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The PreCalc Project: Development of a Dynamic Model for Plutonium Processing

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INTRODUCTION

Nearly all of the plutonium in the world has been manufactured synthetically through large-scale separation and purification facilities. The different processes create specific isotopic, chemical, and physical characteristics, or signatures, and those can be organized to determine whether an interdicted nuclear sample is or is not consistent with a given process. One of the most common processes is the conversion of plutonium nitrate to oxide through Pu(IV) oxalate precipitation process.[1] Recently it has been shown that the morphological and physicochemical signatures produced from laboratory-scale experiments do not translate linearly to the production process because inhomogeneous temperature and pressure gradients dramatically complicate the macroscopic picture. It is our assertion that multi-scale, multi-physics models can provide a basis for the prediction of specific properties, but the approach must capture the atomistic features of nonequilibrium dynamic phenomena at finite temperatures while maintaining relevance at the process scale.

In that context, this presentation will be an overview of the modelling efforts at SRNL to integrate multiple time/length scales for a description of the precipitation and calcination dynamics of PuO_2 from a production facility, entitled the PreCalc Project. This presentation will discuss the framework development and modeling progress thus far in the project.

METHODOLOGY

The simulation system used to model the Pu(IV) oxalate to oxide conversion process consists of three main development areas: Data generation, data storage, and data analysis. The data generation component involves development of a workflow software tool that will automate and manage the computational steps necessary to determine a specific material property. The data storage component will enable the creation of databases from high-throughput calculations to store and query associated datasets. The data analysis component will involve the development of web applications to allow users to interactively analyze specific datasets. The current phase of the project is data generation.

Precipitation occurs through several steps, namely nucleation, crystal growth, and eventually aggregation and breakup.[2] Classical nucleation theory (CNT) models involve supersaturated solutions at supercooled temperatures where the molecules in solution begin to agglomerate and form microcrystalline structures. Once the clusters reach a certain critical size, molecules in solution will more favorably associate with the crystal surface than the solvent, making crystallization a spontaneous process. The net flux of the nucleation is then related to the free energy barrier of nucleation which is used to determine the crystal growth rate in solution. In nonclassical crystallization, nanometer-sized particles are considered to be the primary units in the construction of larger crystals. The nonclassical mechanism helps to explain the formation of nanoaggregates at production scale.

To determine the free energy of nucleation, density functional calculations (DFT) have focused on plutonium nitrate behavior in solution prior to complexation with oxalic acid. The solution is modelled as a continuum solvent with the necessary hydronium and nitrate ions to result in the appropriate nitric acid concentration. Once general behavior is established, the next step is to determine how the free molecules in solution will nucleate and grow on the desired timescale. The crystal free energy generated from MD simulations is then a relationship with temperature, Boltzmann's constant, supersaturation of the solution, and molar volume. Using the quantities derived from the molecular scale enables understanding of the crystallization phenomena at the macroscale when it is strongly influenced by flow turbulence and mixing patterns. The hydrodynamics are described by means of computational fluid dynamics (CFD) to generate growth kinetics, fluid flow, heat and mass transfer, and population balance.

If oxalate precipitation is the key unit operation for dictating the final oxide morphology, then thermal decomposition dictates the fine structural features of the final oxide powder, such as porosity, surface area, and residual carbon content. However, the reaction mechanism is often misunderstood and the intermediate structures are often speculative. Recent thermogravimetric (TG) work has aided in identifying the intermediate species, but the connection between gas release and structural changes is still lacking. In addition, the morphology is still subject to change because structural changes are still occurring over the reaction period.

To obtain information on these experimentally unknown morphology changes and intermediates, density functional calculations are used to determine their relative energies throughout the reaction. Kinetic Monte Carlo (KMC) simulations provide a means of quantifying gas release as a function of heating parameter. These values can then be used to describe the process as a multi-stage, multi-reaction shrinking core model for the gas-solid reactions.

RESULTS AND DISCUSSION

Precipitation

Before modeling work can begin, it is important to understand the plutonium-nitric acid-oxalic acid equilibrium relationships and their significance during model development. Several solubility models have been developed in the past with varying success. We have expanded upon a solubility model for plutonium(IV) oxalate (Figure 1) initially developed by Reas.[3] While there are several equilibrium equations that can be used to describe the solubility, our model shows that the equilibrium in solution can be represented by the following three:

$$Pu(C_2O_4)_2{\cdot}6H_2O + 2H^+ \rightleftarrows [Pu(C_2O_4)]^{2+} + H_2C_2O_4 + 6H_2O \quad (1)$$

$$Pu(C_2O_4)_2{\cdot}6H_2O \rightleftarrows Pu(C_2O_4)_2 + 6H_2O \quad (2)$$

$$Pu(C_2O_4)_2{\cdot}6H_2O + H_2C_2O_4 \rightleftarrows [Pu(C_2O_4)_3]^{2-} + 2H^+ + 6H_2O \quad (3)$$

When represented in this way, the Pu(IV) oxalate solubility can then be expressed as the concentration of Pu(IV) species in solution:

$$[Pu^{4+}]_{total} = [Pu(C_2O_4)]^{2+} + [Pu(C_2O_4)_2] + [Pu(C_2O_4)_3]^{2-} \quad (4)$$

After writing equilibrium expressions for the reactions above and substituting the individual species into equation 4, the total Pu(IV) concentration can be summarized as:

$$[Pu^{4+}]_{total}=[Pu(C_2O_4)_2]\left(K_1\frac{[HNO_3]^2}{[H_2C_2O_4]}+1+K_3\frac{[H_2C_2O_4]}{[HNO_3]^2}\right) \quad (5)$$

Or

$$[Pu^{4+}]_{total}=\frac{K_1K_2}{R_s}+K_2+K_2K_3R_s \quad (6)$$

where R_S is the solubility parameter $[H_2C_2O_4]/[HNO_3]^2$. Application of the solubility model was first verified using experimental results from Reas and then expanded to include all Pu(IV) oxalate solubility information (Figure 1). In addition, solubility information was also obtained for Pu(IV) oxalate at 50°C.[4] Based on the information, the solubility product for Pu(IV) oxalate at 25 and 50°C can determine the solubility at any temperature using basic thermodynamic relationships. The higher temperature data shows a deviation from linear behavior, which is consistent with some experimental information about the formation of thixotropic gels of Pu(IV) oxalate at higher nitric acid concentrations.

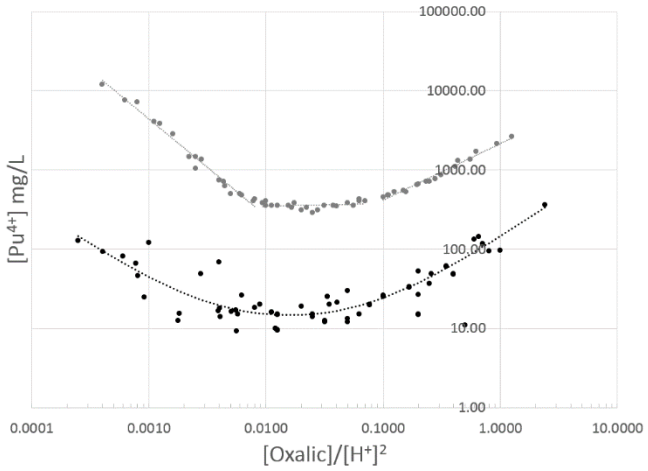

Fig. 1. Log-log plot of the predicted solubility of Pu(IV) oxalate at 25°C (bottom) and 50°C (top).

Once the pertenant Pu(IV) oxalate species were identified, the next step was to use DFT to understand complexation in solution. The complexes $[Pu(C_2O_4)]^{2+}$ and $[Pu(C_2O_4)_3]^{2-}$ are trivial but the oxalate ligands in the neutral complex $[Pu(C_2O_4)_2]$ could have preferencial arrangement to be either in a cis- or trans-like configuration with H_2O molecules completing the coordination environment. Our studies indicate that both species are likely to exist in solution, thereby complicating calculations of the free energy of nucleation (Figure 2).

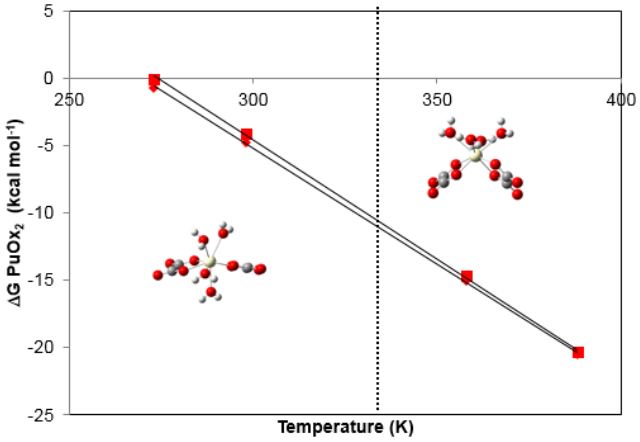

Fig. 2. Free energy of reaction for cis and trans configuration of $Pu(C_2O_4)_2(H_2O)_4$ from $Pu(NO_3)_4$.

Preliminary calculations of the Pu(IV) oxalate molecular species indicate that clusters form almost 2 dimensional sheets and nucleation begins when sheets extend along the z-axis. Status of these results, as well as tank mixing studies, will be presented.

Calcination

The thermal decomposition sequence has been previously investigated using TG analysis where the intermediates were identified by extrapolating the mass loss with structural analyses using XRD, UV-vis, or IR (Figure 3).[5] Some structures could be identified, but others were too short-lived for various reasons. Our attempt to understand the pathways and intermediate species included using DFT calculations to confirm the thermal decomposition pathway.

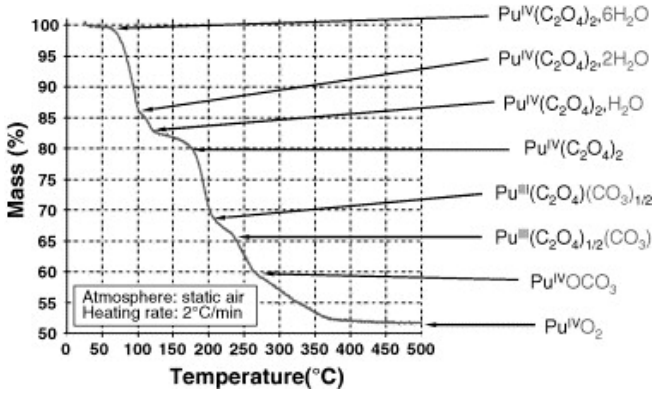

Figure 3. Experimental TG plot starting from $Pu(IV)(C_2O_4)_2{\cdot}6H_2O$ under static air.[5]

Thermal decomposition first involves endothermic dehydration of Pu(IV) oxalate, then oxalate decomposition to CO and CO_2. Structurally, we have identified three different types of water molecules within the oxalate structure; interstitial, void, and coordinated. Our proposed structures are validated by the Vigier experimental results. Once the final water molecule is removed from the void space in Pu(IV) oxalate, plutonium is reduced to +3 charge and a carbonate-bridged species is formed (Figure 3).

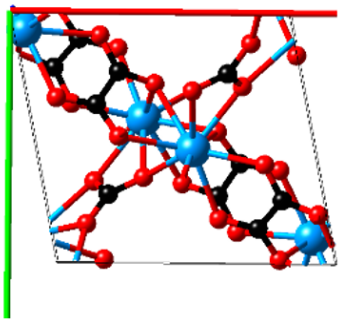

Figure 3. Optimized structure of $Pu_2(C_2O_4)_2CO_3$.

Notice that the structure still contains large void spaces wherein gases could remain trapped. Following the decomposition sequence, the results suggest that subtle changes in the morphology should be expected. Further discussion into the energy profile as a function of the reaction coordinate will be presented including preliminary data on the effects of O_2 on the pathway. In addition, we will also briefly discuss methods for determining gaseous diffusion within the intermediate structures.

CONCLUSIONS

The results described herein provide the theoretical treatment used to understand precipitation/calcination dynamics for plutonium(IV) oxalate to oxide conversion process. Development of a multiscale, multi-physics model to express the influences of operational conditions on physico-chemical properties of PuO_2 will allow for better understanding of the engineering principles associated with the oxide conversion process at the production scale, and allow for more directed experimental work to be performed to verify the observed phenomena at laboratory scale.

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NOMENCLATURE

DFT = Density Functional Theory
IR = Infrared Spectroscopy
KMC = Kinetic Monte Carlo
MD = Molecular Dynamics
TG = Thermogravimetric Analysis
UV-vis = UV/vis spectroscopy
XRD = X-Ray Diffraction

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