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Chem-Prep PZT 95/5 for Neutron Generator Applications: Powder Preparation Characterization Utilizing Design of Experiments

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Abstract

Niobium doped PZT 95/5 (lead zirconate – lead titanate) is the material used in voltage bars for all ferroelectric neutron generator power supplies. In June of 1999, the transfer and scale-up of the Sandia Process from Department 1846 to Department 14192 was initiated. The laboratory-scale process of 1.6 kg has been successfully scaled to a production batch quantity of 10 kg. This report documents efforts to characterize and optimize the production-scale process utilizing Design of Experiments methodology.

Of the 34 factors identified in the powder preparation sub-process, 11 were initially selected for the screening design. Additional experiments and safety analysis subsequently reduced the screening design to six factors. Three of the six factors (Milling Time, Media Size, and Pyrolysis Air Flow) were identified as statistically significant for one or more responses and were further investigated through a full factorial interaction design. Analysis of the interaction design resulted in developing models for Powder Bulk Density, Powder Tap Density, and +20 Mesh Fraction. Subsequent batches validated the models. The initial baseline powder preparation conditions were modified, resulting in improved powder yield by significantly reducing the +20 mesh waste fraction. Response variation analysis indicated additional investigation of the powder preparation sub-process steps was necessary to identify and reduce the sources of variation to further optimize the process.

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Introduction

Niobium doped PZT 95/5 is the material used in voltage bars for all ferroelectric neutron generator power supplies. There is currently no supplier of this material. In 1996, a program was initiated to develop a process for the synthesis of this ceramic powder. A non-aqueous process developed in Department 1846, referred to as the Sandia Process,¹ was selected, and in June of 1999, scale-up of the Sandia Process was initiated by Department 14192. Scaling the process from 1.6 kg to 10 kg was immediately successful with respect to stoichiometry and several powder characteristics (e.g., particle size, surface area, etc.). However, sintered slugs made from the scaled powder batches had unacceptably high variability in bulk density and functional test units (FTUs) fabricated from those slugs did not consistently meet drawing requirements (i.e., output failures and high voltage breakdowns).

The sequence of steps from powder synthesis through component qualification is extremely complex and typically takes over six months to complete. The overall process can be broken down into three sub-processes: powder preparation (synthesis through calcined powder), powder processing (granulation through sintered billets), and voltage bar fabrication (slug grinding through FTU testing). Voltage bar fabrication of chem-prep derived billets is identical to mixed oxide (current WR source material) billets and therefore, the variability mentioned above is thought to be primarily associated with the powder preparation or powder processing processes. Investigation of the powder processing sub-process will be described in future SAND reports. This report focuses on the factors associated with the powder preparation sub-process.

There were three interrelated goals to this study. One goal was to optimize the powder preparation process to meet component requirements. A second goal was to determine the processing space that would meet those requirements and to define the most robust levels of factors within that space. The third goal was to characterize the process sufficiently to identify the effective operating parameters for all factors, those that appear insensitive to the measured responses as well as those that require fine control to meet requirements.

Several issues affected the design of this study. One, mentioned previously, is the complexity of the process. The scope of the process, both in terms of the number of factors and the time it takes to complete a lot, forced several compromises. Time and expense did not allow for a large number of batches to be prepared and processed all of the way through to FTU testing. It was decided to evaluate responses up through component electrical properties, but not functional test evaluation. Although to date we have not been able to identify strong linkages between most powder processing responses and component performance, it was decided that those factors affecting powder processing strongly would reasonably be expected to affect component responses. To evaluate powder preparation factors it was necessary to hold constant all powder processing factors. This had two potential drawbacks. One is that it would miss any interactions that may span the two sub-processes, and two, the optimal powder processing conditions were still unknown. We had to assume that results based on a particular set of powder processing factors would generally hold true for other powder processing factor combinations. It should be noted that characterization of the powder processing factors was being investigated in parallel, and that the lack of understanding of optimal powder preparation conditions created the same difficulties for those experiments as well.

As will be seen in the discussion below, the number of factors in the powder preparation process itself was still quite large. Additional assumptions were made to narrow the scope to a practical number of experiments. Many of these factors were related to the scaling of the process itself. The production scaled process required larger vessels (25 L) for the various solutions, as well as larger diameter slurry filters. Equipment suitable to handle the larger process, such as the drying oven, was different from the laboratory scaled process. Additionally, steps had to be added to handle the amount of material produced, such as transferring the slurry into multiple drying trays instead of placing the filters directly in the drying oven and having to prepare the batch in four consecutive sub-lots rather than in a single reaction. Several of these factors had little flexibility, i.e., the scale of the process drove those conditions. It was recognized that some of these factors might be significant in explaining the differences between laboratory-scale material and production-scale material (e.g., the laboratory-scale process powder had a lower tap density and required more water for granulation, and the laboratory-scale sintered slug density was generally higher despite the greater amount of pore former that was typically added), but the goal in those cases was to optimize the process given those scaling constraints, rather than trying to force the process to more closely resemble the laboratory-scale process.

It was also decided to focus on post-synthesis steps. As mentioned earlier, stoichiometric control was demonstrated immediately. Although the process of precipitation can certainly affect the morphology of the initial precipitant, subsequent steps such as drying, pyrolysis, and ball milling were considered more likely to have significant impact on powder characteristics.

This report will cover the process optimization/characterization study that comprised several screening designs, an interaction design, and subsequent follow on experiments to evaluate the models developed. It should be noted that other experiments, looking at other aspects of powder preparation and optimizing the powder processing operations, were intermixed with the designed experiments. This resulted in restarting the screening design several times and changing some of the fixed factors between designs. The first two years of work, excluding the designed experiments discussed herein, has been previously documented.² The powder processing work and the more recent work on powder preparation will be discussed in subsequent SAND reports.

Procedure

A flowchart of the process from synthesis through calcined powder is presented in Figure 1. Although all other factors outside of each design were held constant, results from other experiments resulted in shifting some of these “fixed” factors between designs. The current, detailed process is described in a series of Work Instructions³⁻⁸.

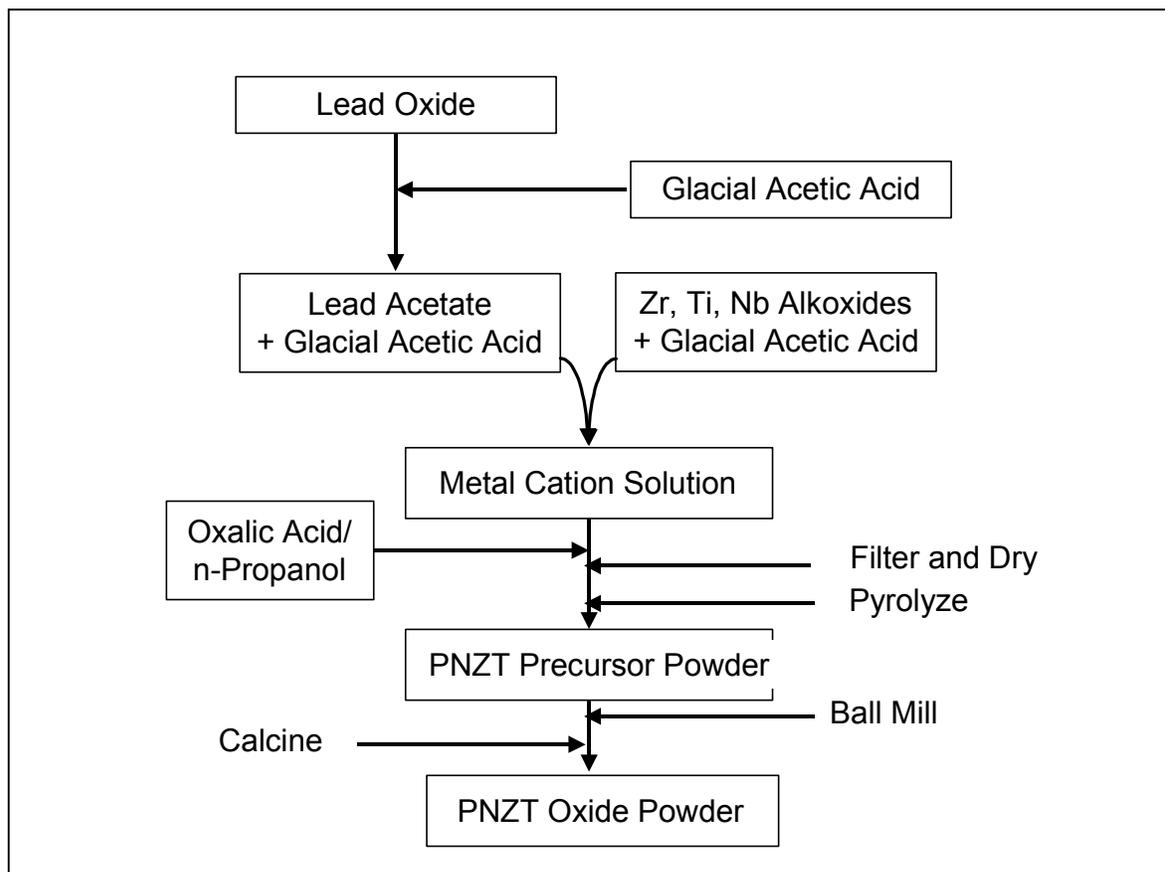
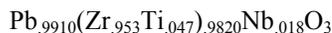


Figure 1. PNZT Powder Preparation Flowchart

The stoichiometry, with the exception of the Zr:Ti ratio, remained constant throughout the period of time covered in this report. The following formulation was synthesized for the screening designs. The Zr:Ti ratio was increased for the interaction design and follow up experiments as a result of other experiments and analyses conducted during that time period (see Table 1 and the Results and Discussion Section, below).



An additional 0.5 mole % Pb was added to the formulation to compensate for Pb loss during the process. The quantity of oxalic acid was increased by 20% over what was required to stoichiometrically react all species to ensure complete precipitation.

Results and Discussion

One of the basic tenets of Design of Experiments is that all factors not included in the design be held constant. This tenet was adhered to within each individual design, but there were changes made between designs. These changes were the results of other experiments and analyses that were conducted in parallel with the designed experiments. A summary of processing factors changed between designed experiments (not included in the original designs) is presented in Table 1. These changes were considered critical to meeting component requirements. In some cases the changes were not expected to affect the measured responses, or at least would affect all combinations within a design equally (e.g., Zr:Ti stoichiometry). Others were anticipated to potentially have a large effect (e.g., injector, shear mixer speed, filter drying). This resulted in aborting the screening design twice and modifying the factors that were investigated. These factor changes and how they impacted interpretation of the models will be discussed in detail below.

Table 1. Processing Factors Changed Between Designed Experiments

Experiment	Zr:Ti	Precursor Solution Filtering	Injector	Shear Mixer Speed	Filter Drying	Drying Oven
First Screening Design*	95.3:4.7	Metals	Straight	1400 rpm	1-5 days (Part of Design)	Hot Pack
Second Screening Design*	95.3:4.7	Metals, Oxalic	Straight	1400 rpm	6 days	Hot Pack
Third Screening Design	95.3:4.7	Metals, Oxalic	Angled	1750 rpm	6 days	Hot Pack
Interaction Design	95.5:4.5	Metals, Oxalic, Pb, Alkoxides	Angled	1750 rpm	6 days	Hot Pack
Follow On Experiments	95.7:4.3	Metals, Oxalic, Pb, Alkoxides	Angled	1750 rpm	1 day	Blue M

* Aborted before design completed

Factor Identification

The initial step in designing the experimental sequence was to identify all potentially significant factors (see Table 2.). Fifteen of the 34 identified factors were set at specific values and not investigated further. They were not considered for evaluation for several reasons. For factors 1, 9, 11, and 12 it had already been established that the minimum level to meet the specific response for each of those factors was desired.

Empirical data from earlier batches or analyses had identified factors 2-8 as sufficiently robust. Process constraints did not allow for factors 10 and 15 to be adjusted over a large enough range to make their evaluation significant. Finally, factors 13 and 14 had been deemed sufficiently characterized in the original designed experiment conducted on the laboratory-scale process.¹

Another group of factors, 16-20, were identified as potentially significant, but they were not controllable at that point in time. To control this group, which included factors that were a function of the environment or the process itself, was potentially very difficult and/or expensive. It was decided to continue collecting data on these factors and evaluate them statistically to determine if any of them correlated with important responses that would then merit process modifications to control them.

The final 14 factors (factors 21-34) were deemed sufficiently significant to investigate. This number of factors could not be investigated in a full factorial design (the number of experiments required is 2^n , where n is the number of factors). A screening design, a fractional factorial, was used to down-select the number of factors to the critical few (usually ≤ 5). However, due to the length and complexity of the process, it was necessary to further reduce this number to 11 or fewer. Up to 11 factors can be evaluated in 12 experimental runs. Greater than 11 factors would require a minimum of 16 runs, more than the team was willing to consider. Three factors, 21-23, were identified as factors that could be investigated at the laboratory-scale, because the results from a designed experiment on that scale could reasonably be expected to apply to the production-scale process.

Table 2. Powder Preparation Sub-process Factors

Factor	Approach	
1	N ₂ flow rate	Set range (need minimum flow to ensure blanket over solution)
2	Pb sol'n stir speed	Set range (empirically determined to have no significant effect over the controllable range)
3	Alkoxide stir speed	
4	Metals stir speed	
5	Oxalic sol'n stir speed	
6	Metals pump speed	
7	Reactor stir speed	
8	Stir tank stir speed	
9	AcAc addition time	Set range (want minimum amount - visual observation sufficient)
10	Stir tank mixing time	Set range (controlled by logistics, i.e., timing of sub-lot processing)
11	Alkoxide prep time	Set range (want to minimize exposure to atmosphere)
12	Alkoxide mixing time	
13	Oxalic sol'n conc.	Set range (investigated in laboratory-scale SAND Report ¹)
14	Oxalic to metals ratio	
15	Amount per drying tray	Set range (oven dimensions restrict range)
16	Pb dissolution time	These factors are not controllable. Conduct correlation study to determine the level of significance for each.
17	Pb sol'n vol.	
18	Pb prep RH	
19	Pb prep temp.	
20	Pb sol'n clarity	Lab-scale DOE
21	Metals mixing time	
22	Shear mixer setting	
23	Reactor mixing time	
24	Filter drying time	
25	Filter cake agglomerate size	
26	Filter cake handling	
27	Oven drying time	

	Factor	Approach
28	Drying temp.	Production-scale DOE
29	Ball mill time	
30	Ball mill media	
31	Powder to media ratio	
32	Pyrolysis time	
33	Pyrolysis temp.	
34	Pyrolysis air flow	

Initial Screening Designs

As described above, a maximum of 12 runs was to be allotted to the screening design. A Resolution III Plackett-Burman design was used evaluate 11 factors in 12 runs. This design is highly fractionated, meaning that there is significant confounding of the main effects with the interactions. For this design, each main effect is confounded with multiple two-factor interactions. Unless a specific interaction is known, the results are interpreted based on the assumption that any statistically significant response is due to the main effect. Table 3 lists the factors in the design, the upper and lower values, and the nominal value at the time of these experiments. Where possible, the design levels were chosen to bracket the nominal values.

Table 3. Factors and Levels in 11 Factor Plackett-Burman Screening Design

Factor	Lower Value	Upper Value	Nominal Value
Filtering Time (Days)	1	5	3
Drying Time (Days)	1	5	3
Drying Temperature (°C)	75	95	88
Ball Milling Time (h)	2	15	7
Media Diameter (in.)	0.25	0.50	0.375
Powder to Media Ratio	1	2	1
Pyrolysis Time (h)	4	24	16
Pyrolysis Temperature (°C)	300	500	400
Filter Cake Agglomerate Size	Break Up	No Handling	Break Up
Filter Cake Handling	Break Up	None	Break Up
Pyrolysis Air Flow	0	130	130

The resulting design is shown in Table 4. The first three batches in the design were prepared without incident, but before the fourth could be prepared, two events occurred that altered the remaining batches in the experimental matrix. A strong solvent odor had been noted emanating from the drying oven in the batch prior to the start of the experimental matrix (the precipitate had been dried in the filters the nominal three days before being placed in the drying oven). The Safety Engineering Department was contacted before continuing with the fourth batch to evaluate the nature/severity/health/safety concerns of the odor. Safety Engineering personnel verified that the drying oven was approved for Class A solvents, but were concerned that the levels of volatiles emanating from the powder during drying were at an unacceptably high level. It was agreed to increase the minimum filter drying time for the DOE from one to two days while quantitative monitoring of the solvent levels in the oven were measured. It had also been noted that in batches leading up to the start of the experimental matrix the oxalic acid/n-propanol solution was occasionally discolored. As a result, it was decided that it was important to incorporate filtering of the solution as a factor in the design. There were two options to avoid restarting the matrix. One option was to bundle the oxalic acid/n-propanol filtering factor to one of the other factors that had been run at a single value for the first three batches, or two, to replace one of those factors with the filtering factor. It was decided to replace Pyrolysis Time with filtering of the oxalic acid/n-propanol.

Table 4. Initial 11 Factor Screening Design

Run Order	Filtering Time (Days)	Drying Time (Days)	Drying Temp. (°C)	Ball Mill Time (h)	Media Diameter (in.)	Powder to Media Ratio	Pyrolysis Time (h)	Pyrolysis Temp. (°C)	Filter Cake Agglomerate Size	Filter Cake Handling	Pyrolysis Air Flow
1	5	1	95	2	0.25	1	24	500	Break up	None	130
2	5	5	75	15	0.50	1	24	300	No handling	None	130
3	5	1	75	2	0.50	2	24	300	Break up	Break up	0
4	2	1	75	2	0.25	1	4	300	No handling	None	0
5	2	5	95	2	0.50	1	4	300	Break up	Break up	130
6	2	1	95	15	0.50	1	24	500	No handling	Break up	0
7	2	5	75	2	0.25	2	24	500	No handling	Break up	130
8	5	5	95	2	0.50	2	4	500	No handling	None	0
9	2	5	95	15	0.25	2	24	300	Break up	None	0
10	5	5	75	15	0.25	1	4	500	Break up	Break up	0
11	2	1	75	15	0.50	2	4	500	Break up	None	130
12	5	1	95	15	0.25	2	4	300	No handling	Break up	130

Monitoring of volatiles in the drying oven for the fourth batch in the design (note this batch was run at the increased minimum filter drying time of 2 days) still resulted in very high volatiles concentrations inside the drying oven. A standard batch was then run to determine the minimum filter drying time. It was determined that the filter cakes required a minimum of seven days filter drying to ensure that the volatiles concentration in the drying oven did not exceed 50% of the lower explosive limit. These results lead to a complete redesign of the experiment. Filter drying time and oven drying time were dropped from the matrix. To incorporate these would require adding additional time to those steps, and with the minimum already at eight days (seven days in the filter, one day in the oven), it was deemed impractical to study even longer times. To minimize the amount of time in the filter and reduce the volatiles concentration in the drying oven, the filter cakes were thoroughly broken up while in the filter and when they were placed in the drying trays. Therefore, filter cake handling and filter cake agglomerate size were also dropped from the matrix.

Six Factor Screening Design

With the loss of factors due to safety issues described above, the number of factors was reduced to six. This allowed for the use of an eight factor screening design. It had taken 10 weeks from the time the initial screening design batch had been started until the safety issues had been resolved. To maintain the same finish date for the screening design, a compromise on the number of batches was made. Since several of the factors were post-synthesis processing steps, it was possible to split the batches and generate two of the experimental runs from each batch, reducing the total number of batches to four. It should be noted that this approach is generally not recommended because it destroys some of the randomness of the design (i.e., pairs of runs will have common characteristics not shared with the other runs and a truly random run order cannot be followed). The resulting design is shown in Table 5.

Table 5. Six Factor Screening Design

Batch ID	Run Order	Drying Temp. (°C)	Pyrolysis Temp. (°C)	Pyrolysis Air Flow (cfm)	Ball Mill Time (h)	Media Diameter (in.)	Powder to Media Ratio
TSP-22-1A	1	75	300	0	2	0.25	1
TSP-22-1B		75	300	0	15	0.50	2
TSP-23-2A	2	115	500	0	15	0.25	2
TSP-23-2B		115	500	0	2	0.50	1
TSP-24-3A	3	115	300	130	15	0.50	1
TSP-24-3B		115	300	130	2	0.25	2
TSP-25-4A	4	75	500	130	2	0.50	2
TSP-25-4B		75	500	130	15	0.25	1

Nine responses were initially analyzed. Seven of the responses were associated with powder characteristics, one response was associated with the sintered slug, and one response was associated with fabricated voltage bars. The responses can be grouped into three categories, those with a desired value, those with a target value based on fundamental ceramic powder principles, and those without a known desired value. The responses, with their targets, if known, and the range of values from the completed matrix of experiments is shown in Table 6.

Table 6. Six Factor Screening Design Responses and Target Values

Response	Target	Experimental Range
Yield (%)	100	46.4 - 98.2
+20 Mesh (g/batch)	0	1 - 3266
Defect Density (defects/in ²) ¹	0	0 - 8.4
Voltage bars Cracked (%)	0	10 - 100
Powder Bulk Density (g/cc)	2.0-2.4	1.54 - 2.22
Hausner Ratio ²	1.00	1.08 - 1.12
Angle of Repose (degrees) ³	<40	59 - 79
Slug Density (g/cc)	?	7.23 - 7.37
Surface Area (m ² /g)	?	0.74 - 1.21
Particle Size (µm)	?	3.11 - 5.86

¹ Spots per unit area of V-bar

² Tap Density/Bulk Density

³ Angle formed by the slope of a poured cone of the powder

Later, additional responses were measured. These included three voltage bar electrical properties, remanent polarization (P_{rf}), coercive field (E_c), and hydrostatic depoling charge release (Q), and a slug microstructural characteristic, Type 2 spot count (qualitative scale where 0 is none and 6 is very high). The complete set of results for all responses is shown in Tables 7 - 9.

Table 7. Six Factor Screening Design Results: Responses 1-5

Batch ID	Factors					Responses					
	Drying Temp. (°C)	Media Size (in.)	Milling Time (h)	Powder/Media Ratio	Pyrolysis Temp. (°C)	Air Flow (cfm)	+20 Mesh (g/batch)	Yield (%)	Particle Size (µm)	Surface Area (m ² /g)	Powder Bulk Density (g/cc)
TSP-22-1A	75	0.25	2	1	300	0	2212	46.4	4.62	0.81	1.716
TSP-22-1B	75	0.50	15	2	300	0	533	85.0	5.28	0.74	1.539
TSP-23-2A	115	0.25	15	2	500	0	1586	76.6	4.76	1.16	1.671
TSP-23-2B	115	0.50	2	1	500	0	667	78.6	5.86	1.03	1.703
TSP-24-3A	115	0.50	15	1	300	130	1	98.2	3.11	1.20	2.217
TSP-24-3B	115	0.25	2	2	300	130	3266	55.0	4.42	1.21	1.796
TSP-25-4A	75	0.50	2	2	500	130	350	87.5	4.19	1.05	1.825
TSP-25-4B	75	0.25	15	1	500	130	2470	63.4	3.23	1.12	1.958

Table 8. Six Factor Screening Design Results: Responses 6-10

Batch ID	Factors					Responses					
	Drying Temp. (°C)	Media Size (in.)	Milling Time (h)	Powder/Media Ratio	Pyrolysis Temp. (°C)	Air Flow (cfm)	Hausner Ratio	Angle of Repose	Defect Density	Type 2 Spot Count	Slug Density (g/cc)
TSP-22-1A	75	0.25	2	1	300	0	1.099	77	4.3	5	7.319
TSP-22-1B	75	0.50	15	2	300	0	1.120	76	0.0	1	7.278
TSP-23-2A	115	0.25	15	2	500	0	1.091	78	3.9	4	7.328
TSP-23-2B	115	0.50	2	1	500	0	1.109	79	8.0	4	7.322
TSP-24-3A	115	0.50	15	1	300	130	1.080	59	1.6	0	7.314
TSP-24-3B	115	0.25	2	2	300	130	1.111	75	5.1	6	7.229
TSP-25-4A	75	0.50	2	2	500	130	1.122	73	8.4	5	7.299
TSP-25-4B	75	0.25	15	1	500	130	1.102	73	3.5	3	7.365

Table 9. Six Factor Screening Design Results: Responses 11-14

Batch ID	Factors					Responses				
	Drying Temp. (°C)	Media Size (in.)	Milling Time (h)	Powder/Media Ratio	Pyrolysis Temp. (°C)	Air Flow (cfm)	Voltage Bars Cracked (%)	P _r (µC/cm ²)	E _c (kV/cm)	Q (µC/cm ²)
TSP-22-1A	75	0.25	2	1	300	0	13.5	29.501	10.028	30.06
TSP-22-1B	75	0.50	15	2	300	0	13	29.001	10.134	29.39
TSP-23-2A	115	0.25	15	2	500	0	10	29.358	10.103	29.74
TSP-23-2B	115	0.50	2	1	500	0	13.5	29.926	10.168	29.77
TSP-24-3A	115	0.50	15	1	300	130	100	-	-	-
TSP-24-3B	115	0.25	2	2	300	130	70	27.962	10.632	28.04
TSP-25-4A	75	0.50	2	2	500	130	10	29.645	10.132	29.93
TSP-25-4B	75	0.25	15	1	500	130	100	31.076	10.006	31.13

Regression Analysis and Analysis of Variance (ANOVA) was run for each of 11 responses. Batch TSP-24-3A voltage bars were so badly cracked it was not possible to make electrical measurements on them, and therefore, the responses Pr, Ec, and Q could not be analyzed. The α level chosen was 0.05, meaning that for a factor to be considered statistically significant its P-value must be <0.05 for the given response. Table 10 shows the factors that were statistically significant for one or more responses.

Table 10. Six Factor Screening Design Statistically Significant Factors

Response	Statistically Significant Factor	P	Direction of Factor to Improve Response
Yield	Media Size	0.012	↑
+20 Mesh	Media Size	0.002	↑
Type 2 Spots	Media Size	0.041	↑
Defect Density	Milling Time	0.022	↑
Type 2 Spots	Milling Time	0.009	↑
Voltage bars Cracked	Air Flow	0.035	↓
Powder Bulk Density	Air Flow	0.031	↑
Particle Size	Air Flow	0.019	?

Only three of the six factors were found to be statistically significant for any of the responses. Media size was statistically significant for Yield, +20 Mesh, and Type 2 Spots. Yield and +20 Mesh are closely related and it is expected that they would behave similarly. Many steps in the process contribute to the reduction in yield, with the +20 mesh fraction potentially being very significant. The coefficient for Media Size was negative for +20 Mesh and Type 2 Spots, and positive for Yield, meaning to improve each of those responses, increasing the size of the media was indicated. Milling Time was found to be statistically significant for Type 2 Spots and Defect Density. These two responses are also closely related, with Type 2 Spots being a sub-set of Defect Density. The Milling Time coefficient for these responses was negative, so increasing the milling time reduces the response value, which is the desired direction for improvement. Finally, Pyrolysis Air Flow was found to be statistically significant for Voltage Bars Cracked, Powder Bulk Density, and Particle Size. The significance of Pyrolysis Air Flow was somewhat mitigated by subsequent experiments and analysis of the regression data. It was learned that voltage bar cracking was due to the bisque firing profile. When the bisque fire profile was modified, voltage bar cracking was eliminated for all synthesis processing conditions. A more detailed analysis of Powder Bulk Density and Particle Size responses revealed high residuals. In each case, a single run was responsible for the high residuals. When ignoring the outlier, there did still appear to be an effect due to Pyrolysis Air Flow, but whether it was still statistically significant could not be determined. Nevertheless, it was decided to include Pyrolysis Air Flow with Media Size and Milling Time for the next phase, an Interaction Design.

Interaction Design

To more quantitatively examine the significant factors identified in the screening design, an interaction design, a full factorial with a center point, was employed. With the addition of replicates at the center point to estimate response variation, a total of 11 runs were required. The center point runs were spread throughout the run order, with all other runs being randomized. For Milling Time and Media Size, the screening design indicated that increasing the value of those factors improved the responses for which they were significant. For the screening design the upper value for Milling Time was set to 29 h, nearly twice the nominal value of 15 h. It was recognized that there is a trade off in processing time, efficiency, and logistics to be made with maximizing that factor range. However, the result from the screening design indicated that widening that range might be important, and it was therefore decided to further expand the Milling Time range such that the upper level in the screening design became the center point in the interaction design. The factor levels for Media Size in the screening design were driven more by available material. Again, based on the screening design results, the factor range was expanded for the interaction design by purchasing larger media. This expanded range resulted in the screening design upper factor level being the center point level in the interaction design. Although the optimal Pyrolysis Air Flow level was equivocal (see Table 10), it was decided to maximize the range in the interaction design by installing a new flow meter to allow for greater air flow. The complete design is presented in Table 11. Nominal baseline conditions at the time of the interaction design were 0.375 in. media, 15 h milling time, and 130 cfm air flow.

Table 11. Interaction Design Matrix

Batch ID	Run Order	Media Diameter (in.)	Pyrolysis Air Flow (cfm)	Ball Mill Time (h)
TSP-36-CP1	1	0.50	150	15
TSP-37-1	2	0.25	0	29
TSP-39-2	3	0.25	0	1
TSP-40-3	4	0.75	300	1
TSP-42-4	5	0.25	300	1
TSP-46-CP2	6	0.50	150	15
TSP-49-5	7	0.75	300	29
TSP-50-6	8	0.25	300	29
TSP-51-7	9	0.75	0	29
TSP-52-8	10	0.75	0	1
TSP-53-CP3	11	0.50	150	15

It may be noted that the 11 runs of the interaction design were not consecutive. Several batches were interspersed throughout the experiment to provide material for powder processing experiments that were being performed in parallel. The total time for synthesizing the powders for the interaction design from the start of Run #1 until the calcination of the powder from Run #11 was eight months. A concerted effort was made to maintain all non-design factors at fixed levels. Those fixed factors are listed in Table 12. There were several other factors that could not be controlled as well as desired. These included environmental factors such as room temperature and relative humidity, and chemical precursor lots. For the environmental factors, their values were recorded, and as will be seen in the discussion below may have contributed to the high response variation that was observed. Precursor lots could have been treated as a blocking factor(s). However, because of limited availability of specific quantities of precursor lots, the unknown number of non-design batches to be interspersed throughout the matrix, the total length of the experiment, and a history that indicated that precursor lot to lot variability did not significantly affect material properties, it was decided not to block for precursor lot. It should be noted that there were two significant factor changes between the screening design and the interaction design. To address depoling pressure and output issues in the voltage bars, the Zr:Ti ratio was changed from 95.3:4.7 in the screening design to 95.5:4.5 in the interaction design. Improved voltage bar electrical properties were correlated with filtering of the Pb acetate and Zr/Ti/Nb alkoxide solutions, and therefore the additional filtering was added as a standard processing step between the screening design and the interaction design.²

Table 12. Fixed Factors for the Interaction Design

	Value		Factor	Value
Pb sol'n stir speed	~50 rpm		Shear mixing setting	75%
Pb sol'n filtering	Yes		Shear mixing time	5 min
Alkoxide filtering	Yes		Stir tank mixing time	90 min
Alkoxide stir speed	~60 rpm		Stir tank stir speed	~50 rpm
Alkoxide mixing time	5 min		Filter drying time	7 days
Metals stir speed	~75/50 rpm		Filter cake handling	Break up
Metals mixing time	30 min		Oven drying schedule	Standard
Metals pump speed	~55 rpm		Pyrolysis soak time	16 h
Metals filtering	Yes		Pyrolysis temperature	400°C
Oxalic to metals ratio	3.5:3.0		Powder to media ratio	1:1
Oxalic sol'n conc.	17.70%		Sieving procedure	Standard
Oxalic sol'n filtering	Yes		Calcination schedule	Standard
Oxalic sol'n stir speed	Not controlled			

Each run from the design was a standard 10 kg batch size. At the time of the experiment, standard processing of the powder into sintered slugs used ~2 kg quantities of powder. This allowed for multiple high fire lots of slugs from each run. High fire to high fire variability within a single powder batch had previously been shown to be very low. Therefore, instead of reaffirming that reproducibility, the multiple high fires were used to look at two different pore formers, Avicel and Lucite, a major powder processing issue at the time. As with the screening design, a large number of responses were measured that ranged from powder characteristics through voltage bar electrical properties. The results for each of the responses are listed in Tables 13-15.

Table 13. Interaction Design Results: Responses 1-8

Factors				Responses							
Batch	Air Flow (cfm)	Media Size (in.)	Milling Time (h)	Powder Bulk Density (g/cc)	Powder Tap Density (g/cc)	Hausner Ratio	Surface Area (m ² /g)	Particle Size (μm)	+20 Mesh Fraction (g)	H ₂ O Addition [Lucite] (vol.%)	H ₂ O Addition [Avicel] (vol.%)
TSP-36-CP1	150	0.50	15	-	-	-	1.37	3.47	577	56	57
TSP-37-1	0	0.25	29	1.636	1.883	1.151	1.28	3.59	750	55	56
TSP-39-2	0	0.25	1	1.057	1.227	1.161	1.06	5.33	512	56	57.5
TSP-40-3	300	0.75	1	1.048	1.218	1.162	1.10	6.56	50	55.5	58
TSP-42-4	300	0.25	1	0.989	1.166	1.179	1.00	4.03	638	56.5	59
TSP-46-CP2	150	0.50	15	1.324	1.460	1.103	1.18	5.21	136	56	59.5
TSP-49-5	300	0.75	29	1.423	1.582	1.112	1.28	4.88	59	57	57
TSP-50-6	300	0.25	29	1.360	1.544	1.135	1.32	3.65	1472	58.5	58
TSP-51-7	0	0.75	29	1.544	1.748	1.132	1.18	4.18	68	-	56
TSP-52-8	0	0.75	1	0.919	1.047	1.139	1.27	4.60	42	59	62
TSP-53-CP3	150	0.50	15	1.504	1.679	1.116	1.18	3.60	47	55	56

Table 14. Interaction Design Results: Responses 9-15

Factors				Responses					
Batch	Air Flow (cfm)	Media Size (in.)	Milling Time (h)	Slug Green Density [Lucite] (g/cc)	Slug Green Density [Avicel] (g/cc)	Sintered Slug Bulk Density [Lucite] (g/cc)	Sintered Slug Bulk Density [Avicel] (g/cc)	Type 2 Spot Count [Lucite] (0=None, 7=Very High)	Type 2 Spot Count [Avicel] (0=None, 7=Very High)
TSP-36-CP1	150	0.50	15	4.03	3.92	7.439	7.382	4	4
TSP-37-1	0	0.25	29	-	-	7.429	7.341	3	1
TSP-39-2	0	0.25	1	3.93	3.93	7.385	7.347	4	2
TSP-40-3	300	0.75	1	3.78	3.67	7.367	7.342	6	0
TSP-42-4	300	0.25	1	3.86	3.74	7.320	7.294	4	4
TSP-46-CP2	150	0.50	15	3.90	3.78	7.358	7.344	7	6
TSP-49-5	300	0.75	29	3.89	3.80	7.433	7.404	4	2
TSP-50-6	300	0.25	29	3.82	3.76	7.386	7.358	4	4
TSP-51-7	0	0.75	29	4.00	3.90	7.347	7.322	2	2
TSP-52-8	0	0.75	1	3.53	3.49	7.262	7.265	7	7
TSP-53-CP3	150	0.50	15	4.07	3.93	7.405	7.331	4	2

Table 15. Interaction Design Results: Responses 16-19

Batch	Factors			Responses			
	Air Flow (cfm)	Media Size (in.)	Milling Time (h)	Q [Lucite] ($\mu\text{C}/\text{cm}^2$)	Q [Avicel] ($\mu\text{C}/\text{cm}^2$)	Depoling Pressure [Lucite] (kpsi)	Depoling Pressure [Avicel] (kpsi)
TSP-36-CP1	150	0.50	15	31.838	30.365	42.807	38.619
TSP-37-1	0	0.25	29	30.737	28.227	47.047	42.237
TSP-39-2	0	0.25	1	31.376	29.860	44.470	39.905
TSP-40-3	300	0.75	1	31.077	30.164	43.887	40.126
TSP-42-4	300	0.25	1	30.294	29.216	47.300	41.730
TSP-46-CP2	150	0.50	15	31.590	30.500	45.560	40.500
TSP-49-5	300	0.75	29	32.020	30.900	45.630	40.620
TSP-50-6	300	0.25	29	31.220	30.150	46.680	41.460
TSP-51-7	0	0.75	29	30.520	29.900	47.410	42.760
TSP-52-8	0	0.75	1	30.460	29.690	43.090	39.450
TSP-53-CP3	150	0.50	15	31.500	30.400	45.980	40.410

Before analyzing the responses within the interaction design framework, some general observations can be made regarding the Avicel and Lucite pore formers. For every design combination, with one exception, the Avicel powders required an equal or higher volume percent of water for granulation. For every design combination, the Avicel containing material had lower slug green densities, lower sintered slug densities, equal or lower Type 2 spot counts, less charge release, and a lower hydrostatic depoling pressure. These results suggested there may be a significant difference in material properties as a function of pore former. However, as will be seen in the discussion below, the center point variability rendered most of response variation statistically insignificant.

Factorial analysis was performed on each of the 19 responses. Only three of the responses were statistically significant with respect to any of the factors, and the three significant responses all involved powder characteristics: +20 Mesh, Powder Bulk Density, and Powder Tap Density. None of the responses for billet or voltage bar characteristics/properties were found to be statistically significant. For most of the responses the response variation for the triplicate center point runs overwhelmed the range of responses from the rest of the design. An example of the response variation problem can be seen with Sintered Slug Bulk Density shown in Figures 2 and 3. The “error bars” are the range of values for the center point triplicate runs. Therefore, because of the relatively wide range in density (~ 0.16 g/cc), it was not possible to attribute it to any of the factors. This raised a concern regarding the reproducibility or robustness of the overall process from chemical synthesis through voltage bar fabrication. Although there is inherent variation in each step of the process and the overall process variability is additive, the high response variation observed in the earliest steps of the process (i.e., powder synthesis) suggested that it was important to identify and reduce variation sources here if overall process robustness was to be achieved. As was noted above, it took eight months to synthesize all of the runs. Many factors can be influenced by time (e.g., environmental conditions, operator experience, equipment drift, etc.). Experiments and analysis of variation sources will be the subject of a subsequent report.

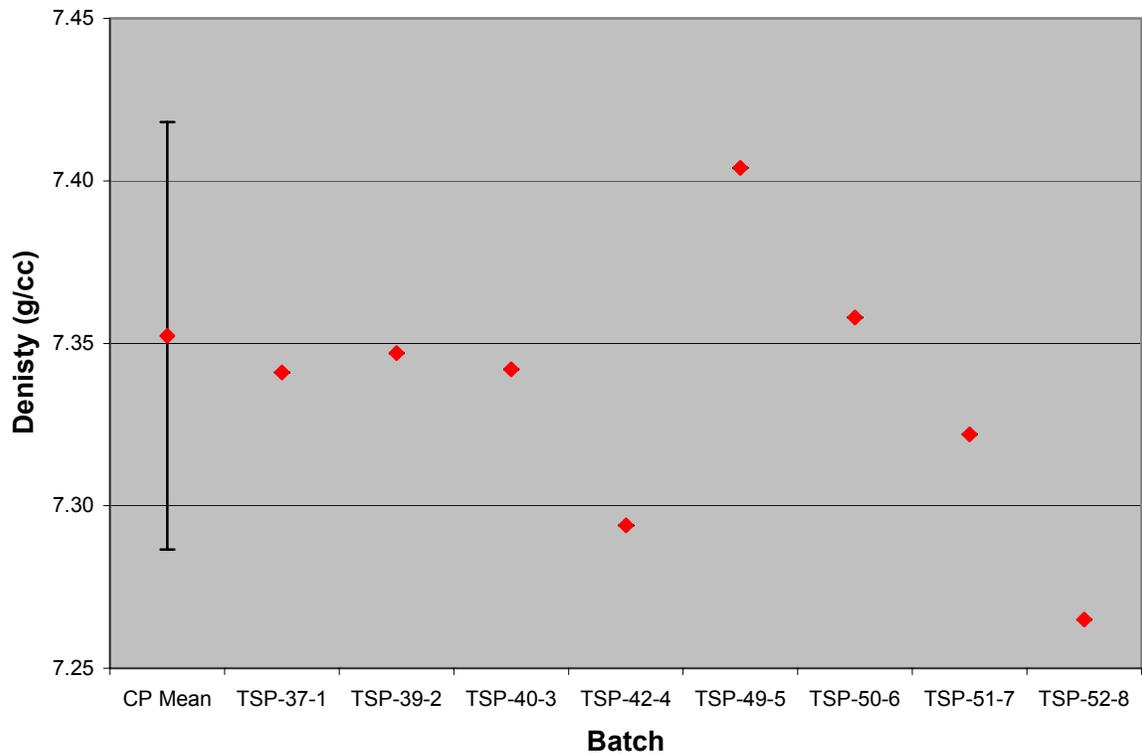


Figure 2. Sintered Slug Density (Avicel)

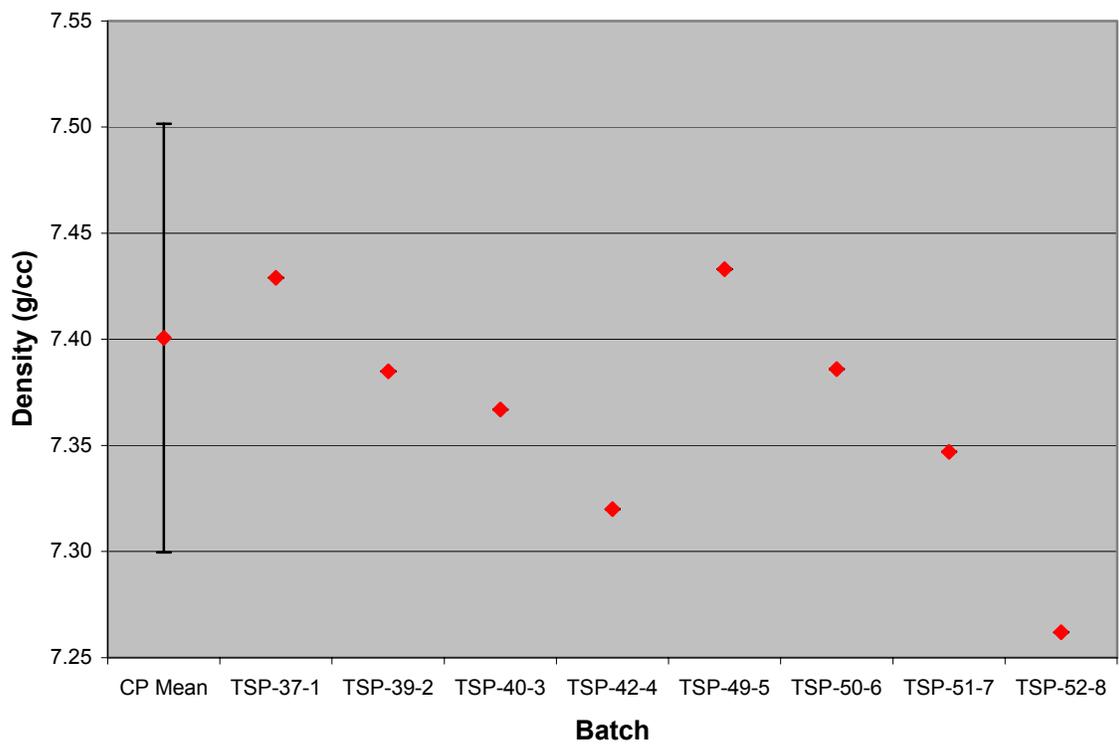


Figure 3. Sintered Slug Density (Lucite)

Powder Bulk Density and Powder Tap Density were found to correlate with Milling Time. They were initially fitted to linear models with R^2 (adjusted) values of ~75%. However, the residuals versus the fitted models were non-random, indicating a non-linear relationship between the responses and Milling Time. When the responses were fitted to \ln (Milling Time), the pattern in the residuals disappeared. The models, given below, also have improved R^2 (adjusted) values.

$$\begin{aligned} \text{PBD} &= 1.00 + 0.146 \ln(\text{Milling Time}) & R^2(\text{adj.}) &= 86\% \\ \text{PTD} &= 1.16 + 0.155 \ln(\text{Milling Time}) & R^2(\text{adj.}) &= 81\% \end{aligned}$$

For these two responses there is not a targeted value. The as-calcined powder, which is what was measured, is not pressed directly, but has pore former and binder added, and is granulated prior to pressing. The granulation conditions are based on the as-calcined powder characteristics. Therefore, a model that accurately predicts those characteristics is useful in optimizing and monitoring the granulation process.

For the +20 Mesh, Media Size was found to correlate. The fit to a linear model was modest with an R^2 (adj.) value of only 56.5%. However, the P-value was 0.005 indicating that Media Size was clearly statistically significant (the significance level, α , is typically set at 0.05). The model for +20 Mesh is as follows:

$$+20\text{M} = 1183.8 - 1576.5 (\text{Media Size})$$

Contributing to the low R^2 value is the wide variation in responses for the smallest media size. As can be seen in Figure 4, the four lowest values, which were of similar values, all corresponded to the larger media size, but the responses for the smaller media size ranged from ~500-1500g, suggesting that there are additional factor(s) associated with that variation.

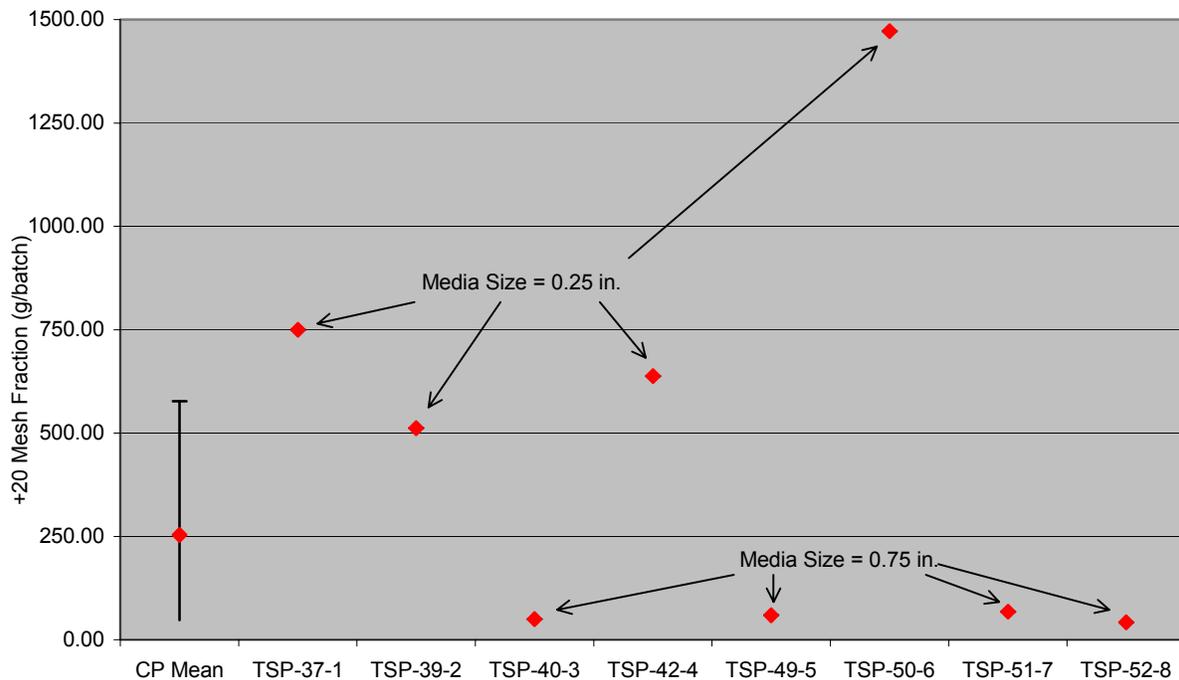


Figure 4. +20 Mesh Fraction

The +20 Mesh Fraction represents the hard agglomerates and is discarded. Therefore, the target value for this is 0, to maximize yield. As a result, the nominal processing conditions were changed to the larger milling media. In addition, Milling Time was set to 1 h (the minimum value in the design) and Pyrolysis Air Flow

was set to 300 cfm (the maximum value in the design). Although neither of these factors were found to be statistically significant, from a processing time and logistics perspective, shorter milling times are more desirable. Similarly, increased air-flow would be expected to help reduce residual organics, and although it was not found to be significant for the responses measured in this experiment, if subsequent processing occasionally resulted in higher levels of organic to be removed, the higher air-flow would be advantageous.

Models Validation

Two batches were prepared to validate the models generated from the interaction design. It is important to note that there was a six month gap between completion of the synthesis of the last powder batch in the design and the analysis of all the responses, which involved the forming and firing of billets from each batch, and the fabrication and testing of voltage bars from the corresponding billets. During that six month period several significant processing changes were made. The drying oven was replaced with one based on a different design. The new drying oven had higher air flow rate and being explosion-proof could tolerate higher concentrations of volatiles. This resulted in reducing the filter drying time to one day, thus loading much wetter slurry into the drying oven. This change had the potential to alter the physical structure of the oxalate, which potentially could carry through to the calcined powder, and possibly affect the powder characteristics that had been modeled. The second significant change was the stoichiometry; the Zr:Ti ratio was changed from 95.5:4.5 to 95.7:4.3. This change was not expected to significantly impact the response models that were being validated.

Table 16 lists the three responses that could be fitted to models, the predicted values based on the models, and the 95% Confidence Limits for the center point in the interaction design, the range of values measured from the interaction design, and the measured values from the two model validation batches (TSP-62 and TSP-63).

Table 16. Model Validation Responses

	Powder Bulk Density (g/cc)	Powder Tap Density (g/cc)	+20 Mesh (g)
Interaction Design Response Range	0.92-1.59	1.05-1.88	42-1472
95% Confidence Limit (center point)	±0.18	±0.21	±321
Model Prediction	1.00	1.16	1
TSP-62	0.87	1.25	57
TSP-63	0.89	1.27	14

It can be seen that the results of the validation batches were reasonably close to the model predictions. When considering the range of values measured during the interaction experiment and the response variation from the center point, one can conclude that the models were able to accurately predict the responses for powder bulk density, powder tap density, and the +20 mesh fraction.

Summary

A series of designed experiments were run to accomplish the following goals: 1) optimize the powder preparation process to meet component requirements, 2) determine the processing space that would meet those requirements and to define the most robust levels of factors within that space, and 3) characterize the process sufficiently to identify the effective operating parameters for all factors, those that appear insensitive to the measured responses as well as those that require fine control to meet requirements. Analysis of the process identified 34 factors, 11 of which were initially chosen to apply Design of Experiments methodology to their investigation. The other 23 factors were to be investigated by other means, or were determined to be sufficiently characterized at the time.

The original screening design had to be restarted twice when other experiments (injector modification and shear mixer speed) and safety evaluations (filter drying and oven volatiles limitations) resulted in significant modifications to the process. These modifications resulted in the final version of the screening design being

reduced to six factors. Fourteen responses, including powder characteristics through component electrical properties, were measured. Three of the six factors, Milling Time, Media Size, and Pyrolysis Air Flow, were identified as being statistically significant for one or more of the responses.

A full factorial design with center point was run to model the three factors. Only three of the 19 responses were found to be statistically significant. This was due in large part to the high response variation measured for the center point triplicate runs. Powder Bulk Density and Powder Tap Density had a log relationship to Milling Time. A simple linear model with the single variable, Media Size, was fitted to the response, +20 Mesh. Two model validation batches were prepared, and although the baseline process had undergone some changes due to the results of other experiments, the measured responses agreed reasonably well with the model predictions, and were well within the calculated response variation. The baseline process was modified in response to the results of the interaction design. Milling Time was decreased and Media Size was increased, resulting in a significant improvement in yield by reducing the amount of the +20 mesh fraction that was generated during processing.

It was also learned from this study that the response variation was greater than expected or desired. Although for most responses, the response variation range was still within specifications, indicating that the process is robust with respect to those responses, there was concern that the process was not adequately controllable for some of the other responses (e.g., slug sintered bulk density). Additional experiments to identify the source(s) of response variation for the powder preparation sub-process will be performed to address this issue.

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