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PARTICLE SIZE ANALYSIS OF CERIUM DIOXIDE SURROGATE MATERIALS AS A SIMULANT FOR PLUTONIUM-238 DIOXIDE FUELS PROCESSING

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Failure attributed to pellet cracking during fabrication of $^{238}PuO_2$ pellets places a severe burden on production efforts through lost time, increased radiation dose due to product rework, and supplementary costs. Unfortunately, the difficulty in working with this material makes identification of root causes, and subsequent correction, infeasible on the production floor. Furthermore, the work presented here begins to experimentally investigate the behavior and variable sensitivity of the grog feedstock at the front end of the pellet production process using CeO_2 surrogate material. This information is critical for establishing a baseline for the grog feedstock, one of the key variables in defining the performance of a $^{238}PuO_2$ pellet during fabrication. Looking forward, this analysis lays the foundation for continued study and training using non-surrogate PuO_2 materials.

I. INTRODUCTION

Radioisotope power sources have been used to power deep space missions for decades. Isotopes such as plutonium-238 produce electrical power through the Seebeck effect as a result of heat generation due to alpha decay (1-3). Plutonium-238 is ideal for this application due to its relatively long half-life, ~87.7 years, and high power density of ~0.5 thermal watts per gram (1-7). Modern applications of this isotope utilize iridium-clad plutonium oxide ($^{238}PuO_2$) in pellet form, generating ~62.5 thermal watts per pellet.

Recent research and development efforts (LDRD 20170531ER) at Los Alamos National Laboratory (LANL) have focused on reducing the rate of failure due to pellet cracking through an understanding of the thermo-mechanical behavior of $^{238}PuO_2$ during pellet fabrication. These efforts make use of experimental work with surrogate materials, such as the studies presented here, to inform the development of the Plutonium Modeling and Assessment (PUMA) computer simulation using the MOOSE framework to fully model the $^{238}PuO_2$ pellet fabrication process. Fabrication of this fuel form has historically proven to be troublesome with a failure rate due to pellet cracking during production often approaching 20-30%, an example of such cracking can be seen in Figure 1.

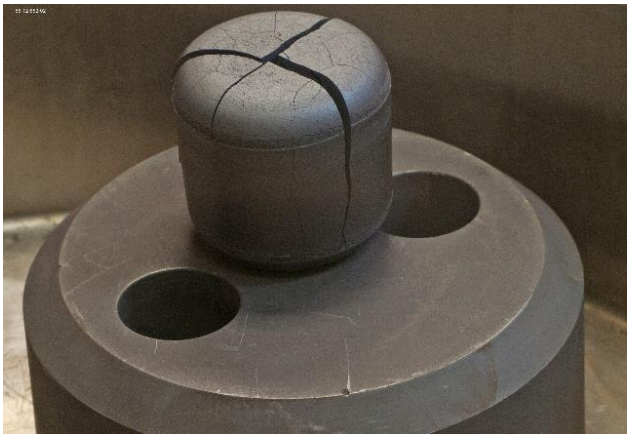

Fig. 1. Example of cracked plutonium oxide pellet during production

Unfortunately, a single, conclusive accompanying root cause of these failures has not been identified through the roughly 40 years of production. With every pellet lost, significant time, effort, and resources are consumed, generating a programmatic loss on the order of $400,000 per pellet failure. Therefore, it is advantageous to begin identifying root causes and implementing process changes in order to reduce such failures for both current and future production campaigns.

The fabrication process begins by seasoning the powdered feedstock at two different temperatures, resulting in a mixture of high-fired and low-fired oxide granules. This grog-type feed mixture has been determined to improve the microstructural homogeneity of the $^{238}PuO_2$ pellets as evidenced by internal cracking patterns observed during pellet production efforts using non-grog feed mixtures. It is reasonable to assume that the more-reactive surface energy of low-fired powder enhances sintering mechanisms, but leads to excessive, rapid shrinkage during powder consolidation. Conversely, the high-fire powder lacks the surface energy needed to ensure pellet integrity during consolidation (4,5,7). While the high-fire and low-fire heating profiles and ratios were determined to be sufficient during process development, they were not

optimized and much room for improvement remains. These parameters are expected to play a large role in the structural integrity of the pellets.

Previous research into PuO_2, as detailed in references 8-10, justify the use of CeO_2 as a valid surrogate material while avoiding the many of the difficulties in working with PuO_2 directly. This study begins to investigate, first, the baseline behavior, then associated effects on process improvements, and varying processing parameters through surrogate analysis. This helps ensure optimum operating parameters via behavioral predictions of $^{238}PuO_2$ pellets from supplementary modeling software and direct, time efficient process improvement verifications. The overall intent of the completed studies and software is aimed to lessen the cumbersome and expensive studies of $^{238}PuO_2$ directly. An optimized, viable software coupled with a process ready, functional ceramics laboratory for continual process changes and improvements will be advantageous for future programmatic strides, lessening the dependence on experimental trials alone.

II. EXPERIMENTAL

Grog materials was fabricated from surrogate CeO_2 (CeO_2 99.99% or 99.9%, Alfa Aesar, Ward Hill, USA) using similar processing parameters and methodology as used for creating $^{238}PuO_2$ grog mixtures. The surrogate powder was first fed into a ball mill to ensure particles are normalized. The milled powder was then cold pressed to achieve a CeO_2 slug to then be screened for granule creation. To create the feeds for the grog, the CeO_2 granules was seasoned at various temperatures and soak times to produce varying material properties. The resulting seasoned granules was screened again to produce a specific particle size distribution. Throughout this procedure, methodology and equipment used was selected to mirror current production as closely as possible. Samples were pulled and analyzed for particle size analysis (Camsizer X2, Horiba) throughout in order to reproduce and determine the baseline of the current process. All particle size analysis results are presented through the minimum chord length of the particles. This method of presentation was selected due to the strict usage of sieves for particle separation, as the smallest chord length permitting or prohibiting passage through the screen.

After establishment of a current process baseline, specific process improvement equipment was then tested for repeatability and alignment to current processing using a particle size analyzer. As results were obtained, data collection methods were updated and revised in order to accurately analyze the lots created. Throughout the processing steps, thermal gravimetric analysis (Thermal Analysis Instruments TGA 5500) was used to determine the necessity of baking out samples prior to particle size analysis.

III. PRESENTED RESULTS

III.A Particle Agglomeration

After creation of fired granule lots, initial particle size analysis results showed the ceria powder's tendency to form larger agglomerates, most notably in the low fire granules. This observation prompted a study into all of the processing steps' agglomeration tendencies. Initially it was thought the time after sieving could strongly influence the tendency of the powder to clump together, making the timing of particle size analysis performance a variable. This was in observed both visibly and through particle size analysis, shown in the upper particle size region. To test this, PSA analysis was performed immediately, 5 hours, 24 hours and 72 hours after sieving to see the corresponding effect of clumping. The intention of this study was to determine if sieving in the ambient environment and controlling the time the powder lot was allowed to sit contributed to the observed particle agglomeration.

Figure 2, below, shows the results of a representative low fire granule lot particle size analysis completed at several different intervals of time after initial sieving. The low fire runs exhibited the more exaggerated, visible clumping and are therefore presented here. Consistently, the lots throughout the process did not exhibit a strong dependence on time after sieving and the amount of larger agglomerations observed, leading to other avenues of investigation.

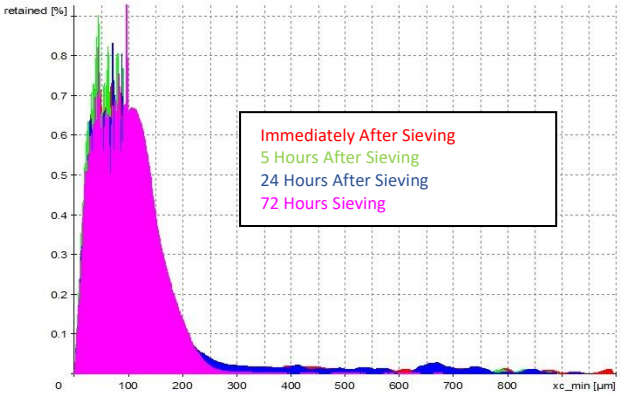

Fig. 2. Particle size analysis as a function of time after sieving on low fire granules, 99.99% ceria

Following the time dependent studies, thermogravimetric analysis was conducted on all processing stages to see if the ceria was absorbing anything from the process or atmosphere itself, potentially contributing to the observed clumps.

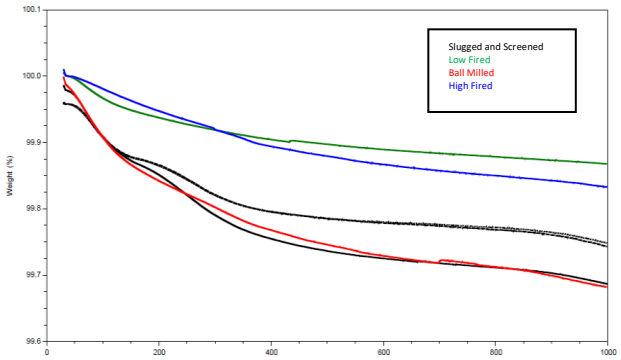

Fig. 3. Thermogravimetric analysis under argon on process material, 99.99% ceria

Figure 3 details the results of thermogravimetric analysis on ceria as it progressed through first ball milling, then slugging and screening process, and finally after firing. All process stages of the ceria itself exhibited mass loss under argon, perhaps attributed to the reduction itself. However, the results indicate an increased mass loss of both the slugged and screened and ball milled material, indicating the reduction or absorbed ambient water were not the only attributing factors. Though these results did not identify the agglomeration concerns in the fired material, they did, however, prompt particle size analysis bake out studies of both the ball milled and slugged and screened material, detailed later in III.C, to determine the potential effects of the notable mass loss on particle size analysis. Investigations into the root cause of the agglomerations in the low fire lots observed are still underway.

III.B Operator/sampling Effects

Throughout the course of the agglomeration studies detailed in III.A it was observed that slight variances in PSA analysis started to surface as more lots were created by different operators. Throughout the process in the ceramics lab and in the current process itself it has been noted that the most operator dependent methods were sampling and screening. Therefore, these two methods were investigated, detailed in Figures 4 and 5.

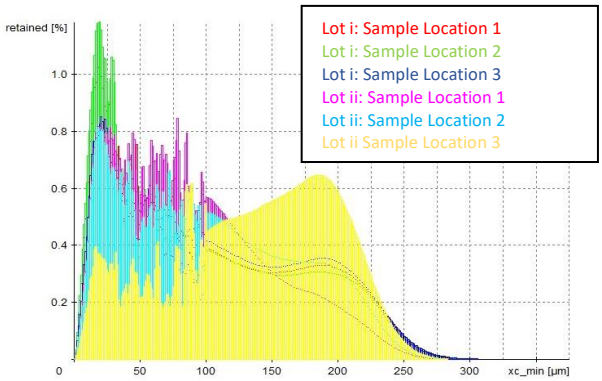

Fig. 4. Differing sample locations effect on particle size analysis, 99.99% ceria

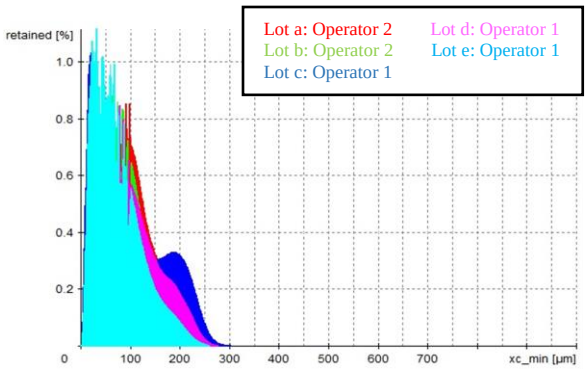

Fig. 5. Particle size analysis as a function of post high fire screening operator, 99.99% ceria

Figure 4 depicts the effects of differing sample locations post high fire screening. This suggests that the post high fire granules do not display a homogenous particle size distribution when collecting samples throughout the settled batch, as utilized in current production. Additionally, shown in Figure 5, different operators screening the high fire lots exhibited varying particle size distribution when sampled from the same location. As operations and process improvement studies continue, further data is being collected to promote further investigations into both identified effects and potentially new effects, such as environment. In both scenarios, the high fire lots alone demonstrated this sensitivity, highlighting the need for a standardized sampling and screening method for data collection. Going forward, a sample splitter has been identified for representative data analysis and a need for an automated sieving process was identified.

III.C Process Automation

To begin addressing both the operator dependencies and the labor intensive sieving in granule formation and post fire screening, an autosieve was employed. Figure 6 conveys the initial process applicability and tests of the autosieve process, coupled with the previous TGA bake out

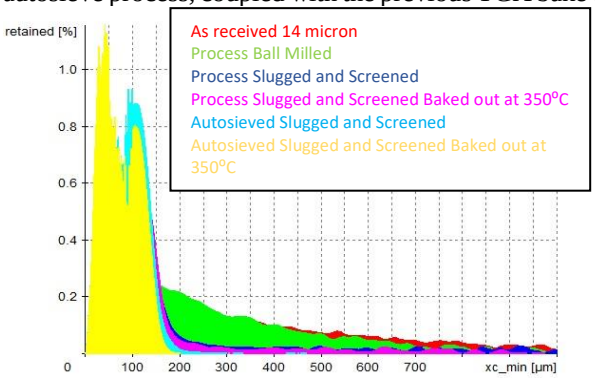

Fig. 6. Particle size analysis as a process improvement tool, 99.9% ceria

findings. The samples baked out to 350 °C showed a decrease in the larger agglomerates, visible from the decreased amount of particles observed above 300 microns for both manual and autosieve processes. Furthermore, the PSA profile of both the baked out and non-baked out autosieved material was further tightened. These initial results show promise towards a smaller range of particles being fed into the process stream while removing direct dependencies on operator's individual expertise and time. Having a more predictable particle size distribution will be beneficial for both repeatability and characterization of both current and future process improvements.

IV. CONCLUSIONS

Overall, a baseline for the currently employed process is still in development. However, by performing these studies we have begun to identify and troubleshoot processing areas of concern with ceria work, which can directly translate into $^{238}PuO_2$ work. After the establishment of an effective system of sampling and sieving ceria, moving the same method into $^{238}PuO_2$ would save time, and therefore dose for the operator while simultaneously providing the process with repeatable, systematic results.

ACKNOWLEDGMENTS

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