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Instrumentation for Studying Binder Burnout in an Immobilized Plutonium Ceramic Wasteform

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INSTRUMENTATION FOR STUDYING BINDER BURNOUT IN AN IMMOBILIZED PLUTONIUM CERAMIC WASTEFORM*

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ABSTRACT

The Plutonium Immobilization Program produces a ceramic wasteform that utilizes organic binders. Several techniques and instruments were developed to study binder burnout on full size ceramic samples in a production environment. This approach provides a method for developing process parameters on production scale to optimize throughput, product quality, offgas behavior, and plant emissions. These instruments allow for offgas analysis, large-scale TGA, product quality observation, and thermal modeling. Using these tools, results from lab-scale techniques such as laser dilametry studies and traditional TGA/DTA analysis can be integrated. Often, the sintering step of a ceramification process is the limiting process step that controls the production throughput. Therefore, optimization of sintering behavior is important for overall process success. Furthermore, the capabilities of this instrumentation allows better understanding of plant emissions of key gases: volatile organic compounds (VOCs), volatile inorganics including some halide compounds, NO_x, SO_x, carbon dioxide, and carbon monoxide.

INTRODUCTION

Binder burnout, loosely defined as the region during sintering where organic compounds are removed, includes the removal of important industrial compounds such as pore formers, binders, dispersants, and lubricants (Ref. 1). They can be removed by directly boiling off, decomposing, combusting, or pyrolyzing. Binder burnout is important to the following industries: traditional ceramics, high temperature ceramics, fuel cell, metal powder, semiconductor technical ceramics (e.g. multilayer tape casting), MOX nuclear fuel, and several nuclear wasteforms. It is also important for determining the airborne environmental releases of such processes from industrial plants. Parameters impacting binder burnout include: selection of binders and other additives, granulation and/or mixing effects, pressing pressure, furnace hold times and ramp rates, furnace atmosphere (e.g. oxiding or inert), composition, and the presence of volatile impurities. Binder burnout limits industrial plant and research laboratory throughput because it necessitates slowing the thermal cycle. Furthermore, it can severely impact product quality, porosity, durability, and structural integrity.

Traditional methods for studying binder burnout are limited for larger samples. The current approach to researching binder burnout is largely a trial and error process of modifying additives, additive addition methods (e.g. mixing and/or granulation), and varying sintering cycles on large samples after small pellet testing provides estimates as to which parameter choices to focus. The materials industry has historically used TGA and DSC on small samples, pellets of less than 5 g, to study this important phenomenon. Strict TGA and DSC techniques only analyze weight loss as a function of temperature, i.e. do not directly determine outgassing regions, and thus are often inefficient means of conducting trade-off studies comparing the advantages and disadvantages of various organic additives. More recently, TGA-FTIR introduced the capability of studying the offgases released during a constant rate heating cycle on small pellets (Ref. 2). This approach has also been shown to have limitations (Ref. 3, 4, 5); small samples often fail to adequately represent the full size or large products typically made on an industrial scale. This is due in part to heat and mass transfer limitations of large, highly compressed matrices – what industry actually makes. As the binder burnout region is both a function of time and temperature, the heating rate and time and temperature of holds all interrelate in large scale ceramics, resulting in behavior not exhibited in small pellets. In comparison to small pellets, Figure 1 shows typical green and sintered pucks which are much larger. Thus, there is a compelling research and technology transfer opportunity to utilize a new LLNL technique to study this phenomenon in industrial products, to move the scope of research from plutonium immobilization to industrial applications.

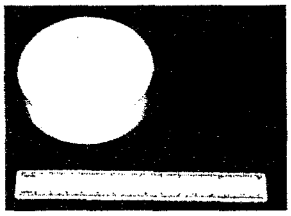

Figure 1. Green and Sintered Pucks.

Analysis of the offgases produced during binder burnout allows the researcher to correlate weight losses to the actual compound being lost. For example, using a hypothetical comparison, offgas analysis provides the researcher a means to know if water, binder A, binder B, dispersent C, and/or lubricant D is the "troublemaker" for product cracking or the "slow poke" for exiting the matrix, and if so, at what time, rate, and temperature. Thus, a replacement compound or a modified schedule can be used to increase product quality and throughput. Figure 2 shows an example correlation between weight loss and offgas behavior for a ceramic puck.

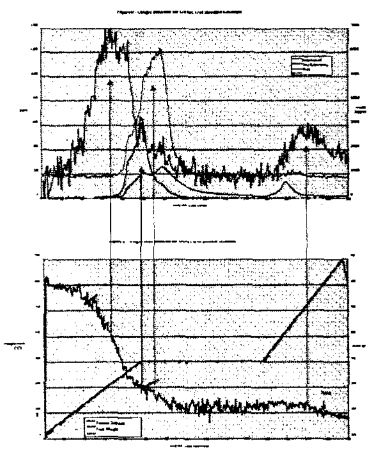

Figure 2. Example Weight Loss Correlation with Offgas Analysis using BBO-FTIR.
This test was conducted prior to the improvement of scale sensitivity.

Binder burnout is important to the Plutonium Immobilization Program because of the bottom line: sintering is the slowest processing step. By optimizing furnace operations, plant throughput may be increased and plant capital and operating cost should be minimized. A recent DOE inter-laboratory collaborative effort to enhance analysis of binder burnout revealed the dearth of research on this important aspect of ceramic processing (Ref. 4, 5, 6, 1).

As a result of these efforts, a binder burnout (BBO) research laboratory was set up at LLNL containing enhanced equipment with new capabilities, specifically BBO-FTIR, expanding the knowledge of this important step in the ceramic processing. The existing binder burnout laboratory can study binder burnout behavior on full-scale samples (pucks) in a plant prototypic fashion. Furthermore, the laboratory can handle radioactive samples, with the exception of the offgas analysis capability. The laboratory includes several furnaces with weight loss, temperature, offgas analysis, and physical integrity analysis capabilities.

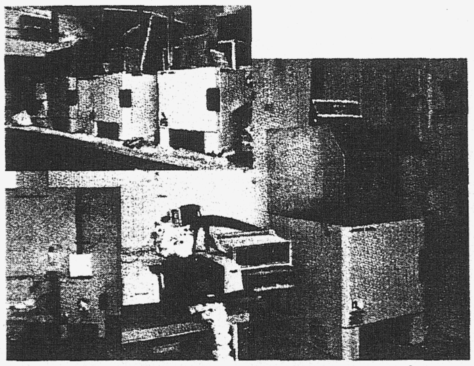

Figure 3. BBO Laboratory. Center: BBO-FTIR. Top left: several BBO furnaces. Bottom left: Visual inspection apparatus.

INSTRUMENTATION

BBO-FTIR is a combination of the capabilities of TGA and FTIR offgas analysis for full scale samples, with a variety of additional useful features. Instead of a small pellet sample chamber, a traditional lab scale box furnace is used to study binder burnout. This furnace easily handles large scale samples such as 500 to 600 g pucks and crucibles. The furnace can be operated in mixed atmosphere conditions, e.g. to introduce reducing conditions, via a gas inlet port. Offgas analysis is conducted using a Nicolet Avatar® FTIR, 0.5 cm^{-1} resolution, with a 2 meter (pathlength) hot gas cell, held a constant 185°C. This is shown in Figure 3 (center). Weight loss measurements are conducted using an externally mounted scale. The sample is suspended on a wire platform from the scale, with the wire going through the port. This setup is very similar to a traditional apparatus used for Archmides density measurements and is shown in Figure 4. Improvements in the stability of the scale mounting are critical to minimizing variations in scale readings, and providing precise measurements. Temperature measurements are taken from furnace thermocouples and a programmable controller that provides both the programmed and actual furnace temperature. The controller has been used for complex, multistep thermal cycles necessary to explore the various offgassing regimes. A Labview® VI was written to measure multiple thermocouple readouts. Additionally, a port for thermocouple connections was added to the front of the furnace for the thermocouple puck capability. A"thermocouple puck" is a sample that is pressed with thermocouples in intimate contact with the sample material. This technique allows determination of the heat transfer gradient to and within the puck. Figure 5 shows an example thermal profile of a puck during binder burnout as measured in a thermocouple puck. An alternate front port allows for visual inspection of the sample via a boroscope-like apparatus, shown in Figure 3 (bottom left). These modifications were conducted in a manner to minimize the impact of the sampling ports on the furnace thermal gradients. Additional furnaces were setup with a mixture of these capabilities to increase testing throughput, shown in Figure 3 (top left).

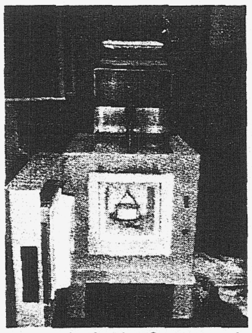

Figure 4. Suspended Platform and Scale Setup.

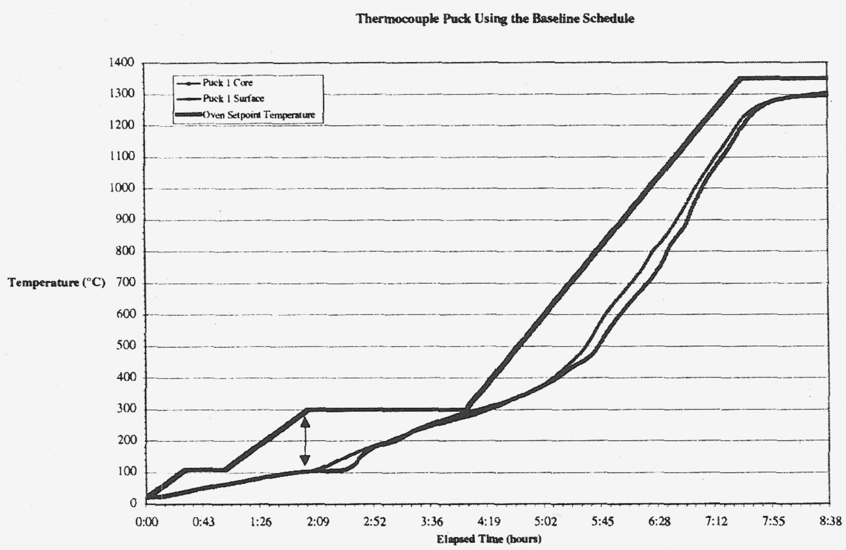

Figure 5. Thermal Profile during Binder Burnout.

BBO-FTIR experiments are conducted by placing the sample in the wire platform, programming the furnace to the desired thermal cycle, using Labview® to record thermocouple measurements, and Nicolet Omnic Series® software to record the FTIR spectra over time. Data from the scale, thermocouples, and FTIR are then analyzed to determine the important weight loss regions and the corresponding materials being lost.

Early research indicated several key points with regard to instrumentation. First, carefully controlled heating of the tubing from the sample port to the hot gas cell is essential. The hot gas cell operates at a constant 185°C, which requires heating of the incoming gases when the furnace is at lower temperatures, and cooling of said gases when the furnace is at higher temperatures. With careful design modifications, the BBO-FTIR was able to obtain furnace operations of up to 800°C. Second, careful construction of the scale platform, hood, and basket are essential. The uncertainty of the weight measurements were dramatically reduced by later improvements, allowing the measurement of previously unnoticed carbonate ingrowth in cooling ceramics. This ingrowth confirmed the results of high temperature XRD experiments performed by Dr. Jim Marra at SRTC, also part of the Plutonium Immobilization Program. Third, as the offgases cool, they condense and deposit on the sampling tubes and the hot gas cell, necessitating periodic maintenance of the gas cell mirrors and windows.

RESULTS

Refinement of the binder burnout process depends on variations of three key scheduling parameters, which control offgassing and decomposition. The parameters include ramp rates, hold temperatures, and hold times. These can vary throughout the binder burnout schedule and are a function of volatilizing and releasing the offgas. As shown in Figure 6, several offgassing regimes are present in a PIP puck and are affected by such parameter variations.

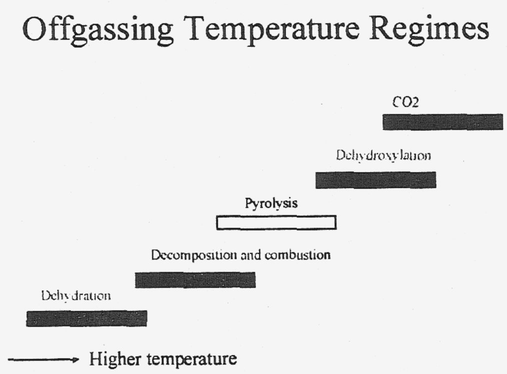

Figure 6. Offgassing Temperature Regimes in PIP Pucks.

Trends related to the PIP pucks—The weight loss behavior of binders, dispersants, and other relevant organic compounds, differs between the organic material as a powder, ceramic powder containing the organic material, compressed small samples of the ceramic and organics (pellets), and full-size pucks. This is illustrated by Figure 7, Morphology Tests. Both holds and slower ramp rates are effective tools to control offgassing and thereby maintain puck integrity. Mass transfer (inflow of oxygen or process gas, outflow of offgases) and heat transfer (heating of the puck surface and to a lesser degree the internal thermal gradient) limitations are important. Time is needed for the puck to reach thermal equilibration as shown in the "thermocouple puck" results.

The combination of understanding the binder burnout mechanisms of the sintering schedule and mass and heat transfer limitations is important to understanding processes that impact product quality, such as cracking. Cracking can be controlled by the binder burnout schedule. Two important examples of successful elimination of cracking in specific temperature regions are: 1) the gradual boil off of water during a range of furnace (dehydration regime); and 2) separating the regions during which water boils off (dehydration) and the organics begin to exit the puck (decomposition).

Low temperature holds are very important for controlling dehydration/ water offgassing. Process parameters have an important influence on puck offgassing behavior and, thus, the binder burnout schedule and puck integrity. Upstream processes that effect green puck dimensions and binder burnout include the: 1) Granulation process—binder type and quantity, binder dispersion method, granulated product particle size distribution, equipment specific parameters dependent on type of granulation; 2) Compaction process—compaction pressure, compaction dwell time; 3)

Preparation of the precursors—choice of raw materials, impurities, mixing method, and the calcination temperature; and 4) Mixing/blending process—ball milling or attritor milling. The particle size of the material resulting from these processes and the composition of the feed material has also been shown to indirectly affect the binder burnout process.

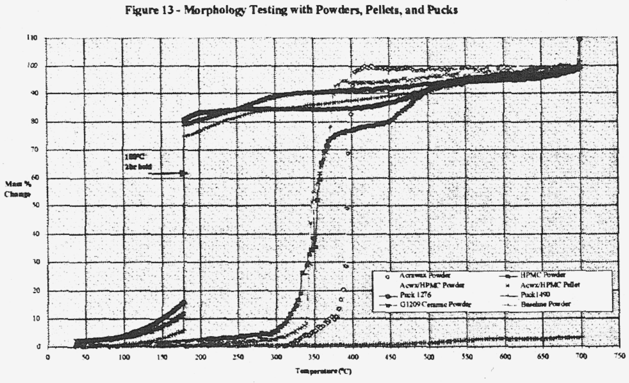

Figure 7. Morphology Tests.

FUTURE RESEARCH

The same technique can be applied to actual plant emissions, by simply sampling smokestack emissions using the hot gas cell FTIR. Used in conjunction with the BBO-FTIR, this allows plant personnel to optimize plant emissions by conducting research in a laboratory setting, using full size samples, and varying the appropriate processing parameters. These results can then easily be confirmed with the actual plant emissions. For plant emission monitoring, hot gas cell FTIR has many benefits over using an array sensors, each for a single gas. First, all IR active chemicals are dedicated – unexpected products of processing reactions are detected, not just the expected compounds. Second, by using the same experimental apparatus, many of the differences between lab scale experiments and plant emissions are eliminated. Third, an array of single gas sensors is more expensive. The next step is to connect the BBO-FTIR to an industrial production furnace in order to determine the effects of thermal gradients within such large furnaces on emissions. Figure 8 is a preliminary experiment towards that goal. The hypothesis is that a blurring of the distinct offgas peaks will result from the multiple pucks experiencing different thermal regimes at the same time.

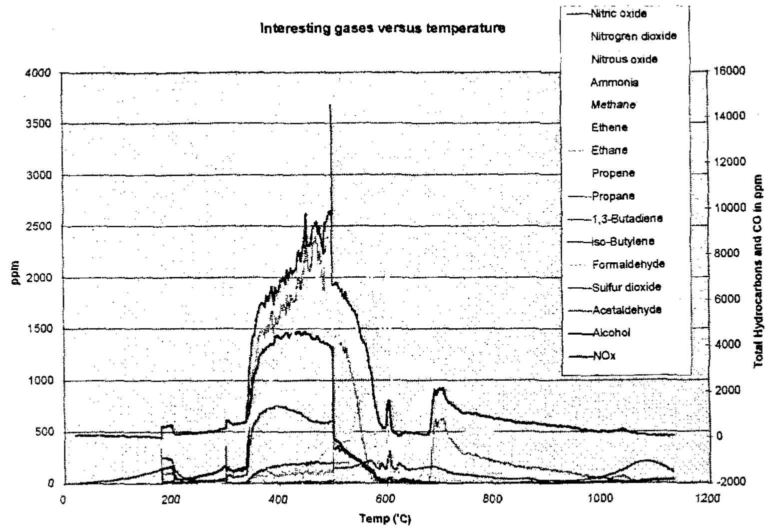

Figure 8. Offgas versus Temperature for full scale furnace.

Binder burnout experiments will continue until the granulation process, and other ceramification parameters, are finalized. A forthcoming LLNL report will consolidate the results of this multi-year research effort. This report will include results from a series of tests using different types, quantities, and dispersal methods for binders and other additives, using both the BBO-FTIR instrument and in a functionally prototypical plant furnace. Additionally, this will include research on binder aging using ^{13}C and ^{1}H NMR, FTIR, and liquid chromatography. Aging of binders in ceramic precursors can be an issue when binder degradation pathways are catalyzed by other compounds in the precursor mix and the material is stored in a hot, humid environment. This results in short molecular weight binders, and thus different binder burnout behavior, depending on the binder types and relevant reactions.

CONCLUSION

Optimization of production quality and throughput by varying the ceramic processing steps, addition of organic additives, thermal cycle development, and other processing parameters, has been greatly aided by the instrumentation developed for binder burnout studies. This technique offers the capability to increase the capabilities of research institutions and improve the profitability of industrial production. Sintering cycles can now be optimized to increase plant throughput and profitability, minimize environmental releases, optimize upstream processing (such as granulation and selection of binders), and minimize product integrity failures thereby reducing production costs and minimizing waste. Additionally, this research approach has the benefit of providing a means to scale up prototype processing developmental research to full scale production. Given the thermal gradients common in such industrial products, this scale up functionality can further optimize processing parameters and improve product quality. Used in conjunction with sampling of smokestacks, this technique can greatly help in optimizing processing to reduce plant emissions. BBO-FTIR allows examination of binder burnout behavior from a more directly representative approach that also has the benefit of examining the actual offgas behavior of full size samples in production environment furnaces.

ACKNOWLEDGEMENTS:

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