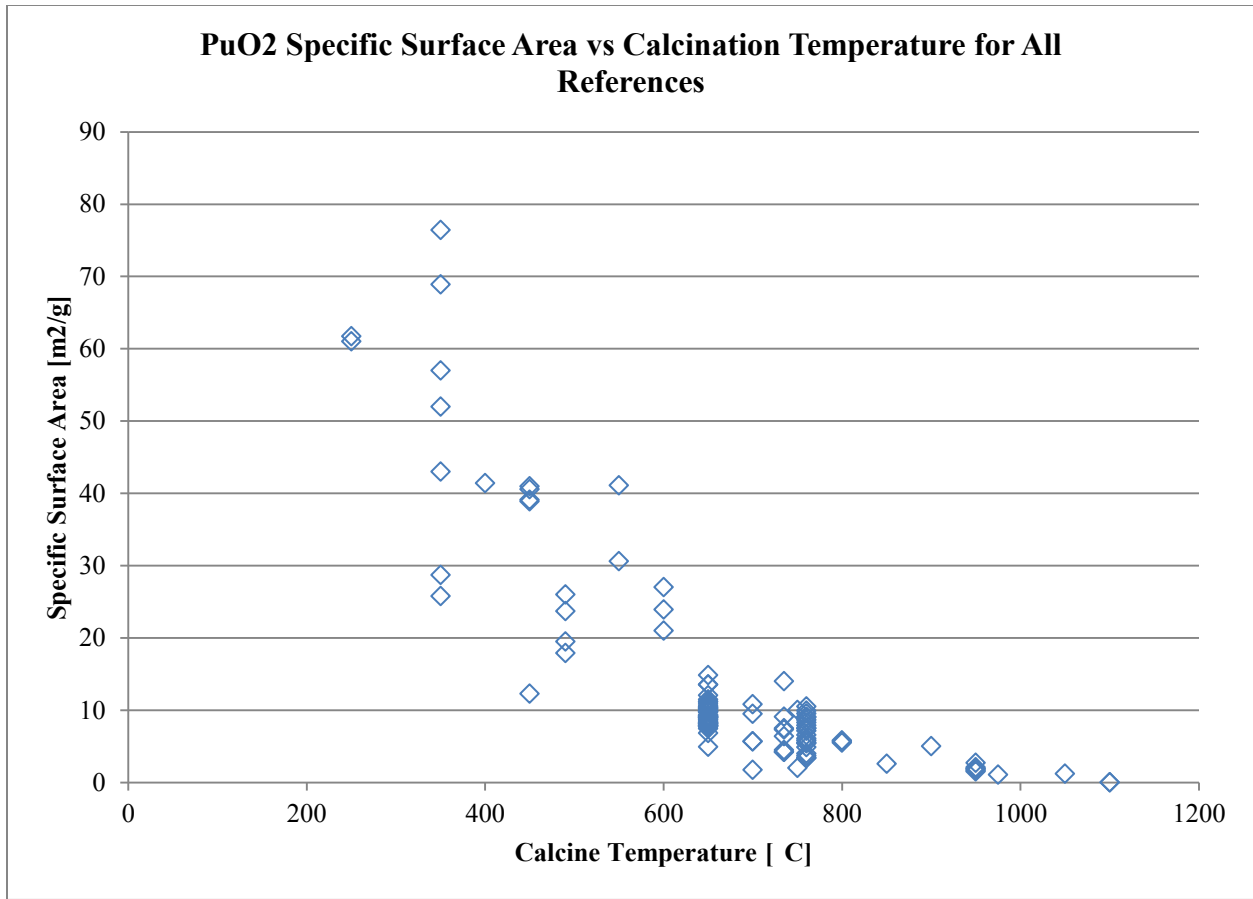


Figure 2-1. PuO₂ Specific Surface Area vs Calcination Temperature for References

To try to identify the relation between calcination temperature and time of plutonium oxalate (Pu(C₂O₄)₂) on the specific surface area of the plutonium oxide (PuO₂) formed, some of the SSA data from the various references was excluded depending on how the PuO₂ was being formed or based on like temperature/time data from the literature reviewed. Note that an * next to a calcination time means that it is an estimated value based on other times from this data set or how the sample was calcined. Should more correct calcination times be identified then the values can be updated. This refined set of data as shown in Table 2-5 will be used to try an empirical fit to examine the effect of calcination temperature and time of Pu(C₂O₄)₂ on the specific surface area of PuO₂ formed. Figure 2-2 is a plot of the calcination temperature versus the specific surface area data for the empirical fit.

Table 2-5. Calcination Data of Pu(C₂O₄)₂ to PuO₂ used for Regression

Calcination Temperature [°C]	Calcination Time [h]	SSA [m ² /g]	Reference	Year
250	2.0	61	58	1975
250	2.0	61.7	58	1975
350	0.25	52	5	1961
350	0.50	43	4	1961
350	1.0	28.7	49	1961
350	2.0	68.9	58	1975
350	2.0	76.4	58	1975
350	2.1*	57	3	1995
400	2.1*	41.4	30	1965
450	4	38.88	17	2003
450	4	39.09	17	2003
450	4	40.56	17	2003
450	4	40.97	17	2003
550	2.0	30.6	58	1975
550	2.0	41.1	58	1975
600	6	21	13	2006
600	3	27	31	1980
600	12	23.9	3	1995
650	4	4.93	7	2007
650	4	10.18	7	2007
650	4	9.76	7	2007
650	4	10.54	7	2007
650	4	10.86	7	2007
650	4	7.89	7	2007
650	4	8.47	7	2007
650	4	9.29	7	2007
650	4	8.64	7	2007
650	4	9.08	7	2007
650	4	8.30	7	2007
650	4	10.31	7	2007
650	4	10.23	7	2007
650	4	8.91	7	2007
650	4	13.56	7	2007
650	4	11.50	7	2007
650	4	10.37	7	2007
650	4	8.04	7	2007
650	4	9.07	7	2007
650	4	8.90	7	2007
650	4	10.54	7	2007
650	4	12.04	7	2007
650	4	13.51	7	2007
650	4	11.14	7	2007
650	4	8.35	7	2007
650	4	8.11	7	2007
650	4	9.82	7	2007
650	4	11.20	7	2007

Table 2-5. Calcination Data of Pu(C₂O₄)₂ to PuO₂ used for Regression

Calcination Temperature [°C]	Calcination Time [h]	SSA [m ² /g]	Reference	Year
650	4	6.85	7	2007
650	4	7.45	7	2007
650	4	7.70	7	2007
650	4	7.82	7	2007
650	4	8.11	7	2007
650	4	8.22	7	2007
650	4	7.87	7	2007
650	4	8.75	7	2007
650	4	9.01	7	2007
650	4	9.89	7	2007
650	4	9.07	7	2007
650	4	7.77	7	2007
650	4	8.19	7	2007
650	4	9.07	7	2007
650	4	9.37	7	2007
650	4	9.26	7	2007
650	4	14.86	7	2007
650	8.46*	7.9	1	1996
700	4.57*	9.48	17	2003
700	4.57*	10.83	17	2003
700	12	5.7	3	1995
735	2	4.2	8	1976
735	2	4.2	31	1980
735	2	4.5	8	1976
735	2	6.4	8	1976
735	2	7.3	8	1976
735	2	7.5	8	1976
735	2.0	9.1	58	1975
750	8*	2	1	1996
760	0.08	10.5	3	1995
760	0.28	7.5	3	1995
760	0.28	7.5	4	1961
760	0.28	9.11	39	1964
760	0.28	9.55	39	1964
760	0.28	9.94	39	1964
760	0.5	3.4	3	1995
760	0.5	3.4	4	1961
760	0.5	3.69	56	1963
760	0.5	3.99	56	1963
760	0.5	4.88	55	1963
760	0.5	5.4	4	1961
760	0.5	5.49	53	1962
760	0.5	5.83	53	1962
760	0.50	6.58	39	1964
760	0.50	7.15	5	1961
760	0.5	7.89	53	1962

Table 2-5. Calcination Data of Pu(C₂O₄)₂ to PuO₂ used for Regression

Calcination Temperature [°C]	Calcination Time [h]	SSA [m ² /g]	Reference	Year
760	0.5	8.3	5	1961
760	0.5	8.66	56	1963
760	1.00	6.1	5	1961
800	2.0	5.5	58	1975
800	2.0	5.7	58	1975
800	10	5.8	3	1995
850	7.65*	2.6	1	1996
950	2	2.7	3	1995
950	3.89*	1.54	17	2003
950	3.89*	1.65	17	2003
950	3.89*	1.87	17	2003
950	3.89*	1.88	17	2003
950	7.37*	2.1	1	1996
975	7.69*	1.09	13	2006
1050	7.14*	1.2	1	1996
1100	2.0	1**	58	1975
1100	2.0	1**	58	1975

*estimated time value, **Treat <1 values as 1 for fits

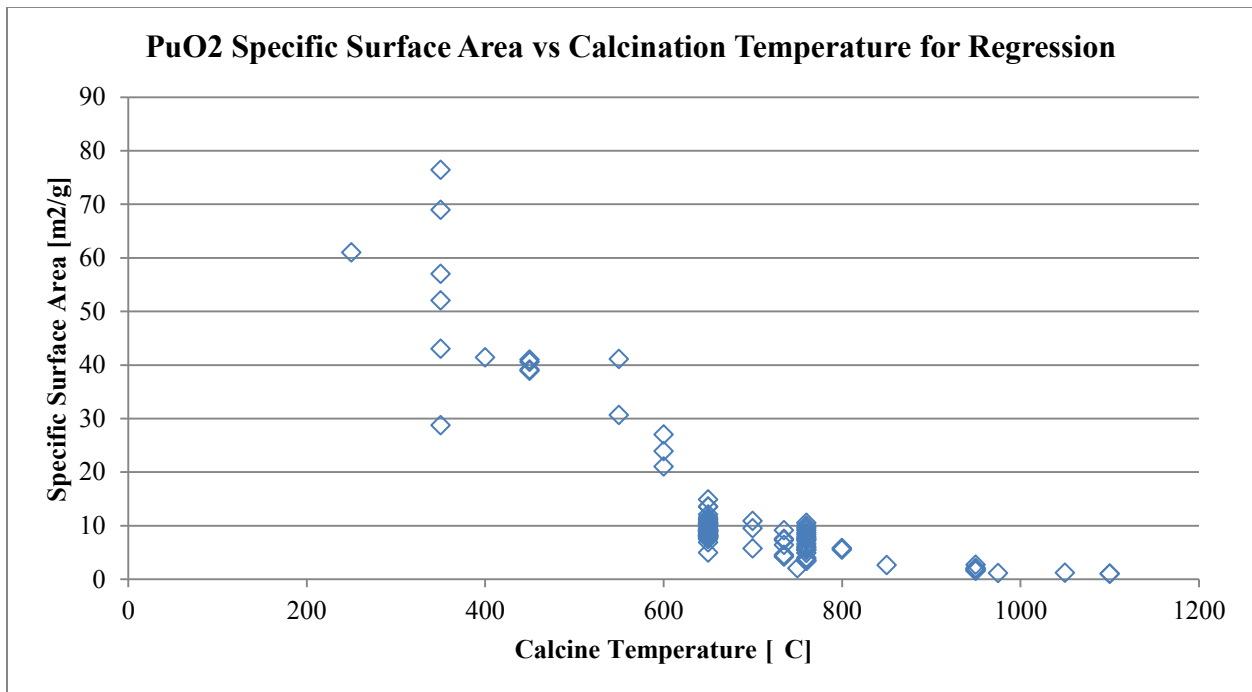


Figure 2-2. PuO₂ Specific Surface Area vs Calcination Temperature for Regression

3.0 Results and Discussion

3.1 Preliminary Regression of 250 -1100 °C Calcination and Time Data for PuO₂ from Pu(C₂O₄)₂

To try to understand the effect of calcination temperature and time of plutonium oxalate (Pu(C₂O₄)₂) on the specific surface area of the formation of PuO₂, the refined data from the literature review in Table 2-5 was imported into the curve fitting program Table Curve 3D version 4.0. Note that this is only a preliminary fit of the data and should be refined as more information or data becomes available. After looking at the various fits that Table Curve 3D derived with and using various knowledge of how the SSA changes with temperature and time, the following equation was chosen:

$$\text{Eqn 3-1} \quad \text{SSA} = A + B * \text{EXP}^{-0.5 * \frac{\text{TEMP}-C}{D}} + E * \text{EXP}^{-0.5 * \frac{\text{TIME}-F}{G}} + H * \text{EXP}^{-0.5 * \frac{\text{TEMP}-C}{D}} + \frac{\text{TIME}-F}{G}$$

where:

SSA = Specific Surface Area of the PuO₂ from Pu(C₂O₄)₂, m²/g
 TEMP = Calcination Temperature in °C
 TIME = Calcination Time in hours
 A = 2.5080E+00, Empirical Fit Parameter
 B = 4.2241E+01, Empirical Fit Parameter
 C = 3.1099E+02, Empirical Fit Parameter
 D = 1.8485E+02, Empirical Fit Parameter
 E = -3.9178E-01, Empirical Fit Parameter
 F = 2.5971E+00, Empirical Fit Parameter
 G = 6.4387E-01, Empirical Fit Parameter
 H = 2.9805E+01, Empirical Fit Parameter
 EXP=exponential function

Using this preliminary fit, the SSA is predicted for the various calcination temperature and time data points of plutonium oxalate (Pu(C₂O₄)₂) from Table 2-5 and shown in Table 3-1. A 2D representation of this empirical fit for the full temperature range of 250 to 1100 °C is shown in Figure 3-1 where the predicted SSA values are shown as lines and the observed SSA values are shown as symbols. The empirical fit shows that the calcination temperature has a bigger effect than time on SSA. The fit also shows that at lower temperatures (< 450 °C) the calcination time has a bigger effect on SSA than at higher temperatures (>650 °C). Figure 3-2 shows an enlarged section of the fit between 600 °C and 700 °C noting that there are only observed SSA data points at 600 °C, 650 °C, and 700 °C at certain calcination times. To better visualize this preliminary fit, the 3D plots from Table Curve 3D have been captured and pasted into this report. Figure 3-3 through Figure 3-7 show the plots of the observed SSA values (the round data points in the figures) versus the preliminary regression (the colored red to blue surface) from Eqn 3-1. There is a slight bump in the SSA surface at the low calcination temperatures (250-350 °C) and low times (0-3 hours) which is a reflection of what References 5 and 58 refer to as a breakdown of the crystallite structure of Pu(C₂O₄)₂ and the escape of decomposition gases as the material transforms into plutonium oxide. This transition from Pu(C₂O₄)₂ to PuO₂ is shown in Figure 3-1 as the specific surface area goes up at 350 °C from 1 to 2 hours but then decreases at 3 hours.

Table 3-1. Calcination Data of Pu(C₂O₄)₂ to PuO₂ for Regression of SSA

Calcination Temperature [°C]	Calcination Time [h]	SSA Observed [m ² /g]	SSA Predicted [m ² /g]
250	2.0	61	61
250	2.0	61.7	61
350	0.25	52	44
350	0.50	43	44
350	1.0	28.7	45
350	2.0	68.9	63
350	2.0	76.4	63
350	2.1*	57	65
400	2.1*	41.4	60
450	4	38.88	36
450	4	39.09	36
450	4	40.56	36
450	4	40.97	36
550	2.0	30.6	29
550	2.0	41.1	29
600	6	21	15
600	3	27	22
600	12	23.9	15
650	4	4.93	11
650	4	10.18	11
650	4	9.76	11
650	4	10.54	11
650	4	10.86	11
650	4	7.89	11
650	4	8.47	11
650	4	9.29	11
650	4	8.64	11
650	4	9.08	11
650	4	8.30	11
650	4	10.31	11
650	4	10.23	11
650	4	8.91	11
650	4	13.56	11
650	4	11.50	11
650	4	10.37	11
650	4	8.04	11
650	4	9.07	11
650	4	8.90	11
650	4	10.54	11
650	4	12.04	11
650	4	13.51	11
650	4	11.14	11
650	4	8.35	11
650	4	8.11	11
650	4	9.82	11

Table 3-1. Calcination Data of Pu(C₂O₄)₂ to PuO₂ for Regression of SSA

Calcination Temperature [°C]	Calcination Time [h]	SSA Observed [m ² /g]	SSA Predicted [m ² /g]
650	4	11.20	11
650	4	6.85	11
650	4	7.45	11
650	4	7.70	11
650	4	7.82	11
650	4	8.11	11
650	4	8.22	11
650	4	7.87	11
650	4	8.75	11
650	4	9.01	11
650	4	9.89	11
650	4	9.07	11
650	4	7.77	11
650	4	8.19	11
650	4	9.07	11
650	4	9.37	11
650	4	9.26	11
650	4	14.86	11
650	8.46*	7.9	10
700	4.57*	9.48	7
700	4.57*	10.83	7
700	12	5.7	7
735	2	4.2	7
735	2	4.2	7
735	2	4.5	7
735	2	6.4	7
735	2	7.3	7
735	2	7.5	7
735	2.0	9.1	7
750	8*	2	5
760	0.08	10.5	5
760	0.28	7.5	5
760	0.28	7.5	5
760	0.28	9.11	5
760	0.28	9.55	5
760	0.28	9.94	5
760	0.5	3.4	5
760	0.5	3.4	5
760	0.5	3.69	5
760	0.5	3.99	5
760	0.5	4.88	5
760	0.5	5.4	5
760	0.5	5.49	5
760	0.5	5.83	5
760	0.50	6.58	5

Table 3-1. Calcination Data of Pu(C₂O₄)₂ to PuO₂ for Regression of SSA

Calcination Temperature [°C]	Calcination Time [h]	SSA Observed [m ² /g]	SSA Predicted [m ² /g]
760	0.50	7.15	5
760	0.5	7.89	5
760	0.5	8.3	5
760	0.5	8.66	5
760	1.00	6.1	5
800	2.0	5.5	4
800	2.0	5.7	4
800	10	5.8	4
850	7.65*	2.6	3
950	2	2.7	2
950	3.89*	1.54	3
950	3.89*	1.65	3
950	3.89*	1.87	3
950	3.89*	1.88	3
950	7.37*	2.1	3
975	7.69*	1.09	3
1050	7.14*	1.2	3
1100	2.0	1**	2
1100	2.0	1**	2

*estimated time value, **Treat <1 values as 1 for fits

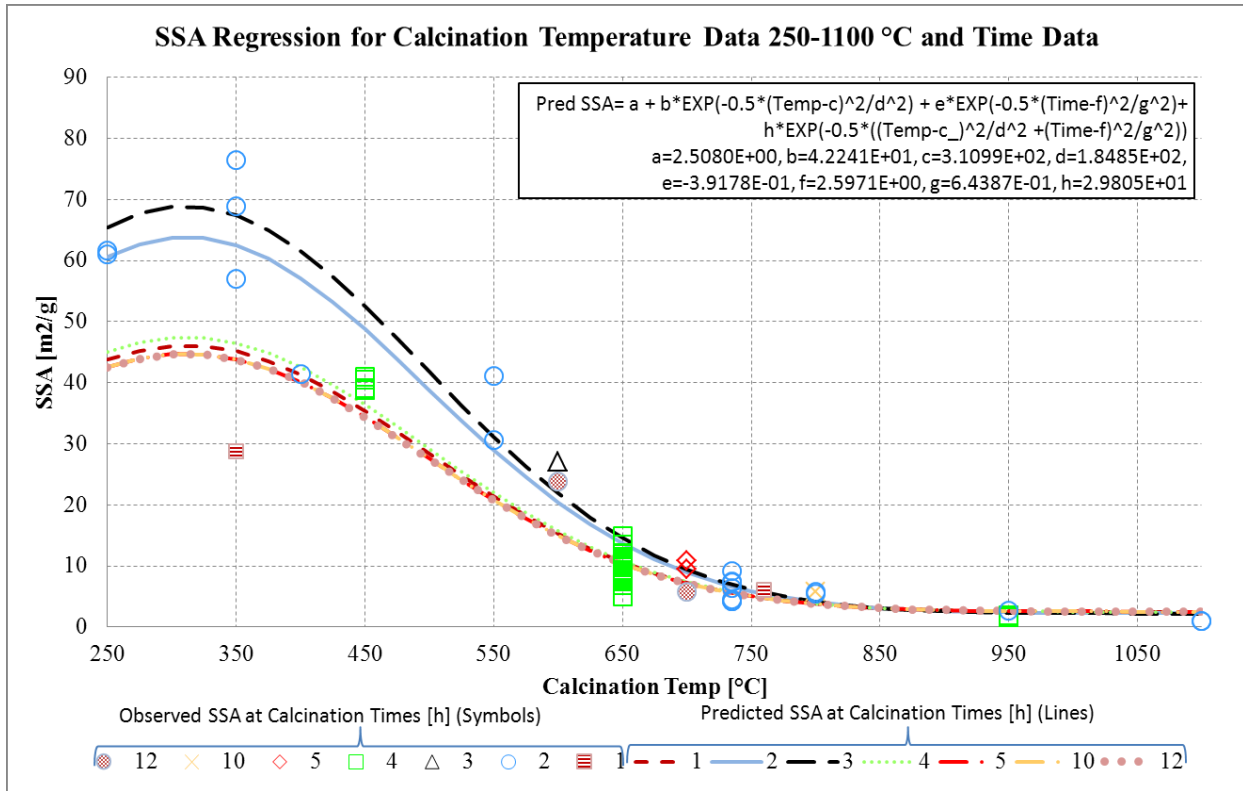


Figure 3-1. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-2D View 1

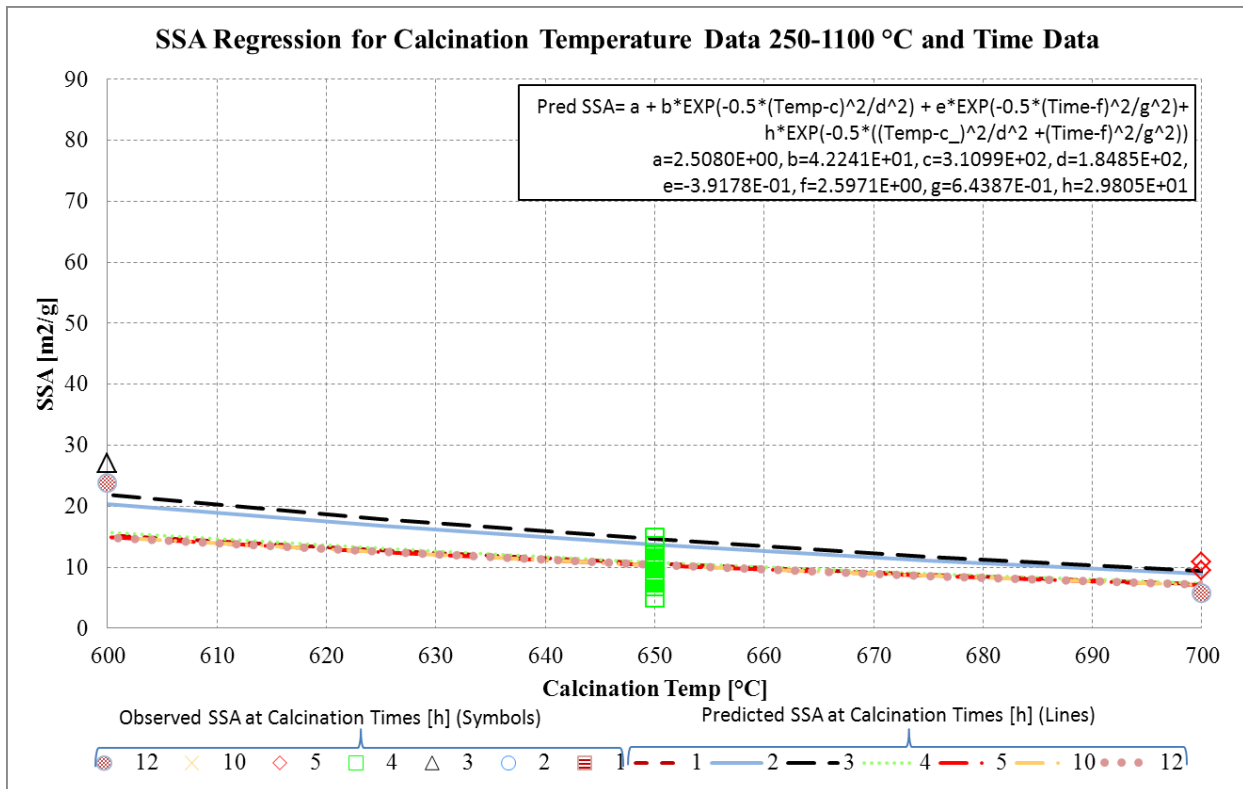


Figure 3-2. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-2D View 2

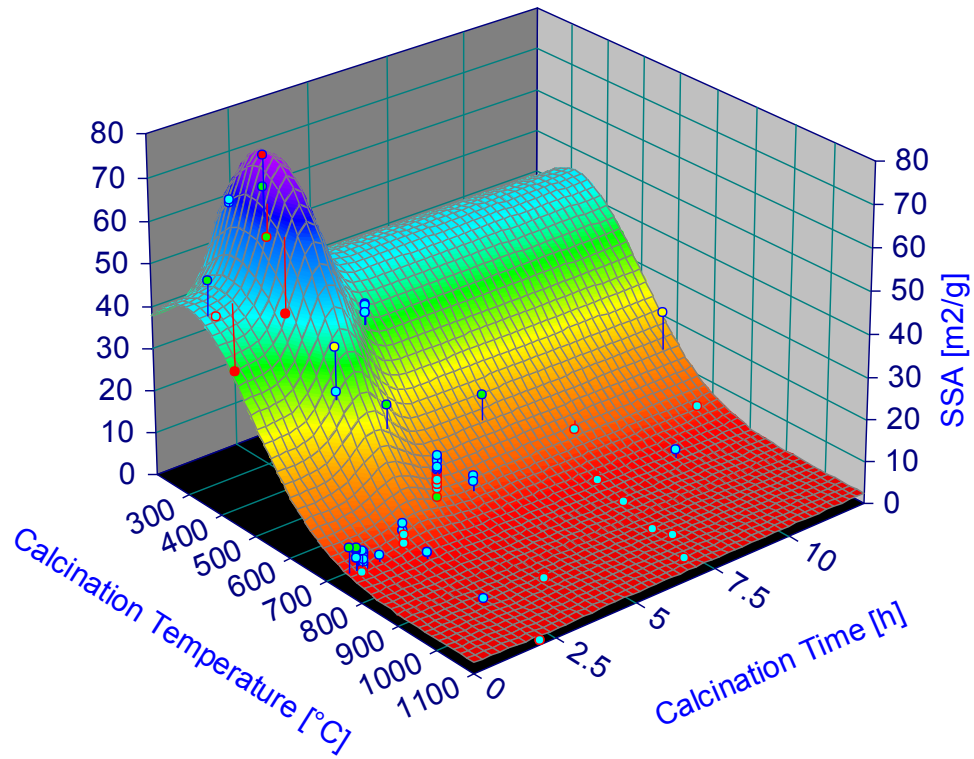


Figure 3-3. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-3D View 1

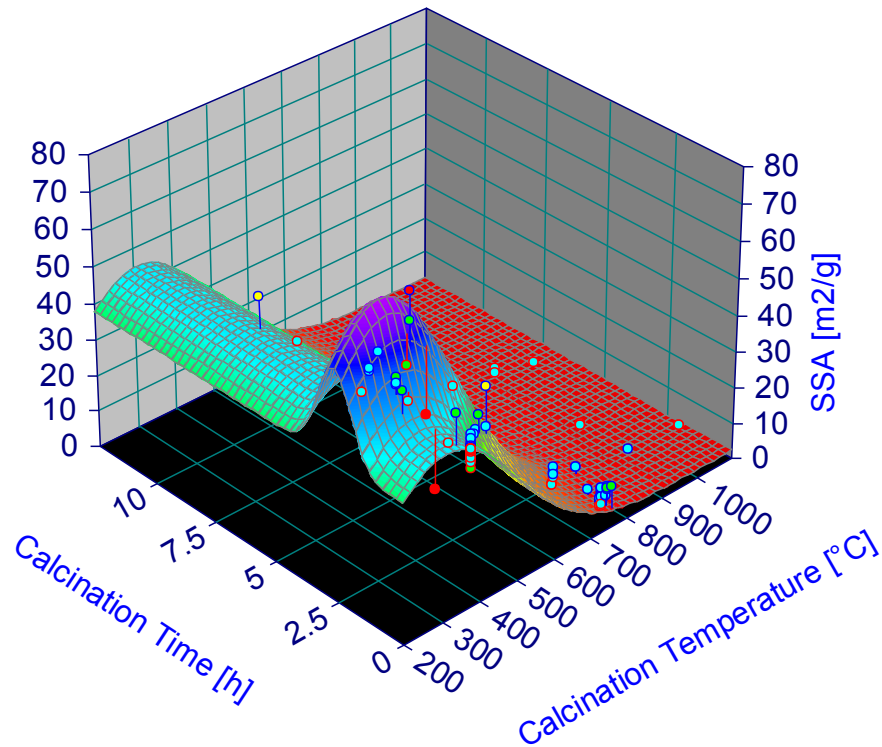


Figure 3-4. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-3D View 2

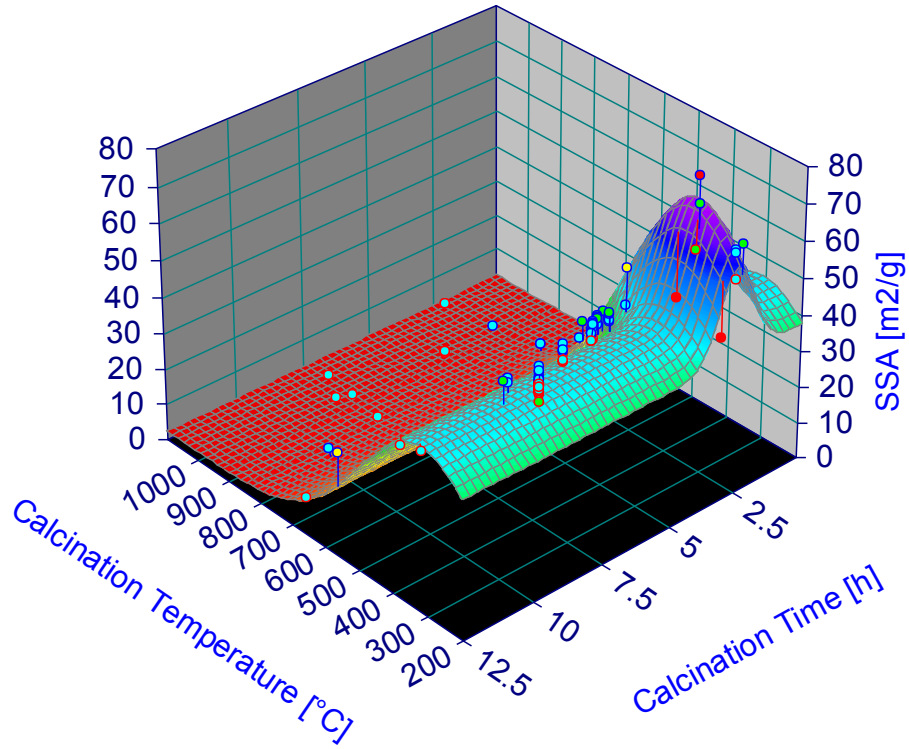


Figure 3-5. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-3D View 3

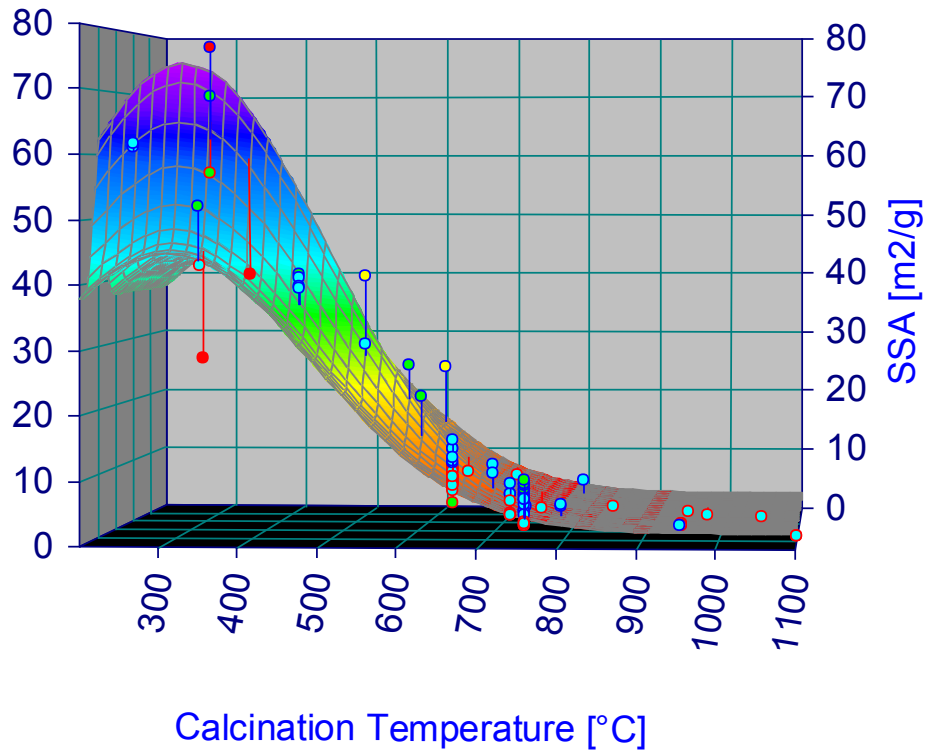


Figure 3-6. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-3D View 4

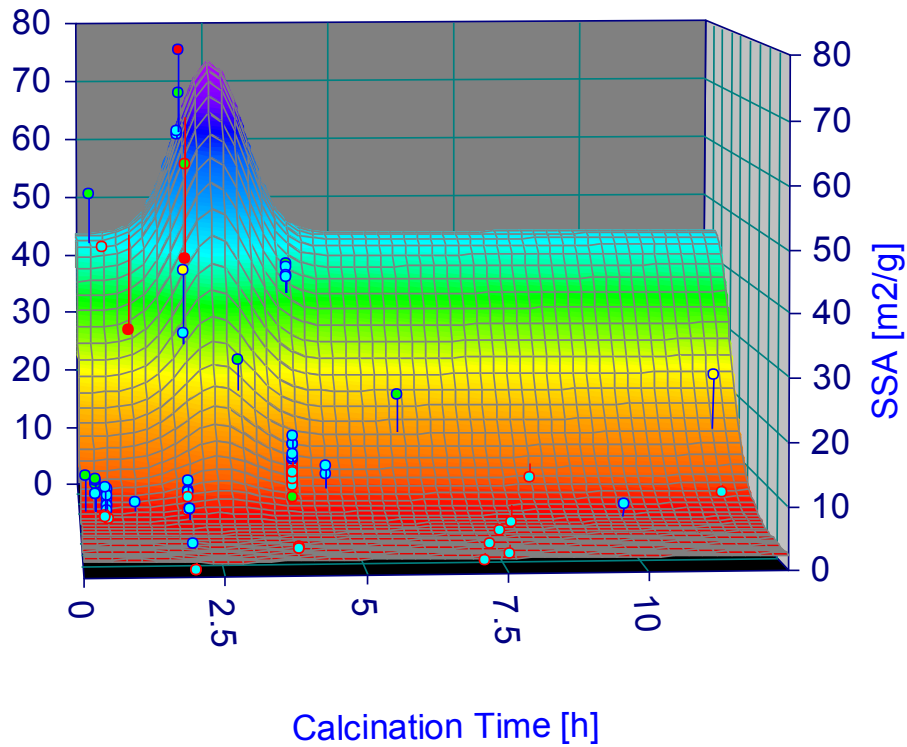


Figure 3-7. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (250-1100 °C) and Time-3D View 5

3.2 Preliminary Regression of 550-760 °C Calcination and Time Data for PuO₂ from Pu(C₂O₄)₂

Since the temperature range of current interest is between 600 and 700 °C, another regression was performed but restricting the calcination temperature and time data to 550 to 760 °C from Table 2-5. Note that this refined regression should not be used outside the temperature range of 550 °C and 760 °C otherwise might get unreasonable predictions. Table Curve 3D version 4.0 was again used to find an appropriate correlation. Note that this is only a preliminary fit of the data and should be refined as more information or data becomes available. After looking at the various correlations from Table Curve 3D and using knowledge of how the SSA changes with temperature and time, the following equation was chosen:

$$\text{Eqn 3-2} \quad \text{SSA} = A + \frac{B}{\text{TEMP}} + \frac{C}{\text{TEMP}^{1.5}} + D \cdot \frac{\text{LN TEMP}}{\text{TEMP}^2} + \frac{E}{\text{Temp}^2} + F \cdot \text{Time}^{0.5} \cdot \text{LN Time} + G \cdot \text{Time}^{0.5} + H \cdot \text{LN Time} + \frac{I}{\text{TIME}^{0.5}}$$

where:

SSA = Specific Surface Area of the PuO₂ from Pu(C₂O₄)₂, m²/g
 TEMP = Calcination Temperature in °C
 TIME = Calcination Time in hours
 A = -1.4972E+05, Empirical Fit Parameter
 B = 1.1665E+09, Empirical Fit Parameter

C = -7.9140E+10, Empirical Fit Parameter
D = 3.7702E+11, Empirical Fit Parameter
E = -1.1193E+12, Empirical Fit Parameter
F = -1.2105E+01, Empirical Fit Parameter
G = 7.1417E+01, Empirical Fit Parameter
H = -3.5063E+01, Empirical Fit Parameter
I = -1.5101E+01, Empirical Fit Parameter
LN=Natural Logarithm

Using this equation, the SSA is predicted for the various calcination temperature and time data points of plutonium oxalate ($\text{Pu}(\text{C}_2\text{O}_4)_2$) from Table 2-5 and shown in Table 3-2. A 2D representation of this empirical fit for the temperature range of 550 to 760 °C is shown in Figure 3-8. The empirical fit has more curvature in it when just fitting the SSA data points between 550 and 760 °C. As done in the prior analysis, the lines in Figure 3-8 represent the SSA predicted values for various calcination times and the symbols represent the observed SSA values. The equation does a fair job representing the observed SSA values over the various times. Figure 3-9 shows an enlarged section of the fit between 600 °C and 700 °C noting that the observed SSA data points in this range is small. The sparseness of the data in this range indicates the need to obtain more data to further refine the fit. Using this equation at 650 °C shows that the calcination time effect is bigger going from 1 to 2 hours (13 to 10 m^2/g) than from 2 to 3 hours (10 to 10 m^2/g) as shown in Table 3-3. However, as the calcination time increases further the predicted SSA value declines such that from 2 to 10 hours of calcination the predicted SSA drops from 10 to 8 m^2/g .

Table 3-2. Calcination Data (550 to 760 °C) of $\text{Pu}(\text{C}_2\text{O}_4)_2$ to PuO_2 for Regression of SSA

TEMP [°C]	TIME [h]	SSA Observed [m^2/g]	SSA Predicted [m^2/g]
550	2.0	30.6	36
550	2.0	41.1	36
600	6	21	24
600	3	27	24
600	12	23.9	23
650	4	4.93	9
650	4	10.18	9
650	4	9.76	9
650	4	10.54	9
650	4	10.86	9
650	4	7.89	9
650	4	8.47	9
650	4	9.29	9
650	4	8.64	9
650	4	9.08	9
650	4	8.30	9
650	4	10.31	9
650	4	10.23	9
650	4	8.91	9

Table 3-2. Calcination Data (550 to 760 °C) of Pu(C₂O₄)₂ to PuO₂ for Regression of SSA

TEMP [°C]	TIME [h]	SSA Observed [m ² /g]	SSA Predicted [m ² /g]
650	4	13.56	9
650	4	11.50	9
650	4	10.37	9
650	4	8.04	9
650	4	9.07	9
650	4	8.90	9
650	4	10.54	9
650	4	12.04	9
650	4	13.51	9
650	4	11.14	9
650	4	8.35	9
650	4	8.11	9
650	4	9.82	9
650	4	11.20	9
650	4	6.85	9
650	4	7.45	9
650	4	7.70	9
650	4	7.82	9
650	4	8.11	9
650	4	8.22	9
650	4	7.87	9
650	4	8.75	9
650	4	9.01	9
650	4	9.89	9
650	4	9.07	9
650	4	7.77	9
650	4	8.19	9
650	4	9.07	9
650	4	9.37	9
650	4	9.26	9
650	4	14.86	9
650	8.46*	7.9	9
700	4.57*	9.48	7
700	4.57*	10.83	7
700	12	5.7	6
735	2	4.2	7
735	2	4.2	7
735	2	4.5	7
735	2	6.4	7
735	2	7.3	7
735	2	7.5	7
735	2.0	9.1	7
750	8*	2	2
760	0.08	10.5	10
760	0.28	7.5	9

Table 3-2. Calcination Data (550 to 760 °C) of Pu(C₂O₄)₂ to PuO₂ for Regression of SSA

TEMP [°C]	TIME [h]	SSA Observed [m ² /g]	SSA Predicted [m ² /g]
760	0.28	7.5	9
760	0.28	9.11	9
760	0.28	9.55	9
760	0.28	9.94	9
760	0.5	3.4	6
760	0.5	3.4	6
760	0.5	3.69	6
760	0.5	3.99	6
760	0.5	4.88	6
760	0.5	5.4	6
760	0.5	5.49	6
760	0.5	5.83	6
760	0.50	6.58	6
760	0.50	7.15	6
760	0.5	7.89	6
760	0.5	8.3	6
760	0.5	8.66	6
760	1.00	6.1	3

Table 3-3. Predicted SSA values of PuO₂ from Pu(C₂O₄)₂ at Calcination Temperature 650 °C for various times

TEMP [°C]	TIME [h]	SSA Predicted [m ² /g]
650	1	13
650	2	10
650	3	10
650	4	9
650	5	9
650	10	9
650	12	8

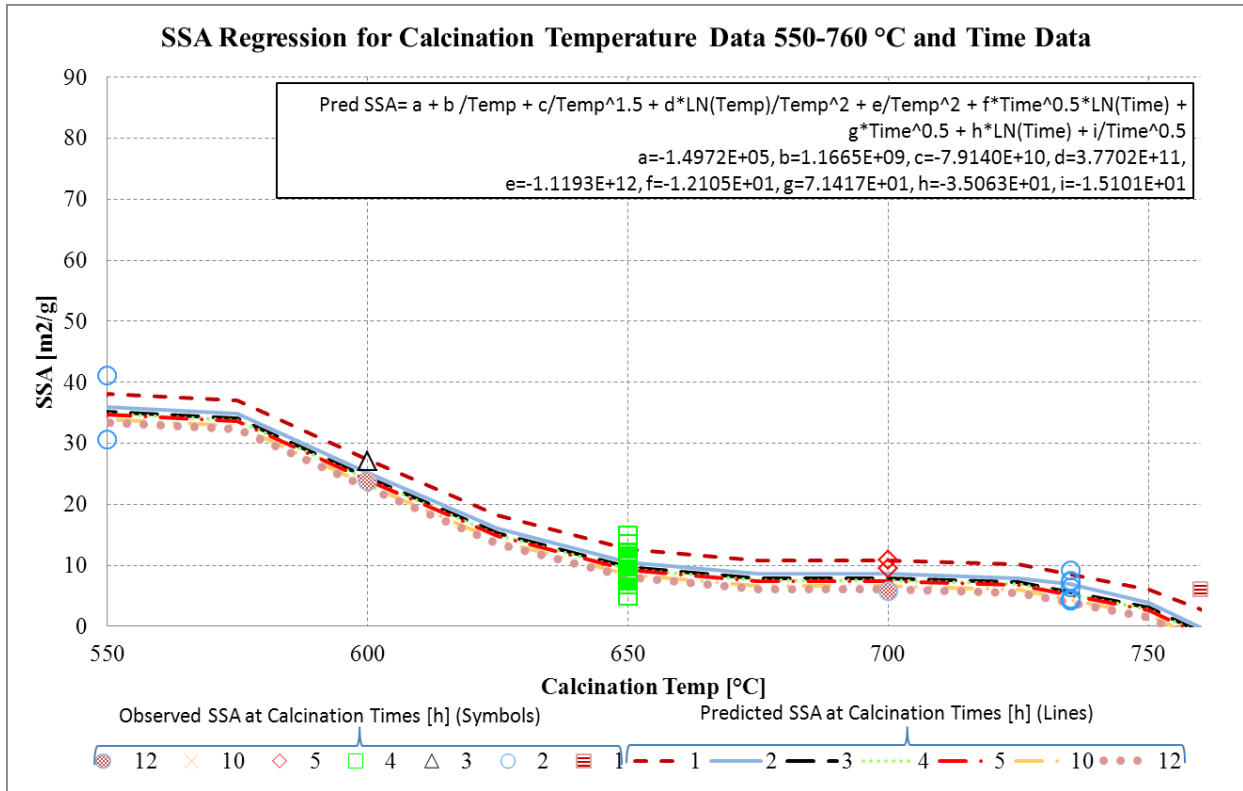


Figure 3-8. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-2D View 1

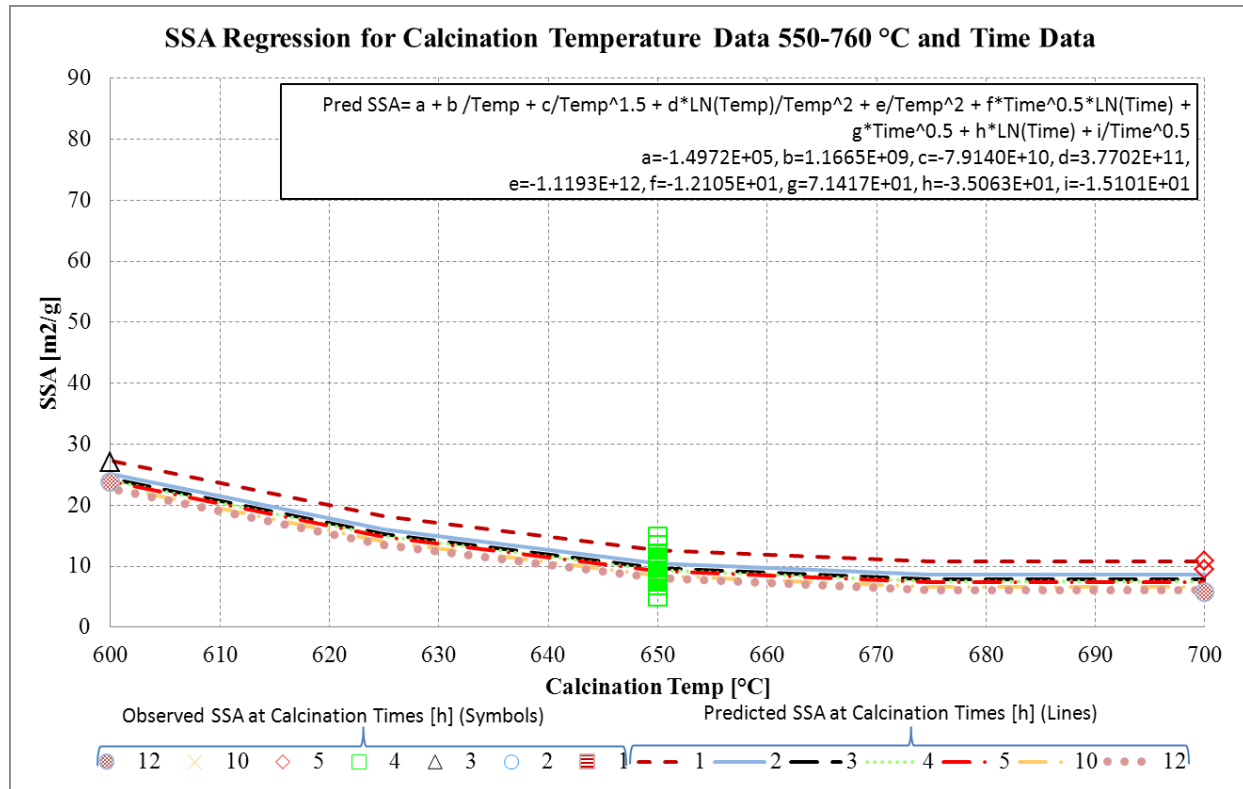


Figure 3-9. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-2D View 2

To help visualize the 3D fit of calcination temperature between 550 and 760 °C and time to the SSA data, the 3D plots from Table Curve 3D have been captured and pasted into this report. Figure 3-3 through Figure 3-7 show the plots of the observed SSA values (the round data points in the figures) versus the empirical fit (the colored red/orange to blue surface) from Eqn 3-2.

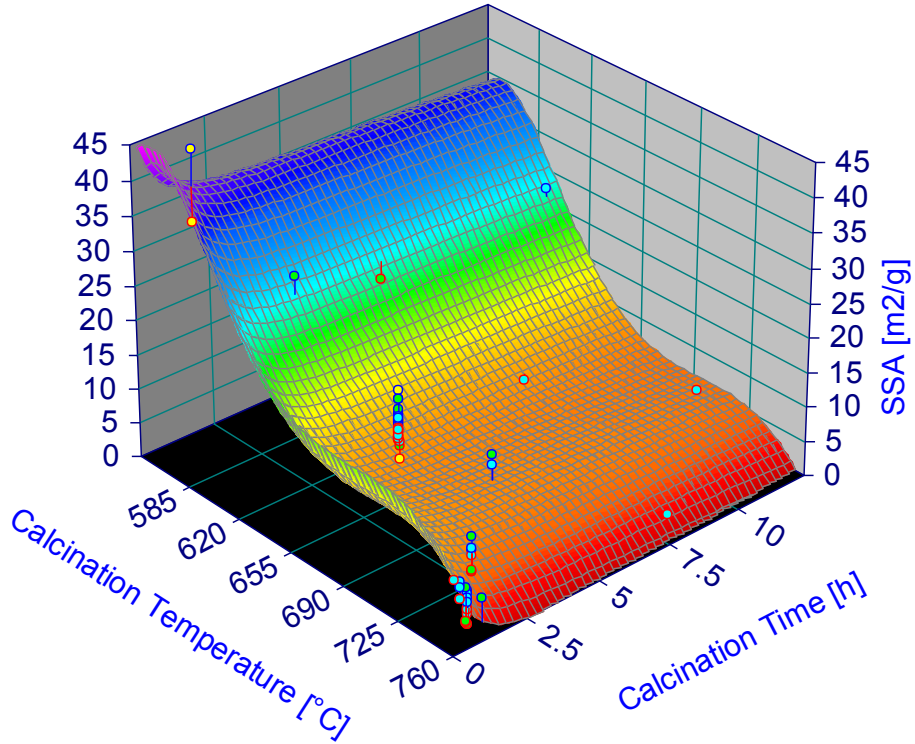


Figure 3-10. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-3D View 1

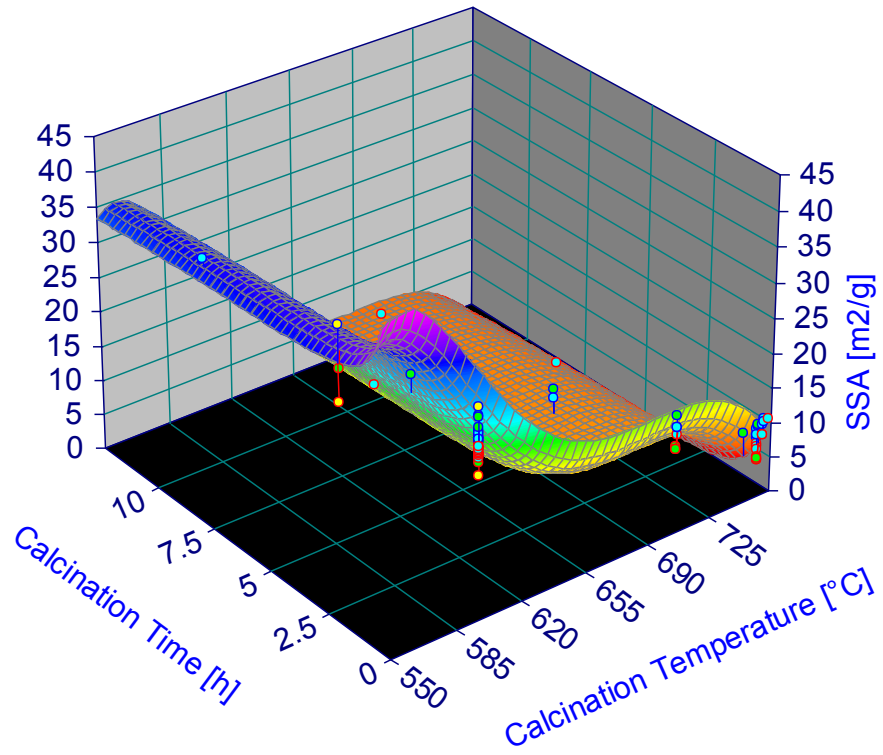


Figure 3-11. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-3D View 2

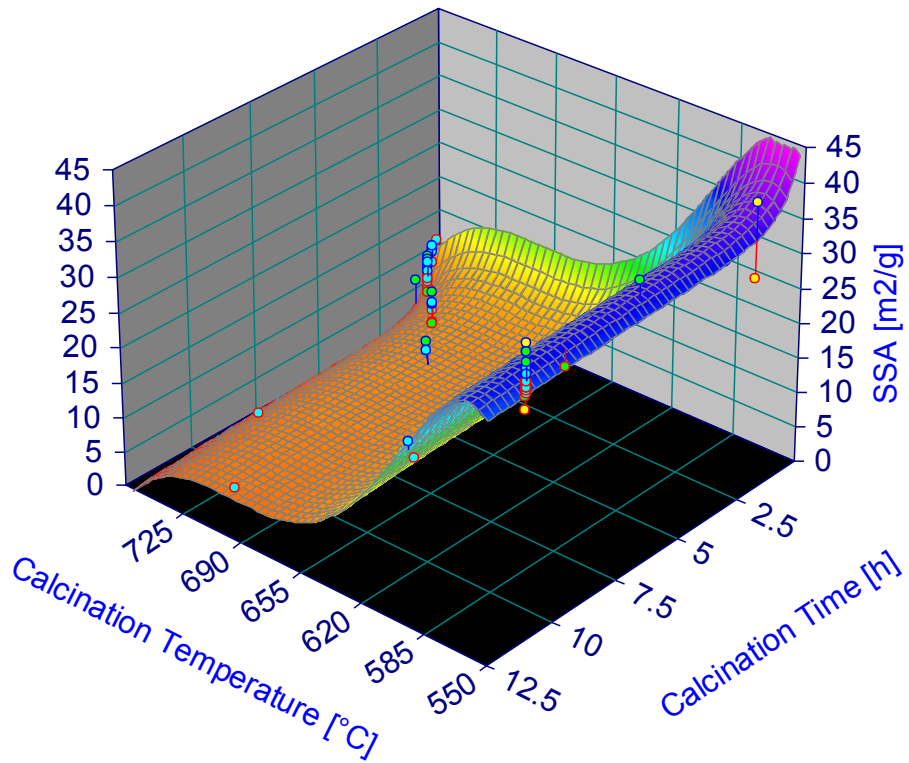


Figure 3-12. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-3D View 3

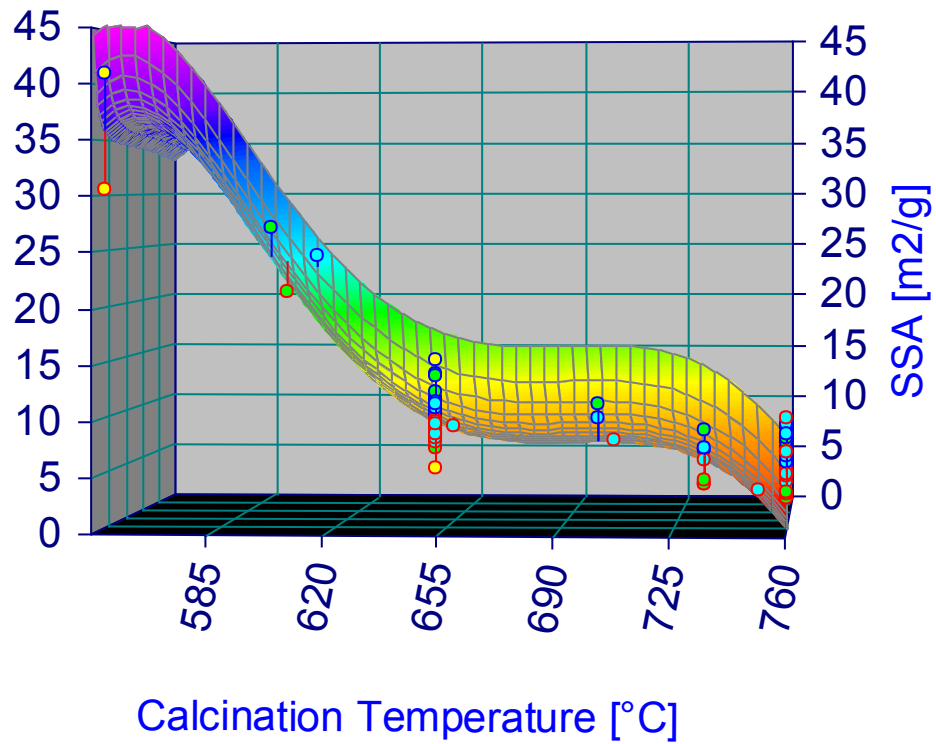


Figure 3-13. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-3D View 4

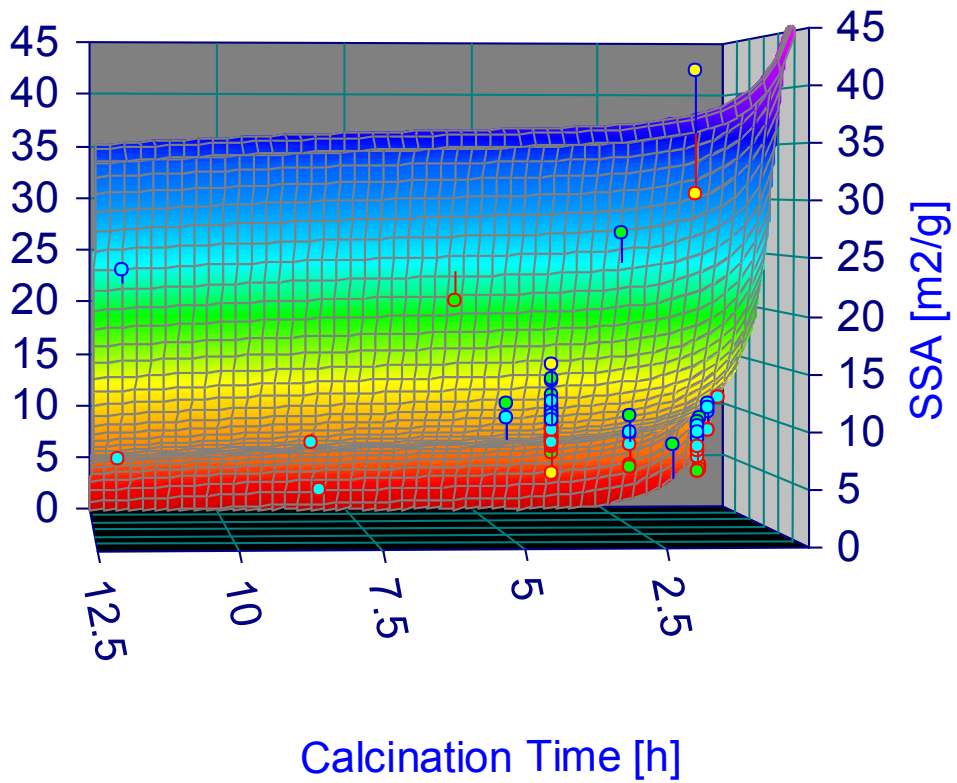


Figure 3-14. PuO₂ from oxalate-Correlation of SSA to Calcination Temp. (550-760 °C) and Time-3D View 5

4.0 Conclusions

The literature has been reviewed using multiple electronic databases searching for calcination data for plutonium oxide (PuO_2) from plutonium oxalate ($\text{Pu}(\text{C}_2\text{O}_4)_2$) with respect to its specific surface area (SSA). A summary of the literature has been presented for what are believed to be the dominant factors on SSA, the calcination temperature and time. The PuO_2 from $\text{Pu}(\text{C}_2\text{O}_4)_2$ calcination data from this literature review has been regressed to better understand the influence of calcination temperature and time on SSA. Based on this data set, calcination temperature has the bigger impact on SSA versus time. However, there is still some variance in this literature review data set that may be reflecting differences in plutonium oxalate preparation or different calcination techniques.

5.0 Recommendations

It is evident from this review that more calcination temperature and time data for plutonium oxide (PuO_2) from plutonium oxalate ($\text{Pu}(\text{C}_2\text{O}_4)_2$) needs to be collected and evaluated to better define the relationship. This literature data has a lot of calcination times around 2 hours and therefore may be underestimating the impact of calcination time on SSA. It is suggested that more calcination temperature and time data for PuO_2 from $\text{Pu}(\text{C}_2\text{O}_4)_2$ be collected in the specific temperature range of current interest (600 to 650 °C) for various calcination times (2 to 5 hours). From an empirical fit point of view, three calcination temperatures each at three different calcination times in the range of interest would improve the fit and better refine the relationship between the SSA of PuO_2 from $\text{Pu}(\text{C}_2\text{O}_4)_2$ and the calcination parameters.

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