

Characterization of Ceramic Powders through Powder Rheology

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Samuel Weimer

May 2024

© by Samuel Weimer, 2024
All Rights Reserved.

COPYRIGHT NOTICE

This document has been authored by Consolidated Nuclear Security, LLC, under Contract DE-NA-0001942 with the U.S. Department of Energy/National Nuclear Security Administration, or a subcontractor thereof. The United States Government retains and the publisher, by accepting the document for publication, acknowledges that the United States Government retains a nonexclusive, paid up, irrevocable, world wide license to publish or reproduce the published form of this document, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, or allow others to do so, for United States Government purposes.

Dedication

This is dedicated to my parents who have supported me endlessly, tirelessly, and unconditionally, always having high hopes for me, but never demands. They have provided to me in many ways, despite never having had those experiences themselves.

Acknowledgments

There are many in my life I wish to acknowledge. However, as I think of what to write, my only thought is that nothing I say could truly describe that which has been given to me. The memories I've been gifted are lasting, as are the friendships they came with. The opportunities I've been given have allowed me to achieve goals which were once dreams. I can only hope that along the way I've shown at least a fraction of gratitude relative to all the support I've received, and I can only hope that I'll continue to have the opportunity to do so.

DISCLAIMER

The information or opinions expressed herein by the author are solely those of the author. Neither the U.S. Government, Consolidated Nuclear Security, LLC, nor any of their employees warrant, or assume any legal liability for, the accuracy, completeness or usefulness of any information contained herein.

Abstract

Frequently in the literature, it has been shown that any single characterization technique is incapable of sufficiently describing the overall rheology properties of a powder. Consequently, much work has gone into exploring multivariate relationships between common rheological tests. However, such efforts have been primarily focused on powders used in pharmaceutical and food industries. Much less rheology work has been conducted for powders of other industries, such as ceramic powders used in making grinding media and crucibles. Yet, it has been shown that supplementing particle size distribution and chemical composition measurements of ceramic powders with powder rheology techniques can greatly increase characterization capability. This work aims to advance said knowledge by investigating relationships among rheological parameters and the general importance of each parameter towards powder characterization for multiple ceramic powders.

Rheological characterization methods used were the Freeman Technology FT4 Powder Rheometer Stability and Variable Flow Rate, Compressibility, Shear Cell, and Direct Pressure Consolidation tests. As the last test has not been used in other works, a novel methodology and data fitting method were developed herein. Additional tests were conducted using the GranuTools' GranuPack, GranuHeap, and GranuFlow equipment. All tests were conducted on grades of varying size of the materials of aluminum oxide, boron carbide, silicon carbide, silicon nitride, and tungsten carbide.

Correlative and principal component analyses were used to ascertain how rheological parameters related with one another, and the relative importance of each based on information captured. Additional rheological parameters to analyze were created from novel calculations and fits to data. It was found that tested powders could be sufficiently characterized using just two tests, the Direct Pressure Consolidation test and Stability and Variable Flow Rate test. One calculated parameter, and a novel parameter from fitting data, from the Stability and Variable Flow Rate

test were found to be key contributors to captured information. Most notably, all Direct Pressure Consolidation measurement points and fit parameters were found to capture the majority of information. This novel test was observed to be the strongest characterization method out of all applied tests.

Table of Contents

1	Introduction	1
1.1	Powder Rheology	1
1.2	Ceramic Grinding Media and Crucibles	5
2	Characterization through Powder Rheology	10
2.1	Introduction	10
2.2	Particle Size Distribution	10
2.3	Traditional Methods and Measurements	12
2.3.1	Bulk Density	12
2.3.2	Flowmeters	15
2.3.3	Angle of Repose	16
2.3.4	Shear Cell Properties	17
2.4	FT4 Powder Rheometer	22
2.4.1	Conditioning	22
2.4.2	Stability and Variable Flow Rate Measurements	23
2.4.3	Compressibility Measurements	28
2.4.4	Direct Pressure Consolidation Measurements	29
3	Ceramics for Grinding Media and Crucibles	30
3.1	Introduction	30
3.2	Consolidated Ceramic Properties and Measurements Thereof	31
3.2.1	Density	31
3.2.2	Green Density	33
3.2.3	Hardness	34
3.2.4	Flexural Strength	36
3.3	Materials Selection	39

3.3.1	Aluminum Oxide	43
3.3.2	Boron Carbide	44
3.3.3	Silicon Carbide	46
3.3.4	Silicon Nitride	48
3.3.5	Tungsten Carbide	50
4	Methodology	53
4.1	Materials and Grades	53
4.2	General Methodology	54
4.2.1	Storage, Blending, and Handling	54
4.3	Mixing Methodology	56
4.4	Freeman Technology FT4 Rheometer Methods	56
4.4.1	FT4 Methods: Stability and Variable Flow Rate	57
4.4.2	FT4 Methods: Compressibility	59
4.4.3	FT4 Methods: Shear Cell	60
4.4.4	FT4 Methods: Direct Pressure Consolidation	61
4.5	GranuTools Methods	64
4.5.1	GranuTools Methods: GranuPack	64
4.5.2	GranuTools Methods: GranuHeap	65
4.5.3	GranuTools Methods: GranuFlow	66
5	Results and Discussion	69
5.1	Freeman Technology FT4 Powder Rheometer Results and Discussion	69
5.1.1	Stability and Variable Flow Rate Results and Discussion . . .	69
5.1.2	Compressibility Results and Discussion	79
5.1.3	Shear Cell Results and Discussion	84
5.1.4	Direct Pressure Consolidation Results and Discussion	88
5.2	GranuTools Results and Discussion	97
5.2.1	GranuPack Results and Discussion	97
5.2.2	GranuFlow Results and Discussion	101

5.2.3	GranuHeap Results and Discussion	105
6	Analysis of Results	106
6.1	Creation of New Parameters	106
6.1.1	Stability and Variable Flow Rate Parameters	106
6.1.2	Compressibility Parameters	108
6.1.3	Direct Pressure Consolidation Parameters	109
6.1.4	GranuTools Parameters	112
6.2	Correlative Analysis	114
6.2.1	Single Test Correlations	114
6.2.2	Multi-Test Correlations	124
6.3	Principal Component Analysis	136
7	Conclusion and Recommendations	146
7.1	Conclusion	146
7.2	Recommendations for Future Work	149
	Bibliography	151
	Appendices	169
A		170
A.1	Sintering and Pressing	170
A.1.1	Pressureless Sintering	171
A.1.2	Hot Pressing	176
A.1.3	Hot Isostatic Pressing	176
B		179
B.1	Particle Size Distribution and Chemical Composition Information . .	179
C		186
C.1	Supplementary Plots and Tables	186

List of Tables

2.1	Flowability scale for Carr Index and Hausner Ratio. ⁵⁸	14
3.1	Typical physical values, or range of values, of select ceramics when densified to $\geq 95\%$ of theoretical density.	42
4.1	Increment/pressure combinations and their mass multiplication factors used in Direct Pressure Consolidation testing.	62
B.1	Average particle size equivalent for select FEPA-F grades.	179
B.2	Particle size distribution information from certificates of analysis for aluminum oxide grades. Mixed grade values were calculated from mass ratios.	180
B.3	Chemical composition information from certificates of analysis for aluminum oxide grades. Mixed grade values were calculated from mass ratios.	181
B.4	Particle size distribution information from certificates of analysis for boron carbide grades. Mixed grade values were calculated from mass ratios.	182
B.5	Chemical composition information from certificates of analysis for boron carbide grades. Mixed grade values were calculated from mass ratios.	183
B.6	Particle size distribution and chemical composition information from certificates of analysis for silicon carbide grades. Mixed grade values were calculated from mass ratios.	184
B.7	Particle size distribution and chemical composition information from certificates of analysis for silicon nitride grades.	184

B.8	Particle size distribution information from certificates of analysis for tungsten carbide grades.	185
B.9	Chemical composition information from certificates of analysis for tungsten carbide grades.	185
C.1	Shorthand names of FT4 Powder Rheometer Stability and Variable Flow Rate test outputs and descriptions thereof. An asterisk indicates the parameter is manually calculated and not directly provided by the FT4.	195
C.2	Shorthand names of FT4 Powder Rheometer Compressibility test outputs and descriptions thereof. An asterisk indicates the parameter is manually calculated and not directly provided by the FT4.	196
C.3	Shorthand names of FT4 Powder Rheometer Shear Cell test outputs and descriptions thereof.	197
C.4	Shorthand names of FT4 Powder Rheometer Direct Pressure Consolidation test outputs and descriptions thereof. An asterisk indicates the parameter is manually calculated and not directly provided by the FT4.	198
C.5	Shorthand names of GranuTools GranuPack test outputs and descriptions thereof.	199
C.6	Shorthand names of GranuTools GranuHeap test outputs and descriptions thereof.	200

List of Figures

2.1	Diagram of linearized yield locus and Mohr circle analysis with angle of internal friction (ϕ), cohesion (τ_c), unconfined yield strength (σ_c), and major principal stress (σ_1). Adapted from El et al. ⁸⁰	21
2.2	Graphic of the FT4 Powder Rheometer helical blade ⁸¹	24
2.3	Stress transmission zones during flow for a cohesive compressible powder (left) and non-cohesive non-compressible powder (right). Adapted from FT4 supporting document W7030. ⁸⁷	26
5.1	FT4 Stability and Variable Flow Rate data for Panadyne aluminum oxide F1200.	70
5.2	(a) FT4 Stability and Variable Flow Rate data for aluminum oxide F1200 grades sourced from Panadyne and Atlantic Equipment Engineers (A.E.E.), and (b) Metallurgical Supplies (M.S.).	72
5.3	FT4 Stability and Variable Flow Rate data for Panadyne aluminum oxide F240, 70/30% mixed F240/F600, and F600 grades.	73
5.4	FT4 Stability and Variable Flow Rate data for Panadyne aluminum oxide F600, 70/30% mixed F600/F1200, and F1200 grades.	73
5.5	Ungrouped FT4 Stability and Variable Flow Rate data for seven separate tests of Panadyne boron carbide F240.	76
5.6	(a) FT4 Stability and Variable data for Panadyne silicon nitride SiN-6 and (b) SiN-9.5.	78
5.7	FT4 Compressibility data for Panadyne aluminum oxide F1200.	80
5.8	FT4 Compressibility data for aluminum oxide F1200 grades sourced from Panadyne, Atlantic Equipment Engineers (A.E.E.), and Metallurgical Supplies (M.S.).	80

5.9	FT4 Compressibility data for Panadyne aluminum oxide F240, 70/30% mixed F240/F600, and F600 grades.	81
5.10	FT4 Compressibility data for Panadyne aluminum oxide F600, 70/30% mixed F600/F1200, and F1200 grades.	81
5.11	FT4 Compressibility data for Panadyne silicon nitride grades of SiN-6 ($\leq 9 \mu\text{m}$), SiN-B ($\sim$ F1200), and SiN-9.5 ($0.6\text{--}0.8 \mu\text{m}$).	83
5.12	(a) FT4 Compressibility data for Panadyne silicon carbide F120 and (b) tungsten carbide FWC 300.	85
5.13	FT4 Shear Cell data for Panadyne aluminum oxide F1200.	86
5.14	FT4 Shear Cell data for aluminum oxide F1200 grades sourced from Panadyne, Atlantic Equipment Engineers (A.E.E.), and Metallurgical Supplies (M.S.).	89
5.15	FT4 Shear Cell data for Panadyne aluminum oxide F240, 70/30% mixed F240/F600, and F600 grades.	89
5.16	FT4 Shear Cell data for Panadyne aluminum oxide F600, 70/30% mixed F600/F1200, and F1200 grades.	90
5.17	FT4 Direct Pressure Consolidation data for Panadyne aluminum oxide F600.	92
5.18	FT4 Direct Pressure Consolidation data for aluminum oxide F1200 grades sourced from (a) Atlantic Equipment Engineers (A.E.E.), (b) Panadyne, (c) and Metallurgical Supplies (M.S.).	94
5.19	FT4 Direct Pressure Consolidation data for (a) Panadyne aluminum oxide F240, (b) 70/30% mixed F240/F600, (c) and F600 grades. . . .	95
5.20	(a) FT4 Direct Pressure Consolidation data for Panadyne boron carbide F240 and (b) silicon carbide F120.	96
5.21	GranuPack tapped density data for Panadyne aluminum oxide F1200.	98
5.22	First 500 taps of GranuPack tapped density data for Panadyne aluminum oxide F1200.	100

5.23	Percent relative standard deviations of GranuPack fitting constant τ , fitted to 9999 taps, for all powders tested.	102
5.24	Percent relative standard deviations of GranuPack characteristic tap number $n_{1/2}$, calculated from 500 taps, for all powders tested.	102
5.25	GranuFlow mass flow rate data for Panadyne silicon carbide F120. . .	104
5.26	GranuFlow mass flow rate data for Panadyne tungsten carbide FWC 300.	104
6.1	Correlation heatmap of FT4 Stability and Variable Flow Rate test and associated parameters. All parameters described in Table C.1.	115
6.2	Correlation heatmap of FT4 Compressibility test and associated parameters. All parameters described in Table C.2.	118
6.3	Correlation heatmap of FT4 Shear Cell test and associated parameters. All parameters described in Table C.3.	118
6.4	Correlation heatmap of FT4 Direct Pressure Consolidation test and associated parameters. All parameters described in Table C.4.	120
6.5	Correlation heatmap of GranuTools GranuPack test parameters. All parameters described in Table C.5.	122
6.6	Correlation heatmap of GranuTools GranuHeap test parameters. All parameters described in Table C.6.	126
6.7	Correlation heatmap of FT4 Stability and Variable Flow Rate test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.	127
6.8	Correlation heatmap of FT4 Compressibility test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.	129
6.9	Correlation heatmap of FT4 Shear Cell test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.	130

6.10	Correlation heatmap of FT4 Direct Pressure Consolidation test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.	132
6.11	Correlation heatmap of GranuTools GranuPack test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.5.	133
6.12	Correlation heatmap of GranuTools GranuHeap parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4 and Table C.6.	135
6.13	Correlation heatmap of parameters from GranuTools GranuPack and GranuHeap tests. All listed parameters are described in Tables C.5-C.6.	135
6.14	Scree plot of first eight components of the principal component analysis.	138
6.15	Plot of loadings of first three principal components (PCs). Residuals along PC 1 are drawn for each loading from the light blue plane that intersects PC 1.	138
6.16	Plot of loadings of first three principal components with select loadings visually removed from plot.	140
6.17	2D scatter plot of loadings from the first and second principal components.	142
6.18	2D scatter plot of loadings from the first and third principal components.	142
6.19	Weighted sum of squares of every parameter across all principal components. Only parameters with a sum value equal to or greater than 100 are shown.	144
A.1	The two forms of isostatic pressing: (a) wet bag and (b) dry bag. Adapted from Rahaman. ¹⁵	173
A.2	Schematic of a uniaxial hot press. ¹⁴⁸	177
A.3	Schematic of a hot isostatic press. ¹⁴⁹	177

C.1	(a) FT4 Stability and Variable Flow Rate data for Panadyne boron carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.	186
C.2	(a) FT4 Stability and Variable Flow Rate data for Panadyne silicon carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.	187
C.3	(a) Ungrouped and (b) grouped FT4 Stability and Variable Flow Rate (SVFR) data for six separate tests of Panadyne tungsten carbide FWC 300.	188
C.4	(a) Ungrouped FT4 Stability and Variable Flow Rate data for Panadyne silicon carbide F240 and (b) 70/30% mixed F240/F600.	189
C.5	(a) FT4 Compressibility data for Panadyne boron carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.	190
C.6	(a) FT4 Compressibility data for Panadyne silicon carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.	191
C.7	(a) FT4 Shear Cell data for Panadyne boron carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.	192
C.8	(a) FT4 Shear Cell data for Panadyne silicon carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.	193
C.9	Plot of loadings of first three principal components (PCs). Residuals along PC 2 are drawn for each loading from the light blue plane that intersects PC 2.	194
C.10	Plot of loadings of first three principal components (PCs). Residuals along PC 3 are drawn for each loading from the light blue plane that intersects PC 3.	194

Chapter 1

Introduction

1.1 Powder Rheology

Powders find far-reaching use in industrial applications, be it in raw form, as an intermediary, or as a final product. Unfortunately, they continue to pose challenges in regard to process performance, product development, and quality assurance. Much of this has to do with lack of understanding as to how powder behaves. This requirement for comprehension begins with the need to characterize the initial state of an acquired powder and extends to all processing that a powder may go through.

A powder is a bulk assembly of solid particles, with possible interspersions of adsorbed liquids or gases. However, it cannot be placed under a distinct phase of matter. Its behaviors can fall under the purview of properties associated with liquids and solids. It can move and compress similarly to a liquid and experience stress and deformation like a solid. Therein lies the difficulties associated with characterizing a powder, its behaviors are not conveniently boxed within one category of matter. Powder rheology is the subject which probes these facets. It is the application of rheology, the study of the deformation and flow of matter, to powders and granular materials. Certainly, much of powder processing is concerned with characterizing the flowability of powder.

It is crucial to note that powder “flowability” relates to much more than what is commonly associated with the flow of a liquid. It is a complex, multidimensional aspect that is dependent upon a myriad of powder characteristics and processing conditions. Flowability, or bulk powder behavior as a whole, generally depends upon

three items. The first item is intrinsic physical properties, or particle properties, such as particle size, surface morphology, and inter-particle forces. Second is bulk powder properties, or rheological parameters, such as bulk density, compressibility, and flow rate. Lastly are environmental and processing factors, or external variables, like that of moisture content, temperature, forces between powder particles and external surfaces, and degree of consolidation.¹

As can be seen, flowability is not a singular quantity to be measured. It entails a multitude of contributing factors and is not an inherent material property that can be described with a single characteristic.² There is not a unified framework capable of describing powder flow.³ In fact, it is inadequate to use any parameter from a single type of rheology test as means to characterize a powder. Multiple particle properties may be considered together in a first principles approach, but ultimately are insufficient to characterize the behavior of a powder as a bulk assembly. Compounding this, external variables can affect behavior further. Direct linking between physics of particle properties and external variables to bulk powder behavior has not been well-achieved.⁴ This demonstrates that bulk powder behavior must be viewed from a holistic framework, i.e., the sum of individual factors cannot account for behavior as a whole. Correspondingly, empirical approaches have prevailed: shear cell methods, uniaxial compression tests, avalanche devices, flowmeters, bulk density measurements, consolidation through tapping (Carr index & Hausner ratio), and so on.^{5,6} Powder rheology gathers flow property data from such methods, which are then used to describe flowability. The important distinction here is that powder flow properties and powder flowability are not synonymous. Properties associated with powder flow ultimately correspond to bulk powder behavior. These data may be used to ascertain flowability but are not constrained to only this single use. These flow properties, or rheological parameters, are factors in many processes: powder transfer, such as through piping, from feeders, into hoppers, die filling, etc.; storage, resulting in caking and/or agglomeration; blending; compaction for pharmaceutical tablets, green bodies for sintering, etc.; and lastly as a way to characterize powders comparatively.²

When selecting which rheological methods to employ, the standard approach is to use techniques which will subject a tested powder to conditions similar to those expected during processing.^{2,5} Of course, it is not easy, or even always possible, to know *ab initio* which characterization techniques are most appropriate for expected processing. One example is the flow of powder through a hopper. It would appear that the only applicable rheological method would be the use of a flowmeter to ascertain mass flow rate. However, this would not account for build-up of powder along the hopper wall near the exit, the resulting compaction, and the inducement of shear forces. This highlights that any given application may expose a powder to stress states ranging from static to dynamic. A study by Krantz et al.⁷ found that it is not appropriate to extend measurements of static stress states to dynamic states and vice versa. It was shown that multiple characterization techniques should be performed at various stress states to accurately predict bulk behavior. What this has resulted in is that purposes for characterizing powder through rheological methods have almost always centered around understanding and predicting flow or deformation of a specific powder, under specific conditions, by means of select rheological measurements that have been determined by extensive testing.

Correspondingly, there has been an increasing focus on utilizing multivariate statistics for rheological characterization of powders. The most prevalent goal has been to create libraries of material data for use as-is⁸ and for the capability to compare newly acquired powders against existing powders.^{9,10} These works, and similar, have demonstrated the value of using multivariate statistics for powder rheology data, but have been limited in that they do not attempt to apply found relationships beyond that of for comparing tested powders. This is not to say found relationships cannot be appropriately applied. For example, Wang et al.¹¹ utilized multivariate statistical methods like those in aforementioned works to analyze shear cell data as a function of material and initial consolidation stress. Multivariate relationships found were used to create a method that augmented shear cell data analysis and greatly reduced the complexity of the respective data. Extending this concept further, multivariate

analysis has also been used to create a methodology that uses an optimized set of tests from a powder rheometer to correlate material properties with process performance of a powder feeder.¹² Works like these evidence that found multivariate relationships can be appropriately applied. However, these specific studies highlight the second limitation commonly found; only data from a single, or minimal number of, rheology tester(s) or equipment are utilized, despite the fact use of a single test or equipment for rheological characterization of a powder is known to be insufficient.

Summarized, it has so far been shown that the rheology properties of a powder cannot be sufficiently described by means of a single type of test or equipment. The typical approach for characterization is to use tests which will subject a sample to conditions similar to those expected of planned processing. This presents significant issue for an innumerable number of processes where powder rheology is of importance; be it flow of powder through hoppers to be mixed into food products, compaction into medicine tablets, or funneling of ceramic powder into a die for sintering into solid products. The issue at hand is one of information. Without significant testing, it cannot be known with sufficient certainty that the rheology test(s) chosen for characterization will acceptably correlate with expected processing. The reverse is also true, one cannot determine *a priori* which types of rheology tests and equipment will not provide any utility for control of processing. As a result, a wide variety of tools and measurement types are commonly used in industry and research.

However, it is reasonable to assume some of the measurement parameters provided by these tests would overlap in the information they convey. It would be useful for many industries and disciplines to determine which of these parameters carry the most information, and which do not, thus allowing for creation of an optimized methodology for rheological characterization. It has been shown that multivariate statistics can be successfully used to ascertain how information from multiple types of rheology tests interrelate. Found relationships among a wide set of test types and equipment have not been applied, though. Only multivariate relationships found with a limited number of rheology tests types have been successfully applied. It is evident that

the current trajectory of research will be the application of multivariate relationships found from many types of rheology tests and equipment. However, unstated so far, the summarized background and projected direction of powder rheology research has been, and is, focused primarily upon powders used in pharmaceutical and food science industries. Little work has been extended to types of powders used in other industries, such as refractory ceramics used as grinding media and crucibles.

1.2 Ceramic Grinding Media and Crucibles

Optimized characterization of powder is desirable for control of properties and quality of products as properties of raw materials can affect the properties and quality of final products.¹³ Raw materials are often characterized to a degree such that final product properties are well-predicted with little variation. Given their bulk nature, this is not as easily achievable for powders. This is exemplified in the sintering of powder for creation of ceramic products.

Ceramics, particularly grinding media and crucibles, are ubiquitous across industry and research laboratories. Grinding media are most commonly used to comminute larger powders or particles of metals and ceramics to form finer powders for powder metallurgy and the formation of monolithic ceramic parts, respectively. Crucibles are containers in which various substances may be held in and subjected to, typically very high, temperatures. The types of ceramics used for grinding media and crucibles are almost always refractory in nature. Refractories are materials that are resistant to heat, exposed to different degrees of mechanical stress and strain, thermal stress and strain, corrosion/erosion from several phases of matter, gas diffusion, and mechanical abrasion at various temperatures.¹⁴ Resistance to thermomechanical stress and erosion is of notable importance for both grinding media and crucibles.

Given the prevalence of ceramic grinding media and crucibles, it would appear that a deep well of knowledge must exist in order for so many of these items to be consistently produced while also having sufficient physical and mechanical attributes

capable of resisting aforementioned stressors. In the simplest approach, a solid-state sintering temperature range of 0.5-0.75 of the material's melting point is acceptable for producing consolidated pieces for most ceramic materials.¹⁵ Furthermore, the general operating conditions required for sufficient sintering of ceramic powders are known for an innumerable number of ceramics. And lastly, specific conditions required for producing higher quality ceramics can be approximately determined by reviewing relevant literature on a per-material basis. All of such knowledge, however, is not enough to be able to consistently produce ceramics with sufficient consolidated properties. As the properties of raw materials affect properties and quality of final products, the properties of ceramic powders must be considered if one wishes to optimize consolidated properties.

Correspondingly, work examining how raw material properties, primarily average particle size of powders, affects consolidated properties and sintering conditions has been conducted to an extensive theoretical and experimental degree.^{16,17} This has been expanded by investigating how a powder's distribution of particle sizes may affect required sintering conditions and consolidated properties.¹⁸⁻²¹ On a material-by-material basis, much work has gone into investigating how the modification of chemical composition through the addition of various elements and compounds, or additives, can improve select product properties and/or increase production efficiency by reducing required operating conditions.²²⁻³¹

As can be seen in the prior referenced works, and overall literature, most efforts have focused upon average particle size and distribution, chemical composition, and sintering conditions required for maximizing consolidated ceramic properties such as green density, density, strength, hardness, fracture toughness, and elastic moduli. Considerable focus has also been given to elucidating empirical relationships between these properties.³²⁻³⁶ It would then appear that by replicating conditions set forth in these works, or extrapolating through use of empirical relationships, one should be able to produce ceramic pieces with property values that can be approximately

known in advance. However, this is neither always applicable, nor necessarily holds true for when it is.

To stress, it is not being claimed that any of the works cited, or relevant literature as a whole, cannot be replicated. There is no reason to doubt that one could produce results similar to those found in the literature if similar conditions were used. However, therein lies the issue, using similar conditions is typically not possible. While exact equipment available to one may vary, the sintering conditions from most works can be reasonably reproduced. However, ensuring the characteristics and behavior of powder used are tolerably similar to those in a specific work can be problematic. Much of this has to do with which powder attributes are typically provided.

When powder attributes are reported in sintering-related literature it is common for only the average particle size, percent purity, and concentration of additives used in the powder to be provided. Less commonly more specific details are provided: a breakdown of various impurities and their concentrations within the powder, the 10th and 90th percentiles of the particle size distribution, or the average particle surface area of the powder. Yet as argued in the first section of this chapter, such details alone have repeatedly been shown in external disciplines to be incapable of sufficiently characterizing a powder and its behavior. This deficiency carries through processing and sintering, arising as further uncertainty as to what values the properties of a consolidated ceramic will have. It is then apparent that more attention should be given to supplementing characterization of ceramic powders with other methods, specifically powder rheology.

To a certain extent this has been accomplished. Powder rheology has been shown to be crucial in that it determines how homogeneously a die is filled; along with the reproducibility of doing so.^{37–39} Preexisting powder agglomerates and those produced during filling can affect green body microstructure, which is then typically preserved in the sintered microstructure of the product.⁴⁰ One detrimental, and common, example is that powder non-uniformly filled into a die may result in micro-cracks when pressed.⁴¹ These micro-cracks in the green body may then be carried over

and intensified during sintering.^{42,43} Ultimately, heterogeneities initially within bulk powder composition, and those introduced during powder processing and die filling, can produce defects that persist throughout pressing and sintering.^{37,40,42,44–48}

Importantly, the relationship between powder rheology and consolidated properties is not limited to bulk density, nor just powder flowability as it relates to good die filling. A recent study by Boehmler et al.⁴⁹ demonstrates this. In the study three ceramic powders of same chemical composition and particle size distribution were sintered under identical conditions, however, conditioning and storage conditions varied across the three powders. Contrary to the standard view that chemical composition and particle size distribution alone are sufficient for characterizing a powder, it was found that the conditioning state of the powder influenced sintered microstructure properties like pore size and distribution, density, distribution of phases, and grain size. While chemistry and particle size distributions were the same, certain rheological parameters measured were found to differ across the powders. While no quantitative work linking rheological parameters with consolidated properties was done, it nonetheless highlights the overall theme herein that the use of powder rheology may provide information beyond that available from measurements commonly taken, like chemical composition and particle size distribution.

A large sum of research has been performed to empirically relate ceramic powder particle properties, like average particle size and size distribution, with resultant consolidated properties post-sintering. Yet for powders in general, it is well-known that bulk powder behavior is more than the sum of its parts, thus inducing the need for methods to quantify the rheology of a powder. As it pertains to ceramic powders, and sintering thereof, aspects of powder rheology have been successfully applied to some degree. However, beyond bulk density, the literature is lacking in how specific rheological parameters of a powder may quantitatively relate to consolidated properties of ceramic products, despite the fact that the existence of qualitative relationships is well-known. A significant contributor to this problem is that, unlike powders used in pharmaceutical/food sciences, it is far less clear which

rheological properties are useful. One cannot begin to find relationships between rheological properties and consolidated properties without having first determined which rheological tests and properties should be explored.

As has been done by others for powders often used in pharmaceutical/food sciences, this work endeavors to explore rheological properties of ceramic powders, with a focus on refractory ceramics used for grinding media and crucibles. By applying multivariate analysis to data collected from a wide range of rheology tests conducted across a varied set of ceramic powders, the objective is to determine how measured rheological parameters correlate with one another; and ultimately, to ascertain which parameters carry the most information. In doing so, insight will be provided onto which rheological tests and properties should be considered in future works focusing on elucidating relationships between consolidated properties of ceramic grinding media and crucibles and their powder rheology properties.

Chapter 2

Characterization through Powder Rheology

2.1 Introduction

Characterizing a powder and its behavior is important for many applications and industries. As mentioned, many techniques for measuring rheological parameters of powder have been developed.^{5,6} It often is unclear which methods and parameters will provide the best qualitative and/or quantitative predictive capability for a given process or application. It is a primary aim of this work to resolve these uncertainties by determining an optimized methodology for characterizing a powder, irrespective of its expected processing. To facilitate this, a variety of rheological tests were selected that best represent those commonly used in the literature. These methods, their associated measurements used for characterization, and other relevant information are discussed within this chapter.

2.2 Particle Size Distribution

The particle size distribution (PSD) of a powder is not a rheological property, but instead considered to be a bulk powder property. It may seem odd to begin a discussion on rheological characterization with PSD, but this is easily clarified. PSD (often represented by an average value) has been repeatedly shown to be a significant factor that affects other bulk properties, rheological properties, and properties of pressed products. Excluding the overall chemical composition of ceramic

powders, PSD (mainly its average) has typically been the primary material property investigated in relation to pressed properties and sintering conditions of ceramics. As such, PSD will be included within the purview of rheological characterization for the purposes of this work given its importance.

The most commonly referenced values are d_{10} , d_{50} , d_{90} , and span. The first three values correspond to the particle size at the 10th, 50th, and 90th percentiles. The span is calculated as:

$$\text{span} = \frac{d_{90} - d_{10}}{d_{50}} \quad (2.1)$$

The way in which particle sizes and distribution are determined depends upon the measuring method used. The classical method is sieve analysis. In this method, powder is allowed to flow through multiple sieves with increasingly smaller mesh sizes. The amount of powder remaining on each sieve is then weighed. Assuming a constant density across particles, the particle size distribution is then given by a number weighted histogram with bin sizes corresponding to sieve sizes used. Like most methods, size measurements from sieve analysis are also reported as diameters. These particle diameter values are found by calculating the equivalent diameter of a perfect sphere. As actual particles are not perfect spheres, sieve analysis tends to emphasize the second largest dimension of particles due to how particles must be oriented in order to pass through mesh openings. Furthermore, the method is not conducive to making precise size measurements as it is inherently limited by its binning nature.

Today, the most commonly used method for measuring particle size is laser diffraction. In this method, a small sample of powder is dispersed in liquid or air and then passed through laser light. The main premise is that small particles will scatter light weakly at wide angles and large particles will do so intensely at narrow angles. Spatial intensity mapping of diffracted light is then used to calculate volumes of particles, providing a volume weighted size distribution. Older laser diffraction methods utilized the Fraunhofer Approximation, a solution to Maxwell's

equations for scattering from spheres, for calculations. Contemporary methods tend to use a similar, but improved theoretical basis; that is, Mie scattering theory, a closed form solution (not approximation). Like other methods, some assumptions are made with Mie theory-based laser diffraction: particles are spherical, the ensemble is homogeneous, and the refractive indexes of the particle and dispersion medium are known.⁵⁰

2.3 Traditional Methods and Measurements

2.3.1 Bulk Density

Bulk density is similar to particle size distribution (PSD) in that it is a bulk powder property and not necessarily (historically) considered a rheological property. Yet, it too is relevant to the flow and deformation of powder and used in various calculations for describing powder characteristics and behavior. Furthermore, bulk density and its relative change are reflective of the state of a powder after having been compressed, aerated, tapped, consolidated, and affected by other means. Consequently, regardless if past workers have or have not defined bulk density as a rheological parameter, it has commonly been included as an important measurement in powder rheology work.

Moving forward, bulk density is the ratio of bulk solid mass to its total volume. Bulk density is always less than particle density, or solid density, as voids exist between particles.⁶ As such, its value accounts for density of individual particles and void space between particles. Bulk density depends upon particle size distribution, particle shape and surface texture, and cohesive/adhesive forces. Furthermore, it depends greatly upon the degree of packing and how particles are packed, like compaction, compression, etc.⁵¹ As packing affects bulk density measurement, two states of density are commonly measured: aerated and tapped.

Aerated, or apparent or loose, bulk density is determined by allowing a powder to settle into a container under the influence of gravity. A powder with strong structural

strength will resist collapse, resulting in a low bulk density and vice-versa for weak powder. However, bulk density is inversely affected by friction, therefore meaning a structurally weak powder may exhibit a low aerated bulk density if inter-particle friction is high.⁵¹ Tapped bulk density is acquired by tapping a powder n times (typically $n = 500$), wherein a vessel containing powder is tapped upwards 1 to 3 mm by use a punch tapping the base of the vessel. To note, aerated/apparent bulk density is typically referred to as just “bulk density” in much of the literature.

Methods for measuring aerated and tapped densities have been standardized.⁵² Very often aerated density ρ_0 and tapped density ρ_T (or respective volumes V_0 & V_T) are used for the purpose of obtaining the Hausner Ratio^{53,54} (HR), a characteristic indicative of powder flowability and cohesiveness.⁵⁵ A corollary to the Hausner Ratio is the Carr (Compressibility) Index⁵⁶ (C), which is used as an indicator for compressibility of a powder. Both measures are used to generally describe the flowability of a powder as given in Table 2.1. Equations for the Hausner Ratio (Eqn. 2.2) and Carr Index (Eqn. 2.3) are provided below.

$$\text{HR} = \frac{\rho_T}{\rho_0} = \frac{V_0}{V_T} \quad (2.2)$$

$$\text{C} = 100 \cdot \frac{V_0 - V_T}{V_0} \quad (2.3)$$

Tapped density and the above parameters highlight that a significant facet of density measurements is focused on relative changes and not a single, absolute value (e.g., aerated density). Relative changes of bulk density are responsive, and often sensitively so, to slight changes in the characteristics of the constituent particles within the process.⁵⁷ As tapped density measurement requires a powder sample to be repeatedly tapped, modern testers like the GranuTools’ GranuPack, used in this doctoral work, can record the change in bulk density as a function of the number of taps made, providing insight into compaction dynamics. Two parameters commonly used for describing these dynamics are the characteristic tap number $n_{1/2}$, which is

Table 2.1: Flowability scale for Carr Index and Hausner Ratio.⁵⁸

Flow Character	Carr Index	Hausner Ratio
Excellent	≤ 10	1.00-1.11
Good	11-15	1.12-1.18
Fair	16-20	1.19-1.25
Passable	21-25	1.26-1.34
Poor	26-31	1.35-1.45
Very poor	32-37	1.46-1.59
Very, very poor	> 38	> 1.60

the number of taps required to reach one half of ρ_T , and the extrapolated density ρ_∞ , which is found by extrapolating the compaction curve to an infinite number of taps.

2.3.2 Flowmeters

The most common of rheology devices are those like the Hall flowmeter, based upon funnel discharge time measurements. Flowmeters are used to measure flow rate, and optionally aerated density, of free flowing powders through an orifice of given size; with methods provided in multiple standards (ASTM,⁵⁹ ISO,⁶⁰ and MPIF⁶¹). While flowmeters are advantageous in their cost and simplicity, they are limited in the case of cohesive non-flowing powders. However, funnels adapted to this case exist, such as the Carney flowmeter. Furthermore, as claimed by Schulze, use of flow rate measurements should not be used to make quantitative statements and instead should be relegated to only comparative use as measurements can be heavily influenced by the operator and aeration of the powder.⁶ A cursory glance at the literature concerning powder rheology gives credence to this claim, as it is not uncommon for flowmeters to be unable to discern different powders.

Be that as it may, flowmeters are a staple in rheology testing by industry, and consequently given a fair degree of attention in research. Considering these facts, it would be of use to include flowmeter-based measurements in a multivariate analysis of rheology methods. Doing so would provide further insight into the uniqueness and limitations of flowmeters relative to other commonly used methods. Accordingly, the GranuFlow flowmeter from GranuTools is used in this doctoral work.

The GranuFlow is a semi-automated flowmeter with orifices of varying size. The instrument uses an electronic balance to measure mass flow rate as a function of aperture size. Like other flowmeters, over time, experimental work has shown that under the influence of gravity, the flow rate of non-cohesive granular material does not depend on fill height (hoppers, silos, flowmeters, etc.), but does non-linearly depend on orifice size. In 1852, the German hydraulic engineer Gotthilf Hagen⁶² was the first

to experimentally determine a relationship for describing mass flow rate as a function of orifice size:

$$Q = C\rho\sqrt{g}(D - d)^{5/2} \quad (2.4)$$

where Q is the mass flow rate, C a dimensionless fitting constant related to material properties, ρ the bulk density of the powder, g the acceleration due to gravity, D the orifice diameter, and d the particle diameter (a translation of Hagen’s publication may be found in the work by Tighe and Sperl⁶³). Over a century later, through dimensional analysis and experimentation without reference to Hagen’s work, Beverloo et al.⁶⁴ found a more suitable relationship for predicting mass flow rate, commonly called the Beverloo equation:

$$Q = C\rho g^{1/2}(D - kd)^{5/2} \quad (2.5)$$

where the fitting constant k (varying from 1.4 to 3 depending on shape/size distribution of grains) has been added to Eqn.2.4 previously produced by Hagen. While other attempts have been made to find a better fit for mass flow rate, the Beverloo equation has persisted as the most widely accepted expression. Through these attempts and other relevant experimental work, it has been consistently confirmed that flow rate does not depend on powder fill height.⁶⁵ Perhaps of greater interest, experimental results show that $C \approx 0.58$, independent of material tested.⁶⁶ Nevertheless, fitting the Beverloo equation to data of flow rates measured for various orifice diameters provides additional parameters (C and k) that can be useful for characterizing powders.

2.3.3 Angle of Repose

Along with flowmeters, measurement of the static angle of repose (AoR) is one of the oldest methods used in powder rheology. Traditionally, AoR is found by allowing

a powder to loosely fall into a conical heap onto a plate, the AoR is then found by measuring the angle made between the heap and the surface normal. As traditionally measured, it is mostly relegated to comparative use only, and not quantitative, due to inherent operator influence.⁶ On the contrary, modern methods allege to greatly reduce operator bias by automating the pouring of powder and utilizing image analysis to determine AoR. The GranuHeap instrument by GranuTools is one such modern tester.

In the GranuHeap test, a manually pre-filled tube is slowly raised, allowing powder to fall into a conical heap onto a collection base. After all powder has emptied from the tube, the collection base is slowly rotated and pictures are taken of the powder heap at multiple angles. For each picture taken, image analysis is used to project an isosceles triangle with surface area equal to that of the powder heap and AoR is calculated. The deviation between the projected triangle heap interface and the interface of the actual powder heap is calculated to determine the Cohesive Index. Values of each parameter for all pictures taken are then respectively averaged. Typically, powders which flow well have a low AoR and non-cohesive powders will have a Cohesive Index value close to zero.

2.3.4 Shear Cell Properties

Shear cell testing was originally developed by A.W. Jenike, who utilized shearing in a linear fashion to measure flow properties of powders for the purpose of designing reliable bins, hoppers, and silos.⁶⁷ Since then, shear cells have become a common staple in comparing flowability across powders⁶ with standardized testing procedures.^{68–71} While quantitative results from differing testers for a given material may vary, qualitative rankings and comparisons may be made with caution.⁷² In the case of using a specific tester with consistent operating conditions, results from differing materials are generally found to be reproducible and able to be compared quantitatively. The only limitation therein is that free-flowing materials are less

suitable for shear cell testing. In combination with Mohr circle analysis, shear cell data can provide cohesion, angle of internal friction, major principal stress, unconfined yield strength, and other design parameters.⁷³

Testing procedure typically consists of two to three steps: conditioning, preshearing, and shearing. Traditional test methods such as the Jenike translational tester⁵ and annular shear cell testers^{74,75} have an initial conditioning stage which is not robust in conditioning powder into a reproducible state.⁷⁶ For such methods, the sample is preconsolidated in a reproducible manner by the operator in accordance with common procedure of the field.⁵ Preconsolidation is typically accomplished by twisting of the equipment’s shear cell lid while applying a compressive load normal to said lid. Other testers, such as the Schulze ring shear tester,⁷⁷ do not have a conditioning stage at all.⁶⁸ Modern systems which utilize preconsolidation have the tester, as opposed to the operator, pack the powder bed during preconsolidation.^{69,71} However, conditioning by preconsolidation alone is not robust due to variation in powder history among bulk samples. The initial packed state of a powder will affect its final state even if during preconsolidation equivalent force is used across samples of the same kind. More recent testers condition powder robustly, like the FT4, wherein a helical blade moves downwards and then upwards through the powder sample, followed by preconsolidation, to create a reproducible state independent of operator and powder history. Standards for such recent testers have also been created.⁷⁰

Following conditioning, the bulk powder sample undergoes preshearing. This entails the sample being loaded with a normal stress, σ_p , or consolidation stress, and sheared until steady-state flow is achieved. This state of the bulk solid is defined as critically consolidated and indicated by a constant shear stress, τ_p , and bulk density for the given normal stress. For Jenike shear testers, it is claimed that with correctly consolidated samples, individual values of the steady-state shear stress τ_p should not deviate by more than $\pm 5\%$ from the average τ_p value for a given preshear normal stress σ_p . However, it is noted that “with some particulate solids” such tolerance cannot be achieved.⁶⁹

Following preshearing is shearing, or shear to failure. For shearing the normal stress is reduced to a value less than the preshear normal stress $\sigma_{sh_0} < \sigma_p$, corresponding to shearing of an overconsolidated sample. As this directly follows preshearing, shear direction is reversed, temporarily reducing shear to zero. Shear stress is then increased until a maximum shear τ_{sh_0} is reached wherein material begins to flow. The sample is then presheared again under normal stress σ_p until steady-state flow is reached, followed by shearing under a lower normal stress σ_{sh_1} to obtain a new shear value τ_{sh_1} point at failure. This process is repeated 3-4 more times using normal stresses 80-20% of the preshear stress σ_p . The preshear point (σ_p, τ_p) and shear points (σ_{sh}, τ_{sh}) are plotted to create a yield locus, providing a failure limit of the bulk solid, i.e., the shear stress necessary to initiate flow for any given normal stress. A linearized yield locus is created by best fit of the Mohr-Coulomb Criterion:

$$\tau = \sigma \tan(\phi) + \tau_C \quad (2.6)$$

The angle of internal friction, ϕ , is the angle between the axis of normal stress and the tangent to the linearized yield locus. The τ -axis intercept is defined as the cohesion τ_C of the bulk solid, or the shear stress required for failure at zero normal stress. A (linearized) yield locus along with cohesion and internal angle of friction may be seen in Fig. 2.1.

The point where material begins to flow during shearing is denoted as incipient flow, or incipient failure. It is analogous to the point at which during a compression test an unconfined, consolidated bulk sample under increasing compressive strength would break.⁶ The stress at failure is called compressive/cohesive strength, much more often unconfined yield strength σ_c , and sometimes f_c , as introduced by Jenike.⁶⁷ Unconfined yield strength, along with major principal stress (MPS), cannot be directly measured with a shear cell test, but instead can be found through Mohr stress circle analysis of the yield locus. A Mohr stress circle represents the normal and shear stresses at angle θ , i.e., the stresses at any arbitrary cutting plane. Two

Mohr stress circles are constructed to determine unconfined yield strength and major principal stress. For a given yield locus, there is one Mohr circle that represents the stress state of steady-state flow found at the end of preshear and one Mohr circle analogous to the stress state at failure for an unconfined bulk sample. For the first circle, the preshear point (σ_p, τ_p) provides one point upon the circle. It is required that the circle be tangential to the yield locus with one point upon the locus. The second circle must also be tangential to the yield locus with one point located at the origin. Lastly, per definition, any Mohr stress circle must be centered upon the σ -axis. Fulfillment of these criteria allow for the construction of the two Mohr stress circles, as shown in Fig. 2.1.

For a Mohr stress circle, the larger σ -axis intercept is deemed the major principal stress and the smaller intercept the minor principal stress. However, in the context of powder rheology, very often the “major principal stress” refers only to the major principal stress of the Mohr circle containing the preshear point. It is the major principal stress at steady-state flow, denoted by σ_1 , or sometimes MPS, and also referred to as the major consolidation stress.⁷⁸ For the Mohr circle that includes the origin as a point, its major principal stress, σ_c , is the unconfined yield strength (UYS). Taking the ratio between the major principal stress and unconfined yield strength provides the flow function coefficient:

$$ff_c = \frac{\sigma_1}{\sigma_c} \quad (2.7)$$

Jenike proposed the flow function coefficient as a method to characterize flowability of a powder.^{67,79} Jenike would later provide a list of ff_c values for general classification of flowability. This was qualitatively centered around a 2-10, unrestrained, scale with $ff_c < 2$ corresponding to a very cohesive and non-flowing

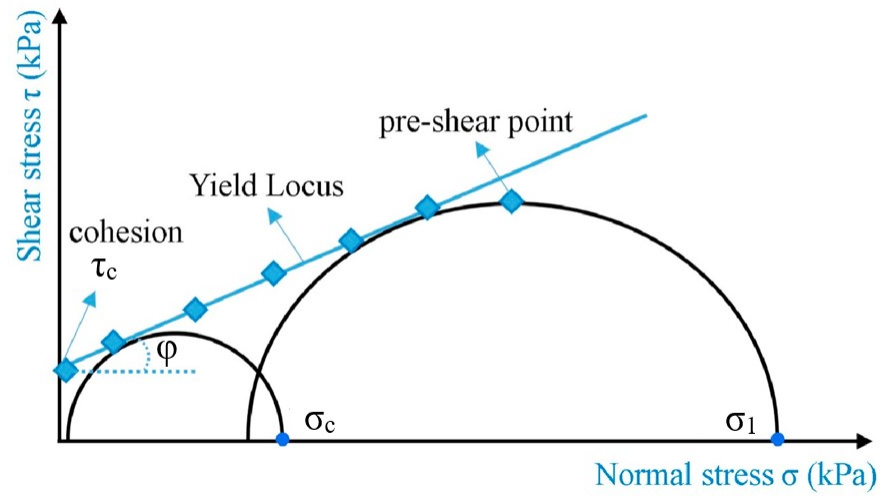


Figure 2.1: Diagram of linearized yield locus and Mohr circle analysis with angle of internal friction (ϕ), cohesion (τ_c), unconfined yield strength (σ_c), and major principal stress (σ_1). Adapted from El et al.⁸⁰

sample, $2 < ff_c < 4$ as cohesive, $4 < ff_c < 10$ as easy-flowing, and any value above 10 representing a free-flowing powder.⁶⁷ Although, the flow function coefficient is insufficient on its own to accurately characterize flowability. Furthermore, as the major principal stress and unconfined yield strength are associated with a single consolidation stress (σ_p), so too is the flow function coefficient. As such, yield loci are measured at multiple consolidation stresses and the major principal stress and unconfined yield strength are extracted from each. Plotting these points (σ_1, σ_c) produces the flow function, which provides a more general relationship between the material's strength, σ_c , and the major consolidation stress σ_1 .

2.4 FT4 Powder Rheometer

Relatively newer commercial equipment incorporates shear cell methods in addition to other characterization techniques, like the FT4 Powder Rheometer (FT4).^{81,82} Beyond shear cell testing and properties thereof,⁸³ the FT4 offers a multitude of other parameters through its Stability and Variable Flow rate, Compressibility, and Direct Pressure Consolidation tests. It provides measurements across static and dynamic states that are needed to support a multivariate analysis approach within one piece of equipment. The following subsections describe functions and tests offered by the FT4 and their associated parameters.

2.4.1 Conditioning

As touched upon previously, conditioning of sample powder is important to ensure accurate test measurements. The FT4 includes at least one conditioning step in almost all of the tests that it offers. The conditioning process employed consists of a traverse of the helical blade downward and then upward. The downward traverse typically uses a 5-degree positive helix so that the blade slices more than compacts. A negative 5-degree helix is used for the upward traverse, gently lifting powder

and dropping it over the blade.⁸⁴ The FT4 helical blade may be seen in Fig. 2.2. Conditioning is usually done before each test cycle so as to remove any compaction from the previous test, or from loading the sample into the vessel. This also helps to remove excess air within the sample. To note, verification in the literature of the manufacturer’s claim that its conditioning cycle does condition powder into a reproducible state could not be found at the time of writing.

2.4.2 Stability and Variable Flow Rate Measurements

The Stability and Variable Flow Rate (SVFR) test of the FT4 Powder Rheometer measures the energy required for powder to flow, yielding various measurements at conclusion. This dynamic testing has shown the ability to differentiate flowability of powders that otherwise display similar behavior under shear cell testing.⁸¹ Beyond this, flow energy has been found to be well-correlated with other common flowability measurement techniques.⁴ The core of this process consists of a rotating helical blade driving downwards and then upwards within a powder bed. The translational and rotational forces required during driving are used to determine total energy consumed, or flow energy, and work done during driving.^{38,85} Before this process the sample is first conditioned by gentle agitation of the powder bed with the blade to create a uniform, reproducible, and lightly packed powder state.⁸¹ Following this, the blade is spun at a rate of 100 mm/s and energy required to induce flow is measured. This cycle, conditioning followed by measurement at a tip speed of 100 mm/s, is repeated six times to yield measured flow energies $E_1 - E_7$. Four more cycles are then conducted, with conditioning steps in-between each. Sequentially, flow energies are measured at decreasing tip speeds of 100, 70, 40, and lastly 10 mm/s. As part of this process, the *Conditioned Bulk Density* (CBD) in g/ml is calculated.⁸⁶ Beyond CBD; [Basic Flowability Energy](#), [Specific Energy](#), [Stability Index](#), and [Flow Rate Index](#) are also measured as part of the SVFR test.

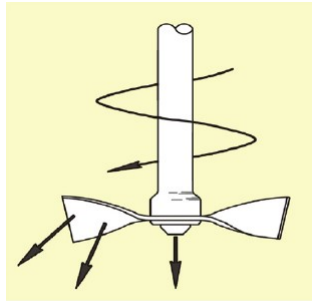


Figure 2.2: Graphic of the FT4 Powder Rheometer helical blade⁸¹

Basic Flowability Energy (BFE) is a measure of the flowability of a powder. It is the energy required to displace powder as the blade moves from the powder surface to the bottom of the vessel.⁸⁷ More specifically, it is the measured flow energy of the seventh cycle:

$$\text{BFE (mJ)} = E_7 \quad (2.8)$$

As evident above, the BFE does not account for varying sample mass. For comparing powders of similar bulk density this is not an issue, but becomes problematic for powders of significantly different densities. As such, the *Normalized Basic Flowability Energy* (NBFE) is more commonly used:

$$\text{NBFE (mJ/g)} = \frac{\text{BFE}}{\text{Sample mass}} \quad (2.9)$$

While a low BFE is typically well-correlated with good flowability (and vice-versa for a high BFE), it must be noted that this is not always the case. Powders with small particle size are often more cohesive than powders with larger particle sizes, which behave less cohesively and typically demonstrate greater packing efficiency. For non-cohesive efficiently packed powders, stress induced by the blade during flow is transmitted deeper into the bulk sample as pockets of excess air that would hinder transmission do not exist. This larger stress transmission zone results in increased particle-particle friction and contact stresses, greatly increasing the BFE. The stress transmission zones for (non)-cohesive and (non)-compressible powders are shown in Fig. 2.3. This inversion of the typical trend seen between BFE and flowability is primarily observed when comparing powders of significantly different average particle sizes.⁸⁷

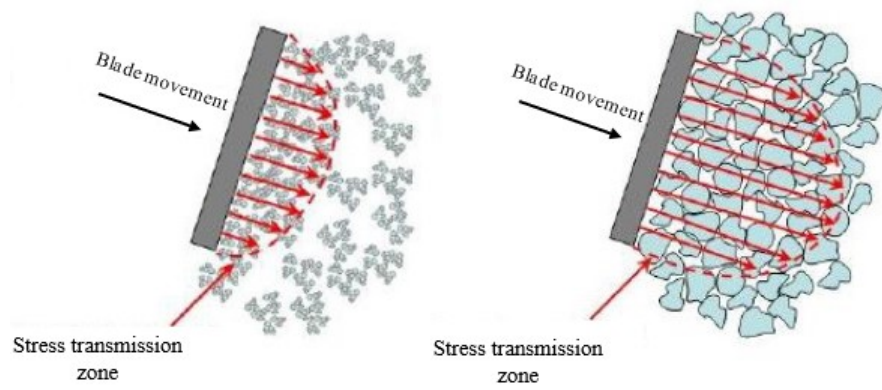


Figure 2.3: Stress transmission zones during flow for a cohesive compressible powder (left) and non-cohesive non-compressible powder (right). Adapted from FT4 supporting document W7030.⁸⁷

Complementary to BFE, *Specific Energy* (SE) is the average flow energy measured during the upward traverses of cycles six and seven divided by the split sample mass:

$$SE = \frac{(E_{6,u} + E_{7,u})/2}{\text{Split Sample Mass}} \quad (2.10)$$

It is representative of the ease with which a powder will flow in a low stress environment.^{38,88} The flow pattern during upward traverse is the same as that of the downward traverse. However, because the blade moves upwards, the powder is unconfined, or in a low stress state. As such, measured energy is more dependent on cohesive forces as opposed to compressive forces as is found during the BFE test.

The *Stability Index* (SI) is representative of the propensity to which the rheological parameters of a powder change when the powder is made to flow. It is the factor by which measured flow energy changes during repeated testing:

$$SI = \frac{E_7}{E_1} \quad (2.11)$$

A robust and non-friable material has an SI value of 1. Deviation from this value indicates that the sample material is prone to change after being made to flow. For $SI > 1$ the material requires more energy over time to be made to flow with possible causes being de-aeration, agglomeration, segregation, moisture uptake, or electrostatic charges. For $SI < 1$ the material requires less energy to flow over time, possibly due to attrition or de-agglomeration.⁸⁹

The *Flow Rate Index* (FRI) describes how sensitive a powder is to changes in flow rate. Cohesive powders are typically more sensitive to changes in flow rate compared to non-cohesive powders due to high air content. Furthermore, compressible powders may cake or agglomerate when exposed to various stresses found at differing flow rates. The FT4 measures FRI by conducting four more conditioning/testing cycles after the first seven flow energy tests. The four testing cycles use blade tip speeds of 100, 70, 40, and then finally 10 mm/s. The FRI is the ratio of the last and first

measured flow energies:

$$\text{FRI} = \frac{E_{11}}{E_8} \quad (2.12)$$

Average FRI values fall between 1.5 and 3.0, with a moderate increase in energy consumption as flow rate decreases from 100 to 10 mm/s. Increase in energy consumption can be explained by the reduction in air content as flow rate decreases. At lower flow rates more air is excluded as the powder becomes locally consolidated by the blade, with the consolidation zone extending out further. This is similar to the comparison between cohesive and non-cohesive powder shown previously in Fig. 2.3. Air reduces interparticle contact and increases compressibility of the powders, thus reducing energy consumed to flow. The reverse applies for the required energy to flow for lower amounts of entrapped air. Values above 3.0 are typically exhibited by very cohesive powders. Powders with large particle size or surface treatments usually have an FRI of 1.0, whereas powders that require even less energy to flow (FRI < 1.0) typically contain flow additives.⁹⁰

2.4.3 Compressibility Measurements

The Compressibility test measures the change in bulk density, or volume, as a function of applied normal stress. More specifically, following conditioning the powder is compressed by a vented piston (in-lieu of the helical blade) under a set normal stress and held for 60 seconds. The distance traveled by the piston is used to calculate the percent change in volume, and therefore density given an initial mass. This compression/calculation step is repeated eight more times under increasing normal stress, in total spanning 0.5 - 15 kPa. Hold time, stress range, and number of compression steps may be modified. The compression test yields [Compressibility](#).⁹¹

Compressibility (CPS) is the percent change in volume after compression by an applied normal stress of m kPa. Cohesive powders with small particle size are significantly more compressible than non-cohesive granular, and/or powders with

large particle size.⁹¹

$$\text{CPS}_m = \% \text{ Volume Change (Normal Stress } m) \quad (2.13)$$

2.4.4 Direct Pressure Consolidation Measurements

The Direct Pressure Consolidation (DPC) test measures flow energy of a consolidated powder. As part of this program, the FT4 offers two tests: one that uses direct pressure applied by the FT4 for consolidation and another that requires use of an external tapper for consolidation. Unlike other FT4 tests, the DPC test does not condition the powder. For the test, a set number of increments and single pressure is selected. The vessel is filled with a fractional amount of powder and then compressed under the pre-chosen normal stress with the vented position. This process is repeated for all remaining increments. Finally, the vented piston is then replaced for the twisted blade and flow energy is measured.⁹²

Notably, at the time of writing, no other work could be found in which this test was utilized in any form. There are no known recommended increment/pressure combinations to use. The associated operating manual for the test as provided by Freeman Technology does not provide any recommendations.⁹² Presumably, it would be expected that higher degrees of consolidation would result in higher measured flow energies. How, exactly, this might scale is unknown. How varying the number of compression increments may affect measured flow energy, if at all, is also unknown. Consequently, work herein has aimed to answer some of these questions by measuring flow energy of various powders for multiple increment/pressure combinations. Exact details are available in [FT4 Methods: Direct Pressure Consolidation](#), a subsection in the methodology chapter of this work.

Chapter 3

Ceramics for Grinding Media and Crucibles

3.1 Introduction

Ceramics, notably crucibles and grinding media, are of important use to industry and research. As covered in Chapter 1, it is reasonable to expect that the addition of rheological methods could considerably complement currently knowledge regarding relationships between powder properties and consolidated properties. The primary objective of this work is to therefore determine which rheological tests and parameters would likely be most fruitful for construction of such relationships. However, this work initially had a secondary objective. Having determined the most useful rheological parameters, the secondary objective was to then investigate how said parameters might relate to consolidated properties of ceramics. This could not be explored due to significant external delays. However, much of the literature review conducted for the secondary aim overlapped with review conducted for the primary objective of this work.

Post-introduction, this chapter first begins with discussion on some of the properties of importance to grinding media and crucibles, along with suitable measurement methods; as an original intent of this work was to measure said properties. Additionally, as initial research plans included the sintering of powders, background was written on the topic. Due to not being as relevant to the work which was accomplished, this background on common methods for sintering and

consolidating ceramic powders may be found in [Appendix A](#). Despite not having sintered ceramic powders or measured some of their consolidated properties, both of these aspects were utilized in determining which ceramic materials should be used for rheological work. The process applied to ascertain which materials to use is provided after discussion of consolidated properties. Finally, how the selected materials are produced, their common uses, typical sintering and consolidation conditions, and other pertinent information are then provided.

3.2 Consolidated Ceramic Properties and Measurements Thereof

The specific properties associated with ceramics are vast. However, they generally fall within one or more of the following categories: chemical, thermal, electrical, radiation, physical, and mechanical. Many properties within some of these categories are either innate to a material or can be modified only by altering specific physical or mechanical properties. For example, aluminum oxide does not dissolve in liquid water; no modification of the material properties can make it do so. However, the probability for a material to interact with a given type of radiation does depend in part on how dense it is. As a result, physical and mechanical properties typically receive more attention because they can be directly influenced to some degree. Of these, [density](#), [green density](#), [hardness](#), fracture toughness, and [flexural strength](#) are some of the primary properties usually investigated.

3.2.1 Density

The theoretical density of a crystalline ceramic is fundamental, essentially determined by the material's chemical composition, unit cell volume, and number of formula units per unit cell. Given that calculation of theoretical density relies on experimental measurements, reported theoretical densities have uncertainty to a minor degree.

However, the actual density of any given ceramic sample can vary significantly more, depending on phase composition, impurities, and typically the largest factor, open and closed porosity. As such, it is common for density measurements to be reported relative to the material's theoretical, and maximum possible, density, i.e., the percent theoretical density. Often total porosity is provided instead, which is given by 100% minus the percent relative density. Furthermore, as long as the theoretical density used in calculations is provided, comparisons of relevant density can still be made with other works that utilize slightly different values for a material's theoretical density.

Whether a material will be used as grinding media or crucibles, the relative density, or more specifically total porosity, of a material is of great importance. The elastic properties of Poisson's ratio and Young's, shear, and bulk moduli all depend on porosity. Additionally, flexural strength, fracture toughness, electrical conductivity, and thermal conductivity depend upon porosity in the same manner as elastic properties. Over the porosity range of 0-30% (where the majority of ceramic applications are concerned with), the aforementioned properties very closely follow an e^{-bP} dependence, where (b) is the slope of a semi-log plot of relative property values vs. the relative porosity (P).³⁵

Fortunately, even though density is an important property, it is relatively one of the simplest properties to measure. Depending upon specimen size and surface finish, one of two methods is commonly used. The first is to determine density by use of mass and length measurements, termed the mass-volume method. Specimen dimensions are usually measured by a caliper, or for utmost accuracy laser interferometry. This is particularly suited for specimens of simple geometry with smooth surface finish. For specimens whose surface roughness or geometry make accurate length measurements difficult, use of Archimedes' principle is an alternative option.⁹³ In this method the weight of the sample is measured in air and then measured again when suspended in an auxiliary liquid (usually water). These two weights combined with the density of air and the density of the liquid are then used to calculate density.

3.2.2 Green Density

The density of a powder once cold pressed into a green body, but not yet sintered, is commonly called green density. Other properties of a green body also follow this naming convention, e.g., green body strength is referred to as green strength. Such green properties determine the capability of which a green body can be machined. This is of importance for production quality and cost. Sintered bodies have significantly higher hardness and brittleness compared to green bodies, thus also an increased propensity for the introduction of microcracks and other defects during machining. Moreover, expensive diamond cutting and grinding tools are often required, insomuch that it has been estimated that the machining of sintered bodies accounts for at least 70% of total production costs.⁴³

To fully cement the utility of green density measurements, the values may be measured non-destructively. The most accurate methods are those using gas pycnometry, typically with helium, wherein density is determined by sample mass combined with the displacement of gas and volume/pressure relationship. However, it is common for the die holding a green body to be directly transferred to a furnace for sintering. In such cases the mass-volume method with calipers is a quicker, and still reliable, method for measuring green density non-destructively.

Beyond affecting machinability and manufacturing cost, green density also affects sintering and sintered body shape. Relatively dense green bodies will experience densification faster and more uniformly during sintering, result in higher sintered density, and undergo less volume shrinkage.³⁷ Notably, green density overall correlates with sintered density, not just at high relative densities; the importance of this should be evident given prior discussion on sintered density.¹⁵ Consequently, as green density correlates with other green properties and thereby extending to machinability and costs, sintered shape, and density, it may be seen why it is not only important to grinding media and crucibles, but also how it may be used as a gauge of quality during production.

3.2.3 Hardness

Conceptually, hardness is indicative of how resistant a material is to penetration by a sharp object. Because hardness is a measure of local deformation caused by a disturbing force, it is not a unique property. This means that the various units of measure that may be used for hardness cannot be traced back to a natural standard, therefore making it impossible to directly compare results from different measures of hardness.⁹⁴ It is then crucial to utilize a standardized and widely used method for measuring the hardness of a material.

The most well-known test method, to researchers and laypersons alike, is scratch testing (Mohs test). This method is simply the observation of whether one material is capable of scratching another. This allows for a rudimentary, qualitative ranking system, but little else. Since the inception of Mohs test, hardness testing has evolved considerably. Contemporary testing most commonly utilizes static indentation tests. In such tests a ball, cone, or pyramid is pushed into a material's surface with a set force. Shown in Eqn. 3.1 below, a material's hardness is then given by the contact pressure, or peak load P , divided by the area of residual deformation, A .⁹⁵

$$H = \frac{P}{A} \tag{3.1}$$

Knoop hardness (HK) and Vickers hardness (HV) are the two most common indentation-based hardness measurement methods, with respective standards of ASTM C1326⁹⁶ and ASTM C1327.⁹⁷ The tips of Vickers indenters are square-based pyramids, whereas for Knoop indenters they are rhombus-based pyramids. In calculating HV, the average of the two indentation diagonals is used. For HK, only the long diagonal of the indent is used. As the diagonal of a Knoop indent is generally twice the length of the average Vickers indent diagonal length, measurement precision is less prone to error in Knoop testing compared to Vickers testing; assuming diagonal ends can even be resolved given that Knoop indents have less depth than Vickers indents, a benefit of Vickers testing. However, this benefit for Vickers testing

can also increase the probabilities for specimen cracking and fracture, becoming a detriment at times. The method that will provide the most accurate measurements is therefore material dependent. The idealistic choice is to then take both HK and HV measurements for an un-characterized material, especially so as HK and HV cannot be converted to one another.

Even if both HK and HV measurements are taken, one other factor important to hardness testing remains. From Eqn. 3.1 it would appear that hardness should not depend upon applied load, but this is not the case. The volume of material that yields, and the mechanisms of yielding, can vary with the applied load. Hardness decreases as the volume of material plastically deformed and corresponding indent size increases, thus named the indentation size effect (ISE).⁹⁵ Meyer's law is commonly used for fitting plots of ISE, or hardness versus applied load:

$$P = Cd^n \tag{3.2}$$

where P is applied load, C is a constant, d is the impression size, and n is the Meyer index. Meyer's law original usage was for determining the work-hardening capacity in Brinell hardness testing of metals.^{94,98} Nonetheless, a good empirical fit can often be achieved when applying it to Vickers or Knoop ISE plots, even if no theoretical basis for such fitting exists.⁹⁹ Due to the extensive application of Meyer's law, it has been found that n is almost always less than 2 for ceramics, which Eqn. 3.2 would indicate that hardness continuously decreases as load increases.⁹⁵ However, this is not the case; hardness usually plateaus to a constant with increasing load. This is appreciably noticeable with Vickers testing, where often a constant hardness is abruptly reached at some critical load.⁹⁵

This all brings to attention that after determining which hardness tester(s) to utilize, one must also determine which load(s) to test at. From Eqn. 3.2, assuming $n < 2$, the range of applied loads may be approximately bounded into two regions: a microhardness region, characterized by low loads and significant hardness-load

curvature; and a macrohardness region, denoted by high loads where curvature is low, hardness plateaus or abruptly transitions to a constant value, and increasing possibility for specimen fracture. No definitive point exists separating the two regions, but it is common to define microhardness as the region where applied load is $9.81\text{E-}03$ to 9.81 N ($1\text{-}1000\text{ gf}$).¹⁰⁰ If only one load is to be tested, it is commonplace to use the upper limit of this range; however, historically this has not been the case and loads often went unreported.

As hardness pertains to crucibles, mechanical erosion is detrimental as it can introduce impurities into the material under heat treatment within the crucible. Erosion can also lead to sufficient enough cracking to cause fracture; especially so once thermal stress is considered. However, the number of situations in which mechanical abrasion and/or penetration of a ceramic crucible would occur to a significant degree is limited. Hardness is relevant to crucibles, but considerably more so for grinding media. Given their application, mechanical abrasion and/or penetration of grinding media by the material being ground is not a question of if, but when. Higher hardness reduces the rate at which grinding media are consumed; however, it can increase the rate at which the mill's lining is eroded. As such, the "right hardness" is application dependent. However, ensuring grinding media produced consistently have the right hardness is important regardless of application.

3.2.4 Flexural Strength

As previously discussed, tensile strength values of ceramics are quite low, greatly limiting their use in applications of tensile loading. Inversely, the compressive strength values of ceramics are very high, promoting their use in corresponding applications. Most research has not been concerned with improving, or better controlling, values for either type of strength as such efforts would not necessarily provide much use in practice. For most purposes, it is easiest to simply not use ceramic materials under

tensile loading and for compressive loading to use ceramic materials with respectively higher than average values.

Flexural strength (also known as bend strength, transverse rupture strength, and modulus of rupture) is the maximum stress under bending that a material can withstand before failure. In a homogeneous material free of defects, flexural and tensile strengths would be identical as bending is just a locally concentrated application of tensile stress. In practice this is not true due to the significant number of microscopic defects in brittle materials. In a flexural strength test, tensile stress is concentrated to a small section of the specimen, whereas in tensile strength testing the stress is experienced throughout the entire test piece. As the latter has a higher sampling volume, the statistical probability of the volume containing a larger defect is higher. With a lower chance of significant stress-amplifying defects being found in a smaller volume tested in bending, flexural strength is then usually higher than tensile stress.

As such, values of flexural strength tend to lie between the respectively low and high values associated with tensile and compressive strengths. While use of ceramics in tensile applications can be avoided, failure by bending is nonetheless common as tensile stress can arise from non-uniform loading, e.g., uneven compressive loading. Even for non-tensile applications though, it would appear that tensile strength testing would be more useful than flexural as its application of a uniform stress better accounts for statistical aspects of tensile/bending failure. However, tensile tests require very accurate gripping of specimen ends that is difficult to achieve for brittle materials. Furthermore, test specimens are complex and expensive in shape. In contrast, flexural testing and associated specimens do not have such issues. The primary problem of flexural testing is its statistical deficiency in measuring strength, which can be alleviated by increasing the number of samples tested. With all of this in mind, more attention has therefore been given to improving and better controlling expectant values of flexural strength compared to tensile and compressive strengths.

Flexural strength is commonly measured by three- or four-point bending tests. In such tests a rectangular or cylindrical specimen is placed on two supporting pins a set distance apart and then loaded until failure by two pins equidistant from the center of the specimen, or one loading pin at the center in the case of three-point bending. Both tests, using rectangular specimens, are covered in the standard ASTM C1161, with four-point bending being recommended for most characterization purposes.¹⁰¹ Ten samples having undergone four-point bend testing may then be used to estimate the mean flexural strength. However, a minimum of thirty samples is required for accurate reporting of the form of the strength distribution.¹⁰¹

The requirements for strength distribution form reporting highlight how the random distribution of defects in nominally identical specimens lead to large scattering in strength measurements. While the Gaussian distribution is the most commonly used distribution for general reporting of experimental data, the Weibull distribution is more commonly used for statistics of brittle failure. It is based on a weakest link argument in that failure at any flaw results in total failure and if one assumes that flaws are distributed throughout the entire material, then the strength distribution must depend in part upon volume.^{95,102} For uniform uniaxial tension throughout the full volume of material, the two-parameter Weibull distribution is given in Eqn. 3.3 on the following page. It gives the cumulative probability of failure P_f ; that is, the probability that failure has occurred by a stress σ .^{95,102}

$$P_f(\sigma) = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (3.3)$$

The Weibull scale parameter is σ_0 and is the center of the distribution. Specifically, it is the 63rd percentile; at or below a stress of σ_0 the probability of failure is 63%. The Weibull shape parameter m , or Weibull modulus, inversely represents the distribution width, where a high value of m signifies a narrow distribution. Larger scale and shape parameters imply greater strength and more reliable reproducibility of specimens, respectively. The three-parameter distribution includes an additional

parameter σ_u that shifts the stress ($\sigma - \sigma_u$). It is the stress at which below there is zero probability of failure. As the possibility that a ceramic specimen could contain a very large flaw cannot be discarded, σ_u is assumed to be zero for safety purposes. Uniform uniaxial tension results in the Weibull distribution losing a volume dependence, but this reliance does exist for non-uniformly applied tension, such as in flexure. Other factors like loading rate can further affect Weibull statistics. Fortunately, guidance for proper Weibull statistics are readily available in ASTM Standard C1239.¹⁰³

3.3 Materials Selection

Focusing research on ceramic refractories, as opposed to ceramic materials as a whole, provides more resolute boundaries as to which materials should be examined. However, the category of ceramic refractories is expansive. This begets the question, which specific materials should be examined? One may review the literature, and commercial usage, to determine which ceramic refractories are principally used in high stress applications, particularly those for grinding media and crucibles. However, this limited set of ceramics may also be ascertained by first referring to a fundamental work within the literature, followed by consideration of manufacturing capabilities and mechanical properties.

In 1920 Alan Arnold Griffith published a seminal study on stress and failure in brittle materials due to crack propagation.¹⁰⁴ Prior to Griffith's work, a contradiction existed in that the stresses required to fracture brittle materials were orders of magnitude lower than what contemporary theory predicted. Griffith proposed that such discrepancies were due to microscopic flaws within a material unaccounted for in the current theory. Griffith confirmed this through examination of artificially induced flaws in glass specimens, correspondingly producing an updated theoretical framework by use of a thermodynamic approach.¹⁰⁴ This work greatly advanced understanding of fracture strength for brittle materials, particularly ceramics. By starting from

the theoretical work in Griffith’s study, an expression relating a brittle material’s theoretical fracture strength σ_{th} with enthalpy of sublimation ΔH_{sub} , density ρ , Young’s modulus E , and molecular mass M may be developed:¹⁰⁵

$$\sigma_{th} = \left(\frac{0.33\Delta H_{sub}\rho E}{M} \right)^{1/2} \quad (3.4)$$

Insight into why certain ceramic refractories find more use may be revealed by considering Eqn. 3.4 above. As enthalpy of sublimation and Young’s modulus are dependent in part upon atomic bond strength, it can be seen that a ceramic material will possess covalent and/or ionic bonding.⁹⁴ Stronger materials will tend to predominantly consist of covalent bonding; with greater bond strength correlating to greater modulus values.¹⁰⁶ The relationship of density to molecular weight further constrains the particularly strong materials to consider to boron and borides such as titanium diboride (TiB_2), zirconium diboride (ZrB_2), and hafnium diboride (HfB_2); carbon and carbides like boron carbide (B_4C), silicon carbide (SiC), and tungsten carbide (WC); oxides like aluminum oxide (Al_2O_3), beryllium oxide (BeO), magnesium oxide (MgO), and zirconium dioxide (ZrO_2); and nitrides like boron nitride (BN) and silicon nitride (Si_3N_4).

While reduced, this generalized list of ceramic materials is too broad for the endeavors of this work. It also does not fully account for general costs and difficulties associated with manufacturing the materials listed and those of similar composition. For example, TiB_2 , the other listed di-borides, and unlisted carbides and nitrides such as zirconium carbide (ZrC) and hafnium nitride (HfN), all have melting points greater than 3000°C and maintain high structural stability at temperatures above 2000°C; therefore, they fall under the subcategory of ultra-high temperature ceramics (UHTCs).^{107,108} UHTCs are more difficult to densify due to requiring higher temperatures and/or pressures when sintering.¹⁰⁸ In contrast, refractory ceramics with lower melting points, like BeO (2507°C), will generally be easier to densify into solid parts; although, this is not a steadfast relationship.¹⁰⁹ However, BeO powder

is a known carcinogen,¹¹⁰ demonstrating that the difficulties associated with the safe handling of a material must also be acknowledged.

With all of this in mind, the list of refractory materials which have higher than average physical and/or mechanical property values, do not fall under the domain of UHTCs, and are not overly unsafe to work with may be reduced to the following: Al_2O_3 , B_4C , BN, MgO, SiC, Si_3N_4 , WC, and ZrO_2 . A summary of some physical and mechanical properties for five of these materials is presented in Table 3.1.

The five materials presented above (Al_2O_3 , B_4C , SiC, Si_3N_4 , and WC) were selected as the candidate materials for this work. In addition to being used as grinding media and/or crucibles, each material had a specific reason for its inclusion. Of the three oxides listed above, Al_2O_3 is the most widely used and least costly, thus it was chosen to represent oxides. BN is unique in that it is a superhard material, making it particularly relevant to grinding media and general abrasive applications. However, its cost is prohibitive, it has very low market availability, and its sintering difficulty is clearly known. On the contrary, these issues are much less severe for B_4C , which was chosen for use as a near-superhard replacement. SiC was included to represent carbides due to its low cost and because of its highly covalent nature relative to most ceramics. Si_3N_4 was chosen to represent nitride ceramics. Lastly, WC was included as it provides a significantly different density compared to all other materials, which is of particular interest for rheology work. Further information on each material is provided in the following five subsections. Each subsection begins briefly on the use of (or lack of) its respective material as crucibles and/or grinding media. Consideration is also given to general applications of the material beyond its use as crucibles and grinding media. How the material is produced and its most prevalent crystal structures are then provided. Finally, the methods commonly used for consolidating the material, with a focus on pressureless sintering and hot pressing, are discussed.

Table 3.1: Typical physical values, or range of values, of select ceramics when densified to $\geq 95\%$ of theoretical density.

Material	Density (g/cm ³)	Melting Point (°C)	Vickers Hardness (GPa)	Flexural Strength (MPa)	References
Al ₂ O ₃	3.987	2050	15-20	300-400	[94, 111–115]
B ₄ C	2.52	2350	36.8	350	[112, 116, 117]
SiC	3.21	2545*	25-27	325-550	[118–122]
Si ₃ N ₄	3.17	1900*	14-16	600-800	[111, 112, 123, 124]
WC	15.6	2870	25-30	380-580	[111, 112, 125–127]

*Decomposes at given temperature.

3.3.1 Aluminum Oxide

Aluminum oxide, Al_2O_3 , commonly called alumina, is perhaps the most commonly used crucible material due to its versatility and low cost. The same can be said for its use as grinding media, particularly so in cases where stainless steel media cannot be used for milling a material out of concern for iron contamination. Compared to other refractories, Al_2O_3 has more readily available raw materials, is easier to produce, and easier to sinter; all of these factors contribute to its low cost.

With the above comparisons in mind, it is also typically the first choice of material for most refractory applications. These reasons combined with its high hardness give cause for its prevailing use for abrasive applications over other ceramics.¹²⁸ Al_2O_3 is a widely used biomaterial (hip implants, dental, etc.) due to its chemical inertness and tribological properties.¹²⁹ It is also used in high-voltage applications, particularly for spark plugs, as it is an excellent electrical insulator.

Al_2O_3 is produced from bauxite ore through the Bayer process. Bauxite ore is mainly composed of aluminum hydroxides, with impurities of iron oxides and hydroxides and various clay minerals. In the first step of the Bayer process, the bauxite ore is crushed and milled down in size. The ore is then dissolved in a concentrated sodium hydroxide solution at temperatures up to 270°C . The aluminum species are dissolved, and insoluble impurities are then filtered out. Aluminum trihydroxide ($\text{Al}(\text{OH})_3$; commonly called gibbsite) is then precipitated out by cooling and seeding with gibbsite. The precipitate is washed and then calcined to produce alumina, which typically is multi-phase.¹³⁰ The predominant stable phase of alumina though is $\alpha\text{-Al}_2\text{O}_3$ with a crystal structure containing two formula units per rhombohedral unit cell (space group $R\bar{3}m$). Although, a larger hexagonal cell with six formula units is often used as an equivalent representation for the crystal structure.¹³¹

Al_2O_3 green bodies are most commonly made by casting (slip or tape) and powder compaction. Casting is typically used as means to reduce agglomeration in powder

and for the production of large pieces. Across industry, compaction is typically achieved through uniaxial compression with pressures between 100-200 MPa. Isostatic pressing is utilized in some situations, but its usage is primarily found in works of research. Sintering is principally done by pressureless sintering at temperatures of 1500-1700°C. Higher temperatures in solid-state sintering, even beyond the aforementioned range, are usually required to achieve complete densification of increasingly pure alumina as impurities aid densification and prevent grain growth to some degree.^{114,128}

MgO is one of the impurities commonly found in alumina and often added to ultra-high purity Al_2O_3 , or added in excess to what is naturally found in less pure alumina. Coble was the first to demonstrate that the addition of about 500 ppm MgO limits grain growth in alumina considerably.^{132,133} Since then, MgO has come to be viewed as one of the most, if not subjectively best, sintering additives for alumina. The specific mechanisms of exactly how MgO limits grain growth, and why it is the most effective additive even among other oxides, has yet be determined indisputably. Generally described though, it is commonly accepted that MgO acts by two mechanisms; it increases surface diffusion, thus contributing to pore mobility, and decreases grain boundary mobility.¹³⁴

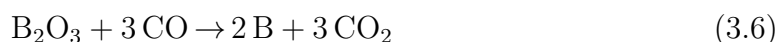
3.3.2 Boron Carbide

Boron carbide, B_4C , finds very niche use, with little commercial suppliers, as grinding media. While it can be useful in reducing contamination when milling B_4C powder, other media materials or milling methods (e.g., jet milling) are usually easier and less costly to utilize. Use of B_4C as crucible material is as rare as its use as grinding media. Its unique attributes, relative to other refractory ceramics, are not as relevant for crucibles; thus, other refractory ceramics tend be preferred.

While B_4C is not a very common choice for grinding media or crucibles, its use in applications directly relevant to these two purposes is extensive. It is immensely hard;

out of well-characterized materials, B_4C ranks as the third hardest material behind diamond and cubic boron nitride. So, while it is rarely used as grinding *media*, it is heavily used as an abrasive in powder form, as sintered coating, and as a sintered piece itself (e.g., grinding wheel). It is further used as coating on cutting tools. As it has good wear resistance, it is also utilized for blasting nozzles, ceramic bearings, and wire drawing dies.^{24,135}

Boron carbide is commercially produced by carbon reduction of boric acid or boron oxide at about 2500°C in an electric arc furnace. The overall carbothermic reduction proceeds by the three steps shown below.¹³⁵



Various parameters of the process are set such that boron carbide with a B_4C composition is typically produced. This introduces an important aspect: “boron carbide” is commonly represented with the stoichiometry of B_4C , corresponding to a carbon content of 20 at.% C; however, a wide range of homogeneity exists for the stoichiometry of stable boron carbide, spanning from approximately 9 to 20 at.% C.^{24,116,135} The homogeneity range arises in part from the crystal structure of boron carbide and the acceptable atomic substitutions within it. The crystal structure of boron carbide consists of 12-atom icosahedra situated at the corners of a rhombohedral unit cell of the $R\bar{3}m$ space group with icosahedra linked by a 3-atom chain along the (111) rhombohedral axis.¹¹⁶ Icosahedra are primarily composed of boron atoms. At most, two of the twelve boron atoms can be substituted with carbon atoms due to internal bonding constraints.¹³⁶ The 3-atom chain is envisioned to consist of only carbon atoms, only boron atoms, and a mix of both depending on the carbon content. While this barely touches upon the subject, it sufficiently

evidences why the stoichiometry of stable boron carbide is so varied. For in-depth treatment of the subject, Suri et al.¹³⁵ and Domnich et al.¹¹⁶ provide excellent reviews.

Densification of pure boron carbide to >90% TD by pressureless sintering is only possible with very high temperatures of $\sim 2300^{\circ}\text{C}$ and particles close to or $<1\text{ }\mu\text{m}$. On the contrary, full densification of B_4C powder without sintering additives and particle size generally falling within the range of $1\text{--}10\text{ }\mu\text{m}$ can be achieved by hot pressing at temperatures $>2100^{\circ}\text{C}$ and pressures $\geq 30\text{ MPa}$ under vacuum or inert atmosphere.^{24,135} Furthermore, hot pressing has a much greater rate of densification and decreased grain coarsening compared to pressureless sintering. As expected, hot pressing is the most common method for consolidating dense, pure B_4C .

3.3.3 Silicon Carbide

Silicon carbide, SiC , is a commonly used crucible material given its sublimation point compared to the melting points of other refractories. It is widely used for the melting of aluminum and aluminum alloys, copper and copper alloys, and precious metals. Similar to B_4C , SiC is used extensively in various forms (powder, coating, sintered) as an abrasive, but not often directly as grinding media. Its use as grinding media is typically reserved for the grinding of SiC powder so as to reduce potential contamination.

Generally, SiC is used in applications typical of most refractories, such as machining and thermostructural components. Its sublimation point, in addition to low thermal expansion and high thermal shock resistance, make it ideal for use in furnaces: as structural components or heating elements. Unless SiC is made into a composite, it is not often used in applications that demand strong fracture toughness given its correspondingly low value. Of note, SiC has long been an important semiconductor. However, SiC semiconductors are made by using physical vapor transport with raw silicon and carbon to grow crystals that are subsequently cut

into wafers or other similar processes; therefore, no sintering is involved in their production.

The Acheson process was the first method created for the synthesis of SiC and is still the primary basis for commercial SiC production today. The Acheson process uses an electric furnace to produce a carbothermic reduction of silica sand and carbon.¹³⁷ The reaction is given below.



Pure SiC is white, less pure is green, and even lower purity results in blue and black coloring. The purity and color varies as a function of distance from the electric heating element, decreasing in purity further away from it.¹¹⁸ It is common for SiC producers to qualitatively classify their products by color, e.g., black SiC and green SiC as products. Another processing factor that affects product properties, specifically crystal structure, is temperature. Lower temperature skews towards producing β -SiC and higher towards α -SiC.

β - and α -SiC are only some of the over 200 reported polytypes of SiC; this high number of polytypes results from the large variety of acceptable stacking sequences.¹³⁸ Of them, the most common are the 3C (β -SiC), 4H, 6H (α -SiC), and 15R polytypes, where the numbers signify the repetition of the Si-C pair and the letters respectively representing crystal structures of cubic, hexagonal, and rhombohedral.¹¹⁹ Notably, 3C (β -SiC) is the only stable polytype with cubic structure. Overall, β -SiC and α -SiC are the most commonly used polytypes. While consolidated properties between the two may differ slightly, there are no differences in sintering mechanisms between the two, and sintering methods are essentially identical for both.¹³⁹

As discussed in section 3.2, [Sintering and Pressing](#), one condition sintering relies upon is that $\gamma_{GB} < \gamma_{SV}$. For SiC, a highly covalent material, this condition is not met. SiC is therefore non-sinterable without the use of sintering aids in pressureless sintering and cannot be fully densified without similar aids in

hot pressing. Successful solid-state pressureless sintering was first developed by Prochazka, who used submicron β -SiC with trace amounts of boron and carbon.¹⁴⁰ The aids are believed to assist sintering by reducing γ_{GB} at grain boundaries.¹³⁹ For hot pressing, it was first discovered by Alliegro et al. that the addition of Al metal produced SiC with density of 3.10-3.20 g/cm³, significantly better than the 2.7 g/cm³ found for pure SiC.¹⁴¹ While not as frequently used due to increased costs and shape limitations compared to pressureless sintering, contemporary hot pressing utilizes oxides like Al₂O₃ for liquid-phase sintering. However, Al in addition to C, and sometimes also B, is still used for pressureless sintering with the B-C system finding the most use.

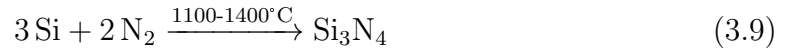
3.3.4 Silicon Nitride

Silicon nitride, Si₃N₄, is not as commonly used for lab-scale crucibles as less costly options are typically available. On the contrary, industrial use of Si₃N₄ crucibles and furnace components is more substantial. Si₃N₄ exhibits good resistance to acid and weak alkaline corrosion and excellent corrosion resistance to many molten nonferrous metals. It has been a staple refractory in the iron and steel industry for a long time.¹²⁸ Its use as grinding media is like that of SiC, primarily utilized when grinding Si₃N₄ powder in order to reduce contamination. However, its low density compared to other grinding media, particularly steel, combined with its other thermomechanical properties make it ideal for grinding of certain powders which also have low density.

Si₃N₄ has higher strength relative to other refractories, giving it a leg up for use in high-temperature, mechanically stressful applications, such as engine components. Its thermal stability, hardness, and wear resistance make it a very useful material for cutting tools. The same can be said for use as bearings, which is reflected in the extensive use of Si₃N₄ bearings in industry, automobiles, wind turbines, and more. In fact, these properties taken together with its low density also make it an ideal

material specifically for high-speed bearings and similar applications, like automotive turbocompressor rotors.¹²⁸

The dominant method across industry for silicon nitride synthesis is by direct nitridation of elemental silicon, shown in Eqn. 3.9 below. In this method piles of silicon powder are heated in a nitrogen atmosphere, producing Si_3N_4 powder and agglomerates that are then milled until a suitable particle size distribution is achieved. Too high temperatures during the process result not only in strongly sintered agglomerates which require more intensive milling, but also the formation of $\beta\text{-Si}_3\text{N}_4$. On the contrary, lower temperatures are less likely to produce such agglomerates and also form $\alpha\text{-Si}_3\text{N}_4$, the generally most desirable phase of silicon nitride.¹⁴²



$\alpha\text{-Si}_3\text{N}_4$ with a trigonal unit cell built up by SiN_4 tetrahedra is the most common crystalline form of silicon nitride powder. During sintering, it transforms irreversibly into the β -modification of Si_3N_4 , consisting of a hexagonal unit cell and SiN_4 tetrahedra, with amount of transformation dependent on many parameters. A γ modification of sintered Si_3N_4 with cubic structure is observed under high temperature and pressure. However, the pressure required is on the order of 15 GPa, significantly higher than that typically possible in pressure assisted sintering. As such, the majority of Si_3N_4 ceramics made consist primarily of the β -modification.¹⁴³

The properties of consolidated Si_3N_4 can vary widely, depending upon powder properties like any other ceramic, ratio of α/β content in the powder and densified product, and notably the sintering technique used.¹⁴³ In fact, grades of Si_3N_4 are often classified by the method of which the material was sintered; the five primary grades/methods are (pressureless) sintered silicon nitride (SSN), hot pressed silicon nitride (HPSN), hot isostatic pressed silicon nitride (HIPSN), gas pressure sintered silicon nitride (GPSN), and reaction-bonded silicon nitride (RBSN). GPSN and RBSN

methods operate as their names imply. GPSN utilizes gas as a pressure medium and in RBSN a silicon powder compact is reacted with a nitrogen atmosphere, similar to the method used to produce silicon nitride powder.

Si_3N_4 is a highly covalent material like SiC and particularly difficult to fully densify. As densification during sintering occurs through mass diffusion, a thermally activated process, increasing temperature would help in achieving high density. However, Si_3N_4 disassociates into silicon and nitrogen when heated above 1900°C , thus greatly restricting sintering and densification capabilities. The result of this is that both pressureless sintering and hot pressing require additives if near theoretical density is sought.

Unlike the other materials and their corresponding additives discussed, additives for Si_3N_4 result in liquid-phase, not solid-state, sintering. The most common additives used are oxides (MgO , Al_2O_3 , Y_2O_3 , etc.) which in the temperature range of 1450 - 1750°C form a eutectic with silica or silicon oxynitride adhered to Si_3N_4 crystals.¹⁴² This produces a liquid phase that allows for mass transport through solution-reprecipitation of the nitride crystals.^{142,143} The specific additives used in SSN and HPSN are generally the same (oxides), however lower concentrations are required if hot pressing. Operating temperatures of 1600 - 1800°C are used for SSN and a slightly expanded range of 1500 - 1800°C may be used for HPSN.¹⁴³ Of note, “pressureless” sintering of Si_3N_4 is usually done with a slight over-pressure of nitrogen to prevent decomposition. This is of course significantly lower than the 20 - 30 MPA pressures used in hot pressing.¹⁴⁴

3.3.5 Tungsten Carbide

Tungsten carbide, WC, is one of the materials that are most commonly used for grinding media. It is highly resistant to acid and alkali corrosion. Perhaps more importantly, it is the densest material used for grinding media that also exhibits superior hardness. Grinding media could be made of denser materials, but low

hardness and wear resistance would prove their use as fruitless. As such, WC is an important material for grinding media. This cannot be said for crucibles, for which the material finds little use. WC is extensively used for mining drill bits, rock crushing, and cutting tools due in part to its high hardness.¹²⁴ These applications can lead to high operating temperatures either innately or through increased machining speed. So, while WC may not be used for crucibles, its refractory nature is nonetheless very much utilized.

WC is commonly produced through the direct carburization of tungsten with carbon at 1400-2000°C in hydrogen or vacuum.¹²⁵ Of the two crystal polytypes for WC, alpha with a hexagonal unit cell and beta with cubic, this process produces α -WC. For all practical purposes, WC will remain in its alpha form regardless of application (e.g., even if exposed to high heat). This is because β -WC is only stable at temperatures above 2525°C and will decompose directly back into the alpha polytype below said temperature.¹⁴⁵ Therefore, ensuring that powder or sintered product consists of only a single crystal polytype is not a concern with WC. However, ensuring uniformity in phase composition is of concern. Due to WC having a very limited stoichiometry range, when exact carbon content is not achieved either free carbon or di-tungsten carbide (W_2C) is formed. W_2C reduces fracture toughness as it is a more brittle phase than WC. It also reduces toughness in cemented tungsten carbide by reacting and partially depleting cobalt binder.¹⁴⁴

This reaction issue with cobalt introduces an important actuality; while called “tungsten carbide” in the literature and by commercial entities, it is often actually cobalt cemented tungsten carbide (WC–Co) that is being referred to and not the monolithic form (WC). Cemented tungsten carbide consists of WC bound by a metallic matrix, most commonly cobalt but sometimes nickel or iron. The prolific use of WC–Co over WC may be attributed to multiple factors. Although WC–Co is less hard than WC, it has better flexural strength and fracture toughness. Given the already high hardness of WC, very often this is an acceptable trade-off. Secondly, the simple technology for producing cemented carbides with required properties has, until

recently, led to little interest in monolithic tungsten carbide.³⁰ The final factor of note is that WC is difficult to sinter due to its high melting point and low self-diffusion coefficients, whereas WC–Co may be sintered with relatively low temperatures of 1400-1600°C.³¹

However, the pulmonary toxicity of WC–Co has been proven to be greater than that of single WC and Co, leading to sintered WC–Co being classified as carcinogenic to humans by the International Agency for Cancer Research.^{146,147} This reason in part has spurred increased research interest in the sintering of monolithic tungsten carbide. Much of this work has been focused on use of field assisted sintering technologies like spark plasma sintering, which are highly restrictive in size and shape of the consolidated body. Conventional sintering methods that offer greater size and shaping, like pressureless sintering or hot pressing, typically require temperatures above 1800°C, submicron powders, and usually the use of an additive.^{30,31,126}

The primary additive used is carbon, which increases densification by a carbothermic reduction of surface oxide impurities.³¹ Furthermore, it can improve fracture toughness as it also acts to unify phase composition, reducing the initial content, or further formation during sintering, of W_2C . However, excess carbon addition very commonly leads to abnormal grain growth that is deleterious to consolidated properties and prevents full densification. Additionally, cavities and pores can result due to excess carbon forming graphite within the total structure.¹²⁶ As costly and size/shape restrictive technologies (field assisted sintering), or high temperature, submicron powders, and strict carbon content control for conventional methods are necessary for optimal densification of WC, it should be evident as to why industry has yet to shift towards monolithic tungsten carbide and away from the production of WC–Co.

Chapter 4

Methodology

4.1 Materials and Grades

The five base materials used were aluminum oxide (Al_2O_3), boron carbide (B_4C), silicon carbide (SiC), silicon nitride (Si_3N_4), and tungsten carbide (WC). To ensure a sufficient amount of data for rheology work, three different base grades were acquired of each material. The grades to use were chosen by examining what was commonly used in the literature. Across all materials, the average particle size of material used typically fell within the range of 1-10 μm , with occasional work having used values below 0.1 μm or between 50-100 μm . FEPA grit sizes of F240, F600, and F1200 were accordingly chosen as the three base grades to obtain per material. Provided for reference, Table B.1 in Appendix B lists average particle size equivalents for select FEPA-F grades.

Further grades beyond the base selection were also acquired for various purposes. To better ascertain how rheology properties may vary across a material, F120, F180, and F360 grades of SiC were obtained. Two additional F1200 grades of Al_2O_3 sourced from different vendors were acquired to compare how origin source may affect rheology properties. A grade of B_4C , having a particle size distribution resembling an F1000 grade, with a 1% addition of Al_2O_3 as a sintering aid was procured to examine how the addition of an additive may affect rheology properties. However, the received product had a claimed size distribution that more closely resembled an F1500 grade and contained a 10% addition of Al_2O_3 sintering aid. To provide further rheology datasets, two mixed grades for Al_2O_3 , B_4C , and SiC were produced by creating one

70/30 wt.% mixture comprised of F240 and F600 grades and a second 70/30 wt.% mixture comprised of F600 and F1200 grades, per respective material. Particle size distribution and chemical composition information from certificates of analysis for all grades are available in Tables B.2 through B.9 in [Appendix B](#). Methodologies for mixing of powder grades may be found in [Mixing Methodology](#).

4.2 General Methodology

4.2.1 Storage, Blending, and Handling

Purchased powders arrived confined in some form which prevented exposure to environment, such as zip locked or tied bags within a container or box, or confined within a plastic container with twistable lid. When not being sampled from, all powders were kept in their stock containers and stored in a cabinet. In testing of any material/grade combination, powder was first transferred to a clean glass jar. A clean plastic scoop was used to load the jar to approximately 60% volume by sampling from multiple positions in the stock container to better ensure a representative powder distribution.

A TUBRULA, which rotates a jar along three axes to blend/mix held powder to improve powder distribution homogeneity, was used to blend loaded jars of powder. A speed of 49 rpm was used for blending of all materials and grades. All jars which held a single grade of powder (e.g, F240 SiC) were blended for 5 minutes after being loaded. Jars which held two grades (i.e., for use in mixed grade tests) were blended for 40 minutes after being loaded. Records of when a powder was initially blended, and any subsequent blending, were kept on a run sheet associated with the specific powder. Before testing a powder, its run sheet was checked to see if more than 72 hours had elapsed since it had last been blended. If so, the powder was placed into the TUBRULA, blended for 5 minutes, and the new date of last blending was updated on the associated run sheet. When a glass jar no longer contained enough powder

needed for remaining testing, it was refilled and blended again in accordance with the above procedure.

During all types of testing, the jar containing the virgin powder to be tested was kept closed unless actively being sampled from, which in such case powder was sampled from it using a plastic flared straw or small plastic scoop, depending on the type of test being conducted. A new straw and/or scoop was typically used per grade/material of powder. Rarely, a straw and/or scoop was reused for powder grades of like material after being thoroughly cleaned.

All powder samples used for Freeman Technology FT4 Rheometer (FT4) or GranuPack tests were stored in containers designated for no further use. However, powder samples used for GranuFlow and/or GranuHeap tests were taken to be effectively identical to their pre-test state. That is, if used in another test, the already tested powder sample would provide results indistinguishable to results of virgin tested powder. This was assumed as it is very unlikely either test could have affected powder in any way which would influence future testing. As such, GranuFlow and/or GranuHeap tested powders were considered to still be virgin and were put directly back into their respective glass jars after testing. Whenever this occurred it was noted on the associated run sheet for a powder.

A powder sample was deemed as “used” if it had undergone any of the following tests: Stability and Variable Flow Rate (FT4), Compressibility (FT4), Shear Cell (FT4), Direct Pressure Consolidation (FT4), or Tapped Density (GranuPack). Due to the nature of these tests, it was assumed that tested powder could produce different results compared to virgin powder if reused in another rheology test. This does not mean that all five tests are as equally destructive to powder samples. Without regard to material tested, it is likely that a sample used in a less destructive test (e.g., Stability and Variable Flow Rate) could be successfully reused in a more destructive test (e.g., Direct Pressure Consolidation). However, this was not assumed in-practice so as to be able to better isolate potential relationships in future data analysis. All powder samples deemed as “used” were put into clean plastic jar(s) allocated to the

specific material/grade combinations, similar to the glass jars. “Used” jars were kept closed unless actively being filled with used powder. When not conducting tests, glass jar(s) of virgin powder and plastic jar(s) of used powder were kept at room temperature in a humidity monitored cabinet.

4.3 Mixing Methodology

All mixed powders were made to have a bimodal distribution consisting of 70 wt.% of a larger grade and 30 wt.% of a smaller grade of like material (e.g., F240 and F600 of SiC mixed). All mixed grades were made by the same method. First, a clean glass jar with lid on was tared on a Sartorius Lab Scale (maximum mass = 10,200g, d = 0.01g). The larger grade of powder to be used in the mixed grade was sampled from its stock container by use of a clean plastic scoop and/or flared straw to fill the jar to approximately 50% volume. The mass was measured and recorded. This value was then taken to be equivalent to 70 wt.% of the desired combined mass of both grades so as to calculate the amount of smaller grade needed. A separate clean plastic scoop and/or flared straw was used to sample the smaller grade from its stock container to fill the glass jar until the total needed mass was reached. The glass jar was put into a TUBRULA and blended for 40 minutes. All further handling, storage, etc. of the glass jar followed the methods described previously.

4.4 Freeman Technology FT4 Rheometer Methods

The Freeman Technology FT4 Rheometer (FT4) tests conducted for every material/grade combination included Stability and Variable Flow Rate (SVFR), Compressibility, Shear Cell, and Direct Pressure Consolidation (DPC). How these tests generally work has been provided in [Chapter 2](#). The operating methods used for each test are found in respectively-titled subsections of this section. Six measurements using virgin powder were taken at minimum for the SVFR, Compressibility, and Shear

Cell tests (i.e., six separate instances of each test with virgin powder were conducted per material/grade). For DPC testing, at least fourteen measurements were taken; a minimum of two measurements per increment/pressure combination. Further described in [FT4 Methods: Direct Pressure Consolidation](#), additional measurements were taken when certain criteria were not met. The same order of FT4 testing (SVFR, Compressibility, Shear Cell, and then DPC) was used for all powders tested. As a material/grade combination of powder was tested, a run sheet associated with the powder was updated with additional information. Information recorded included the: date, test type conducted, instance of test (of six minimum), FT4 operator, temperature, humidity, duration of test, and the ID number of the run as recorded by the FT4. Because some FT4 tests had sufficient hands-off time, GranuHeap and GranuFlow tests were conducted while these FT4 tests ran. Furthermore, GranuPack testing was done concurrently with other testing as after initial setup the test is fully hands-off. When GranuHeap and/or GranuFlow testing concluded, the tested powder was put back into the glass jar which was drawn from for FT4 testing. Each time this occurred it was noted on the run sheet of the powder being tested. After all FT4 tests had been conducted for a powder, equipment (e.g., FT4 blade, FT4 vessels, brushes used, etc.) were cleaned. If the next powder to be tested was of like material, then wet wipes and dry Kimtech wipes were used for cleaning. If the next powder to be tested was of a different material, then everything was cleaned using 99% isopropyl alcohol and dry Kimtech wipes.

4.4.1 FT4 Methods: Stability and Variable Flow Rate

The Stability and Variable Flow Rate (SVFR) test measures the flow energy of a powder as function of tip speed of a blade that traverses up and down through the sample. Details on how it functions, along with its measured and calculated parameters, have been previously given in [Chapter 2](#). The following paragraphs describe the operating method used for every SVFR test conducted in this work.

In the Standard Test Programs of the FT4 software application, the SVFR test for the 25 mm x 25 mL vessel was selected. The 23.5 mm blade was installed into the FT4, if not already present, and the 25 mm x 25 mL vessel (with funnel attached) was placed upon the raised base platform of the FT4. The base clamp was positioned onto the vessel base as its presence affected mass readings. The vessel was then tared through the SVFR program. After, the vessel was removed and filled with virgin powder to approximately the top of the plastic ring of the vessel. This was done using a clean, plastic flared straw. After every few scoops the straw was used to lightly move, but not compact or impact, the powder so as to maintain a fairly flat surface as necessary. The vessel was put back onto the FT4 base platform and the FT4 base clamp secured into the slots of the vessel base ring. The vessel was then attempted to be twisted to ensure the clamp prongs were fully engaged in the base-ring slots. The knob on the base clamp was rotated to tighten the vessel in place. Preliminary testing showed that SVFR results were dependent on FT4 operator as “appropriate clamp tightness” varied by person, resulting in more or less energy dissipation during testing, thereby affecting SVFR measurements. To account for this, the knob was rotated until it first made contact with the base clamp, then rotated further until drawn marks on the knob and base clamp aligned. Markings corresponded with the level of clamp tightness naturally used by the author of this work, coincidentally also the highest degree of clamp tightness out of all operators. Next, the mass of the loaded vessel was recorded by the FT4. Material description was input into the application prompt following mass measurement. On this screen humidity and temperature were also input, both measured by an external Big Digit Hygro-Thermometer located beside the FT4. After all information was filled in, the test was started.

At the onset of the test a conditioning cycle automatically ran. Once over, powder was brushed off the blade into a small plastic weigh boat. A dry Kimtech wipe was used to clean the blade further if necessary. The vessel was then manually split by pushing down on the split pin and rotating the top portion of the vessel towards the

operator. The weigh boat was used to catch excess powder as the vessel was split. Next, a brush was used to clean the top glass portion of the vessel and the top of the split mechanism without disturbing the conditioned powder. This was done to ensure the best accuracy of any mass measurements to be made during the remainder of the test. The split vessel was then closed. If stray powder remained on the exterior of the vessel, or on the base clamp, it was brushed off for the same reason given before. A software prompt was clicked and the SVFR test automatically ran. Once finished, the vessel contents were dispositioned into the “used” jar of the given powder. The vessel was then cleaned with brushes and/or dry Kimtech wipes.

4.4.2 FT4 Methods: Compressibility

The Compressibility test measures bulk density of a powder as a function of applied normal stress. How the test generally works, along with its measured and calculated parameters, has been described in [Chapter 2](#). The following paragraphs describe the operating method used for every Compressibility test conducted in this work. The operating method used closely follows that of the SVFR method, but with a few differences. Unlike the SVFR method, the Compressibility test for the 25 mm x 10 mL (not 25 mm x 25 mL) was selected within the Standard Test Programs of the FT4 application. From here, the same steps as laid out in the SVFR methodology were followed up until the point in which the vessel would be split. Instead, for the Compressibility test the funnel was removed and a prompt clicked in the application right after the conditioning cycles finished as the FT4 takes another mass measurement after funnel removal. The blade was brushed, vessel split, and vessel and exterior brushed as described in the SVFR methodology. Following this, the vessel was kept open and not closed. The blade was exchanged for the vented piston. A software prompt was clicked and the Compressibility test automatically ran. Once finished, the vessel contents were dispositioned into the “used” jar of the given powder. The vessel was then cleaned with brushes and/or dry Kimtech wipes.

4.4.3 FT4 Methods: Shear Cell

Shear cell testing provides the unconfined yield strength of a powder in addition to other shear-related properties. Shear cell testing fundamentals, along with measured and calculated parameters, have been given in [Chapter 2](#). The following paragraphs describe the operating method used for every FT4 Shear Cell test conducted in this work.

The operating method used is similar to the SVFR and Compressibility methods. To begin, the Shear Cell 15 kPa option with 25 mm x 10 mL vessel option is selected within the Standard Test Programs of the FT4 application. This option applies an initial consolidation stress, or pre-shear normal stress, of 15 kPa, then measures shear stresses for applied normal stresses of 9, 8, 7, 6, and lastly 5 kPa. After selecting the prior option, the same steps as laid out in the SVFR methodology were followed up until the point in which the vessel would be split in the SVFR procedure. Instead of splitting after the conditioning cycles have elapsed, the vessel is kept intact and the blade exchanged for the vented piston. A prompt was clicked in the FT4 application and consecutive normal stresses of 0.25, 0.5, and finally 15 kPa were applied by the piston. Next, the funnel was removed as prompted by the FT4 software. After clicking another prompt, and allowing the FT4 to take another mass measurement after funnel removal, the vented piston was exchanged for the shear cell head and brushed clean if necessary. The vessel was split, portions brushed as was done in the SVFR methodology, and then kept open as was done in the Compressibility methodology. Another software prompt was clicked and Shear cell testing automatically proceeded. At test conclusion, the vessel contents were dispositioned into the “used” jar of the given powder. The vessel and shear cell head were then cleaned with brushes and/or dry Kimtech wipes.

4.4.4 FT4 Methods: Direct Pressure Consolidation

The Direct Pressure Consolidation (DPC) test measures the flow energy of a powder after it has been subjected to X increments of Y normal applied stress. A rudimentary background on DPC testing has been previously provided in [Chapter 2](#). The following paragraphs describe the methodology used for every DPC test conducted in this work.

Unlike the other three FT4 tests, DPC testing required customized programs to be created. A program was made for each increment/pressure combination utilized, with the only differences between each program being the number of increments and pressure used. For every powder tested in this work, 7 different increment/pressure combinations were used. They were selected so as to give fair insight into the 3D DPC curve of a powder, but without requiring an exorbitant amount of time. Each combination was tested at least twice per powder. If the percent relative standard deviation was greater than 7% after the two tests, a third test was conducted, a fourth if $> 9\%$ after three tests, and a fifth if $> 10\%$ after four tests. No more than five tests per combination were ever done as preliminary testing indicated that variance would not reduce further within a feasible amount of required testing time. The 7 combinations (14 separate tests) were conducted in the same order for all powders. The order, in the format (# of increments, pressure in kPa), was as follows: 2 x (5, 88), 2 x (2, 60), 2 x (5, 5), 2 x (1, 5), 2 x (5, 30), 2 x (1, 88), 2 x (1, 30), and any additional tests required in the order they arose if cutoff criteria were not met.

With the above information in mind, the general procedure used for DPC testing may be described. To start, the custom test corresponding to the increment/pressure combination to be tested was selected within the FT4 application. The amount of mass to add per increment was calculated by multiplying the average split vessel mass of previously conducted shear cell tests with a factor for the # of increment/pressure combination, and then rounded up to the nearest tenth of a gram. The factors are given in [Table 4.1](#) and were empirically determined through prior testing.

Table 4.1: Increment/pressure combinations and their mass multiplication factors used in Direct Pressure Consolidation testing.

# of Increments	5 kPa Factor	30 kPa Factor	60 kPa Factor	88 kPa Factor
1	2.78	2.95	-	3.34
2	-	-	1.58	-
5	0.56	0.59	-	0.67

They were found to provide good estimates of the incremental mass required such that the vessel would reach near 100% fill volume after all increments had been added. After initiating the program, the vented piston was installed into the FT4 and the 25 mm x 25 mL vessel with funnel attached was placed onto the FT4 raised platform. The base clamp was positioned onto the vessel base and tightened in the manner as described in the SVFR methodology (tightening of clamp does not affect mass measurement). The vessel was tared through the FT4 application. A small or large plastic weigh boat (depending on mass increment amount) was tared on a nearby scale. The boat was filled with virgin powder with a plastic flared straw or scoop up to the incremental mass amount within the range of +0.3g and -0.0g. The weight as measured by the external scale was recorded on the FT4 run sheet associated with the powder being tested. The boat of powder was then slowly poured into the vessel. The weight of the filled vessel was recorded through the FT4 application. Next, the FT4 conducted the first (or only if doing a single increment) compression cycle. The vented piston lowered until applied stress reached 0.25 kPa. The piston then continued lowering slowly while also slowly rotating, so as to gently level the top surface of the powder. This continued until an applied stress of 0.50 kPa was hit. From here, the piston continued lowering until the target normal stress was reached (5, 30, 60, or 88 kPa depending on program selected). This target force was held for 30 seconds, then the piston moved back up into the parked position. If the test had more than one increment, the next increment was measured out in the weigh boat on the external scale and the mass recorded on the run sheet. The weigh boat was poured into the vessel and a prompt clicked to initiate the next compression cycle, which operated the same as the first. The FT4 did not take mass measurements for subsequent increments, only the first was recorded. This process was repeated for all remaining increments required for the selected # of increments/pressure combination. For the last mass increment added, the piston was used to lightly push down the powder if necessary, as the FT4 requires the piston to lower to an unchangeable height without

force detection before it will begin the compression cycle. If the FT4 measures any force before the height is reached, it will throw an error.

Once all increments had been added and compressed, the vented piston was exchanged for the 23.5 mm blade. The piston was cleaned using a brush and/or dry Kimtech wipes as needed. The vessel was split and brushed clean as described in the SVFR methodology. The split vessel was then closed and a prompt clicked in the FT4 application to initiate the energy flow measurement portion of the test. Once over, the vessel and blade were cleaned as previously described and the powder dispositioned into its “used” container.

4.5 GranuTools Methods

4.5.1 GranuTools Methods: GranuPack

The GranuPack is an instrument by GranuTools that measures tapped density, allowing for calculation of parameters like the Hausner Ratio and Carr Index. Fundamentals of tapped density testing have been provided in [Chapter 2](#). At least three runs were conducted for every powder used in this work. The following paragraphs describe the operating method used for tapped density testing of all powders.

The 1 mm test cell was placed into the GranuPack and the system initialized through the application. The silver measuring cup that came with the instrument was placed onto a scale and tared. The cup was fully filled with virgin powder by use of a flared plastic straw. The mass was taken and input into the GranuPack application, in addition to the temperature and humidity as measured by an external gauge. The tapping parameters were then set within the application. The total number of taps to complete was set to 9999, the maximum amount as allowed by the application. Tap frequency was kept to its default setting of 1 Hz for the first 100 taps, and then 2 Hz for all remaining taps. The test was initiated after confirming all

tapping parameters in the software. The sensor was moved to the right, the funnel placed into the test cell, and the powder poured from the measuring cup into the cell. The funnel was removed and the sensor went down once the door was closed. The door was opened/closed again and the sensor went back up. The sensor was then moved back to the left and the diablo placed into the cell. The door was closed and the sensor lowered. The door was opened/closed again and finally tapping proceeded.

Once all tapping completed, the test cell was removed and tilted into a plastic weight boat to catch the diablo. Powder in the cell was dispositioned into the used container for the respective powder. The bottom of the test cell was removed, and all parts (diablo, test cell, and test cell bottom) were cleaned with a wet wipe and dry Kimtech wipe. The test cell was reassembled and placed back into the GranuPack.

4.5.2 GranuTools Methods: GranuHeap

The GranuHeap is an instrument which measures the angle of repose and related parameters of a powder. Elementary background on angle of repose and related has been given in [Chapter 2](#). At least six runs (each including 16 measurements) were conducted for every powder used in this work. The following paragraphs describe the method used for GranuHeap testing.

At the start of testing, the collection base, 40 mm measurement support, 40 mm cylinder, and funnel were installed inside the GranuHeap. The system was then initialized through the GranuHeap application. Next, the 100 mL supplied beaker was filled with virgin powder. This was poured into a large plastic weigh boat to facilitate future pouring/emptying. The temperature and humidity as measured by an external gauge were input into the application. The testing parameters were set as follows: number of frames to 16 (a picture every 11.25 degrees), tube up speed to 5 mm/s, rotation speed to 1 rpm, camera gain to 3, camera exposure to 1.98 ms, and camera threshold to 83. Other the number of pictures, all other listed parameters are at their default values.

After confirming parameters were set correctly, measurement was initiated. The cylinder and funnel system lowered to the measurement support, forming a seal. The door was opened and the powder from the weigh boat was poured into the top of the funnel. The rate at which it was poured was kept consistent across all runs as much as possible. After closing the door, the cylinder rose, allowing powder to fall onto the flat 40 mm measurement support. Once the cylinder reached its top position, with the powder no longer falling or shifting on the support, the GranuHeap began taking pictures. A picture was taken and the GranuHeap used image analysis to calculate the height of the powder heap, the angle of repose, and cohesive index. The collection base plus measurement support slowly rotated 11.25 degrees, at which point another photo was taken and another set of values calculated. The GranuHeap automatically continued this through all 16 pictures (180 degree coverage). After finishing and saving data, the door was opened and the collection base plus screwed-on measurement support was removed. Powder was poured/brushed out of the base into the large weigh boat. This powder was then used in the next run through the GranuHeap test. This entire process was repeated at least five more times.

4.5.3 GranuTools Methods: GranuFlow

The GranuFlow is a flowmeter by GranuTools which measures the mass flow rate of a powder as a function of aperture size. Measuring flow rates across multiple aperture sizes allows for calculation of further parameters which may be used to describe a powder. Flowmeter fundamentals and associated parameters have been discussed in [Chapter 2](#). The following paragraphs describe the method used for all GranuFlow testing.

To start, the big plate (aperture sizes included 18, 20, 22, 24, 26, 28, and 30 mm) was installed onto the rotating plate of the GranuFlow. The silo with funnel was installed on top of the big plate. The software application was started and a connection was made with the mass balance. The balance was tared and then

calibrated with a 200 g weight per GranuFlow instructions. The supplied 500 mL beaker was fully filled with virgin powder and any powder remaining from GranuHeap testing that occurred immediately prior (GranuHeap tested powder was treated as virgin). Beaker contents were slowly poured into the silo. The empty beaker was placed onto the mass balance and tared. The big plate was selected from a drop-down menu in the application. The testing program was initiated, whereupon doing so temperature and humidity measured by an external gauge were input.

The record button was hit and the plate manually rotated over the first aperture (18 mm). Powder was allowed to flow into the beaker and change in mass automatically recorded over time. After a sufficient number of data points had been recorded, or if all powder had flowed out, the plate was rotated to the next closed position. Recording was then stopped. An upper and lower mass value was input into the application, which then applied a linear fit to the data. The calculated mass flow rate for the aperture size was then added to the flow curve section of the application. If powder did not flow, recording was stopped, no fit was made nor added to the flow curve section, and no data was saved for that aperture. The described process was repeated for remaining aperture sizes (20–30 mm, evens). After all apertures had been tested, data fitted, and flow rates added to the flow curve section of the application, the flow curve data was fitted with a modified Beverloo equation and all data/fits saved. This was all repeated two more times, i.e., measuring flow rates for all apertures of the big disk.

If powder flowed through the smallest aperture of the big disk (18 mm), then further testing with smaller apertures was conducted after all testing with the big disk had finished. For this, the big disk was exchanged with the small disk (apertures of 4, 6, 8, 10, 12, 14, and 16 mm). Unlike the larger apertures, a significant amount of data could be collected per aperture due to flow rates being much slower. As such, all powder was allowed to flow out of the silo into the beaker for all apertures for which flow would occur. Only one measurement was conducted per aperture as the amount of data collected meant a measured flow rate was statistically equivalent to

averaging three separately measured flow that had less data to be fitted. Beyond this, all other steps for flow rate testing with the small disk were identical to those of big disk as described above. Once all GranuFlow testing concluded, the tested powder was added back to its virgin glass jar and noted on the associated run sheet.

Chapter 5

Results and Discussion

5.1 Freeman Technology FT4 Powder Rheometer Results and Discussion

5.1.1 Stability and Variable Flow Rate Results and Discussion

The data provided by the Stability and Variable Flow Rate (SVFR) test include energies required to induce flow at different tip speeds. An example plot of SVFR flow energy data for Panadyne aluminum oxide (Al_2O_3) F1200 is shown in Fig. 5.1. Error bars represent the standard deviation of six repeated SVFR tests of virgin powder. For the first seven runs, or cycles of the test, the helical blade spins at 100 mm/s when traversing up and down into the powder. These seven flow energy measurements collected constitute the stability region of the SVFR test. The remaining four measurements of flow energy, comprising the variable flow rate region of the SVFR test, are collected at consecutive tip speeds of 100, 70, 40, and 10 mm/s. The dashed line connecting all data points is for visual ease in reading only.

Fig. 5.1 demonstrates some aspects of SVFR data common to well-behaved powders tested. The stability region showed little change in measured flow energies across runs 1-7, which was expected under the assumption that the SVFR test does condition powder into a reproducible state between cycles. The variable flow rate region, runs 8-11, exhibited at least some curvature. The standard deviation of run 11 was typically greater than the standard deviations of the other variable flow rate

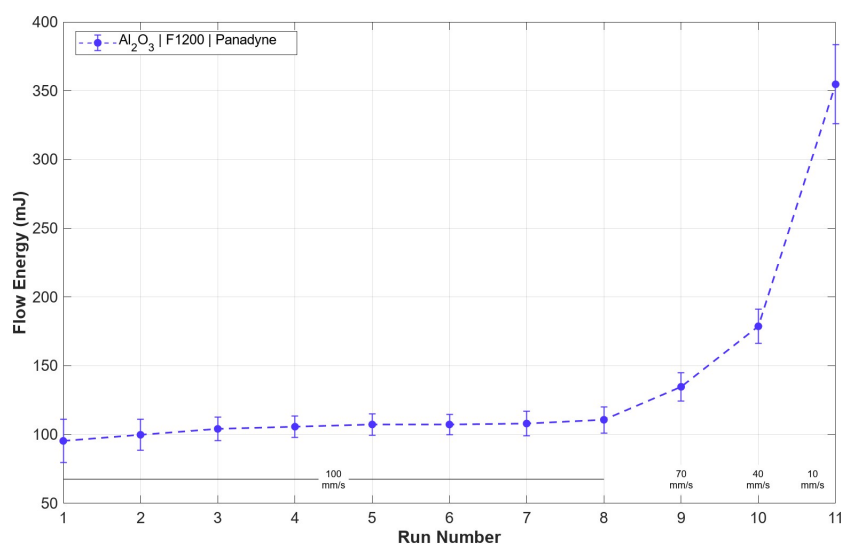


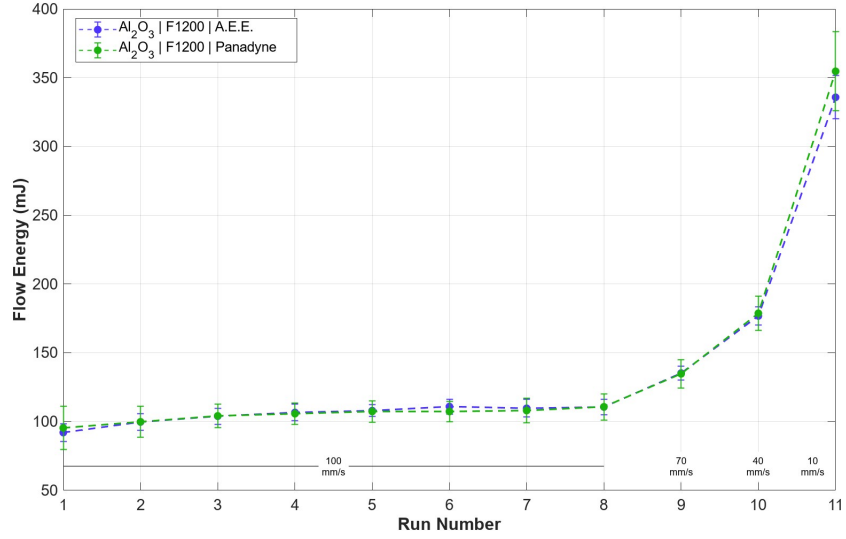
Figure 5.1: FT4 Stability and Variable Flow Rate data for Panadyne aluminum oxide F1200.

runs. If increasing error across runs 8-11 was an effect dependent upon powder tested, an effect caused by the FT4 Powder Rheometer having precision difficulties at lower tip speeds, or a combination of both, is unknown.

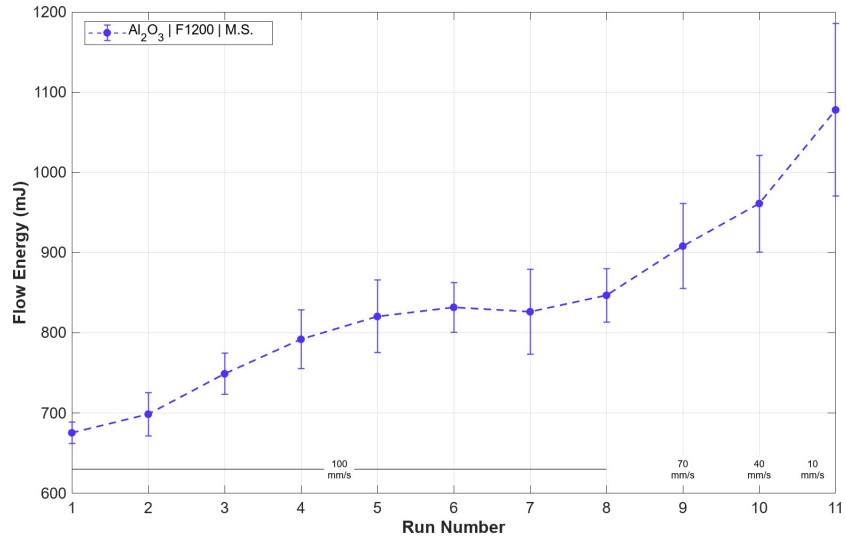
Shown in Fig. 5.2 is a plot of SVFR data for Al_2O_3 F1200 grades from Panadyne and Atlantic Equipment Engineers (A.E.E.) and a plot of SVFR data for a Al_2O_3 F1200 grade from Metallurgical Supplies (M.S.). The plot of SVFR data for Al_2O_3 F1200 M.S. was separated from the other two for clarity. The two F1200 grades of Al_2O_3 from A.E.E. and M.S. were acquired in addition to the F1200 grade of Al_2O_3 from Panadyne to compare how origin source may affect rheological properties. Despite all three having an identical stated grade of F1200, along with similar purity levels (data provided Tables B.2 through B.9 in Appendix B), SVFR data were not similar for all three vendors. Noticeably, the M.S. grade exhibited higher flow energies and inconsistency in the stability region. Although not readily clear visually, the relative standard deviations of measured flow energies for the M.S. grade were similar to those of the A.E.E. and Panadyne grades.

Fig. 5.3 and Fig. 5.4 show SVFR data for Al_2O_3 F240, F600, and F1200 grades from Panadyne along with 70/30% F240/F600 and F600/F1200 grades mixed in-house using the base Panadyne grades. Similar plots of identical grades, those from Panadyne and mixed ones using the Panadyne grades, for the materials of boron carbide (B_4C) and silicon carbide (SiC) may be found in Fig. C.1 and Fig. C.2 in Appendix C.

For Al_2O_3 and B_4C the F240/F600 mixed grade had flow energy values residing between the flow energy values of their constituent grades. For SiC , the flow energies measured in the stability region had values between those measured for the base grades, but it is uncertain if this was true for the variable flow rate region due to overlapping error. For all three materials, the relative standard deviations of the flow energies of runs 2-8 for the F240/F600 grades were typically lower than those of their base grades.



(a) Al₂O₃ F1200 A.E.E. and Panadyne



(b) Al₂O₃ F1200 M.S.

Figure 5.2: (a) FT4 Stability and Variable Flow Rate data for aluminum oxide F1200 grades sourced from Panadyne and Atlantic Equipment Engineers (A.E.E.), and (b) Metallurgical Supplies (M.S.).

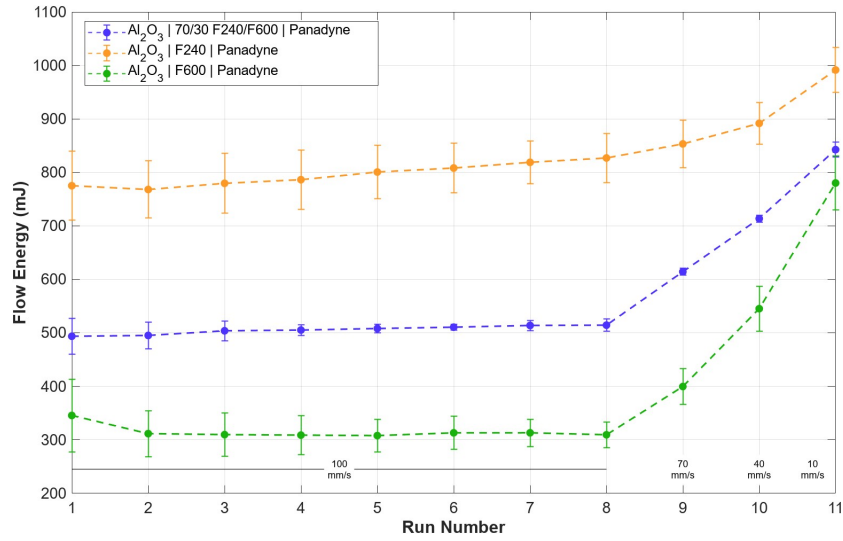


Figure 5.3: FT4 Stability and Variable Flow Rate data for Panadyne aluminum oxide F240, 70/30% mixed F240/F600, and F600 grades.

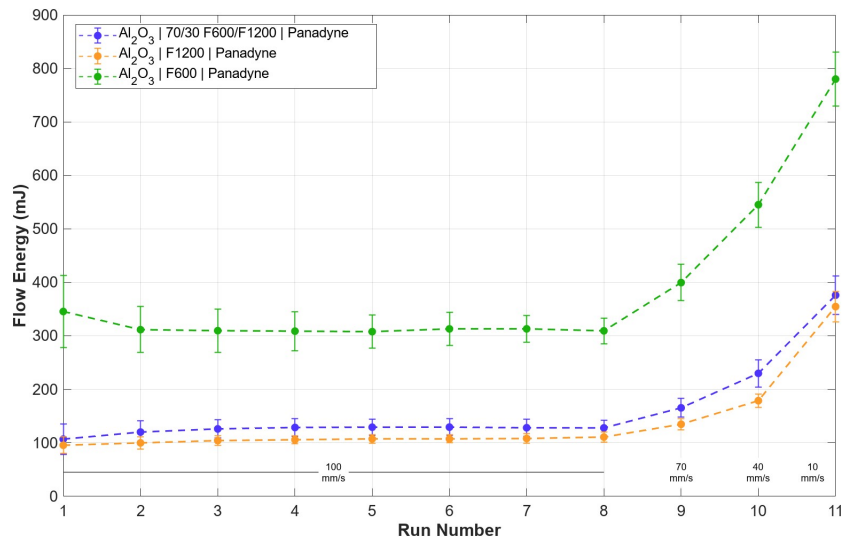


Figure 5.4: FT4 Stability and Variable Flow Rate data for Panadyne aluminum oxide F600, 70/30% mixed F600/F1200, and F1200 grades.

For all tips speeds, the F600/F1200 mixed grade of Al_2O_3 typically required less energy to induce flow than the constituent F600 grade and more, or statistically equivalent, energy than the F1200 grade. This trend was mostly present in the B_4C data for the same three grades. The measured flow energies of B_4C F600/F1200 were less than the energies of its F600 base grade for all tip speeds, excluding 10 mm/s. Unlike the data of Al_2O_3 , none of the measured flow energies for the B_4C F600/F1200 and F1200 grades could be statistically distinguished due to overlapping error. For SiC, only the flow energies of runs 1-9 of the F600/F1200 grade were lower than those of the F600 grade, as run 10 flow energies overlapped in error. Furthermore, the flow energy of run 11 for F600/F1200 was greater than the measured value for F600. Notably, this overlapping and eventual surpassing of measured flow energy in the variable flow rate region for SiC F600/F1200 also occurred for its F240/F600 grade.

Unlike the F240/F600 mixed grades and their components, a clear statement on relative standard deviations of runs 2-8 for the F600/F1200 grades compared to their constituent grades cannot be said with certainty. Comparably, the range of measured flow energies were lower for the F600/F1200 grades and their base grades compared to the F240/F600 grades and their constituents. This may be due to the span of particle size for F240-F600 being greater than that of F600/F1200. The average particle size of F240 is 44.5 μm , 9.3 μm for F600, and 3 μm for F1200.

In the above discussions of the mixed grades above, when looking at relative standard deviations, only those of runs 2-8 were considered. The first reason for this is that all of these runs are conducted at the same tip speed, providing the largest number of comparable samples across powders. Run 1 was excluded despite it being conducted at the same tip speed. Regardless of powder tested, very often run 1 exhibited a higher standard deviation than runs 2-8 and greater/lower average flow energy value than the average value for runs 2-8. This may imply for the affected powders tested that they were not conditioned into a reproducible state from the

onset, only after the first run were they actually conditioned into a reproducible state.

In fact, not all SVFR data were well-behaved. Fig. 5.5 provides one such example, containing ungrouped data from all seven SVFR tests of Panadyne B₄C F240. Each test was conducted with virgin powder, and FT4 parts were cleaned with brushes and dry wipes between tests. Unexpectedly, the measured flow energies increased through test one to test six. Given the odd behavior, a seventh SVFR test of B₄C F240 was ran. Surprisingly, measured flow energies were not only lower, but decreased across runs, seemingly independent of tip speed. With concern the FT4 Rheometer may have been malfunctioning, parts were fully cleaned with isopropyl alcohol and a previously, well-behaved, powder was tested. Its results were in-line with past measured data. This implied that data of, at least, tests 1-6 for B₄C F240 were representative of the powder. As for test seven, it was later discovered during compressibility testing that high memory usage on the FT4 computer can cause it to have issue with applying correct forces, typically occurring if the FT4 Data Analysis Application was also running. Data from the seventh test were excluded from future analysis under the presumption that such an error had occurred.

The increase in flow energies consecutively through tests 1-6 also occurred for Panadyne tungsten carbide (WC) FWC 300 (average size of 25–30 μm), shown in Fig. C.3. Shown in Fig. C.4, measured flow energies also increased across tests 1-6 for Panadyne SiC F240, but decreased for the SiC F240/F600 mix. The SVFR results of SiC F240/F600 were similar to those of B₄C F240 in that one of its tests, its first, flow energies decreased across the runs. However, flow energies did increase across the variable flow rate region (runs 8-11), as would normally be expected. A seventh test was conducted and data from the first test were excluded from future analysis under the previously discussed notion that the FT4 computer encountered memory issues.

Why some tested powders had measured flow energies that increased/decreased consecutively across tests, often appearing to eventually stabilize, is unclear. In the

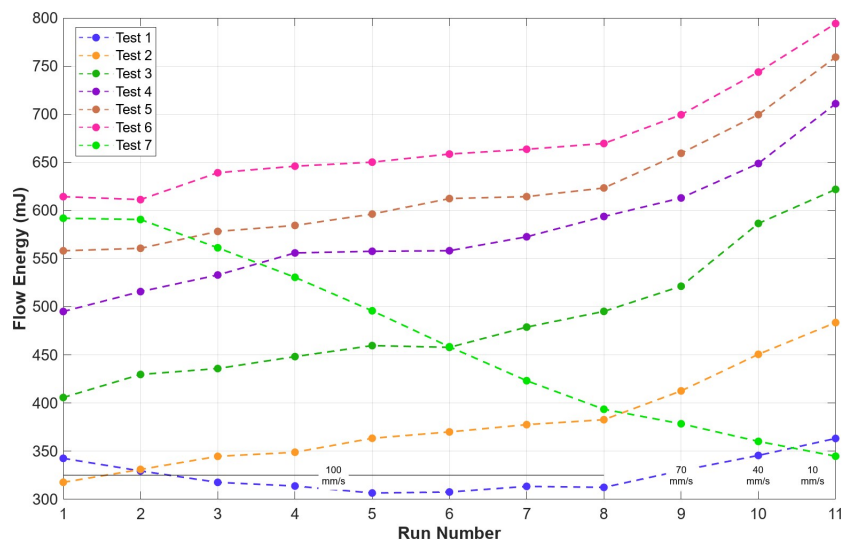
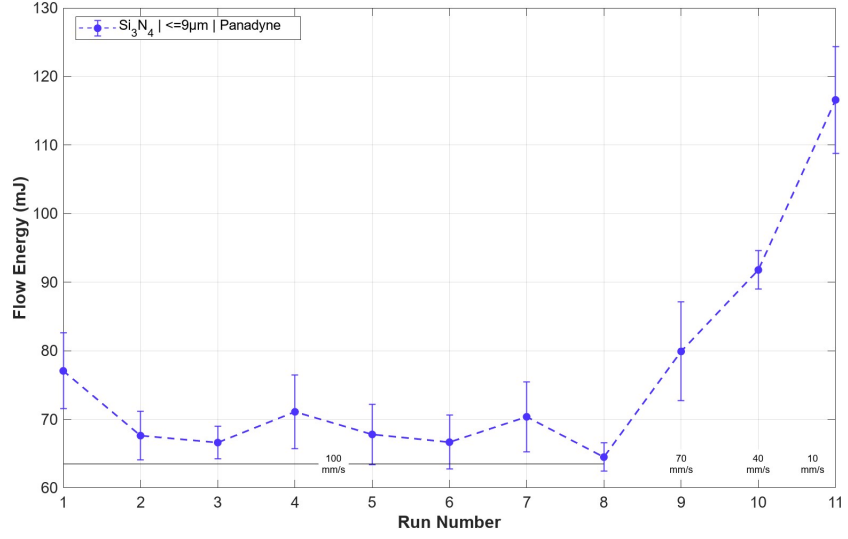


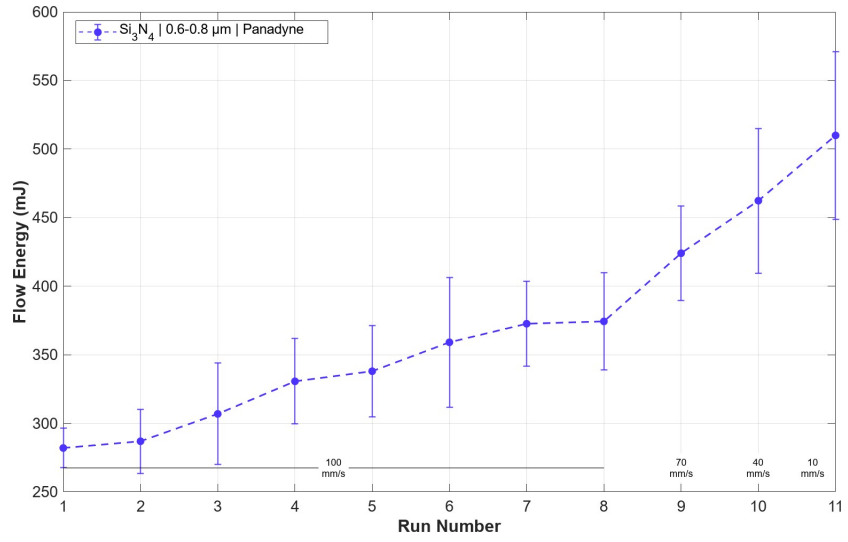
Figure 5.5: Ungrouped FT4 Stability and Variable Flow Rate data for seven separate tests of Panadyne boron carbide F240.

order of testing, described fully in [Methodology](#), powders were first mixed for 5 minutes by use of a TUBRULA and then underwent SVFR testing. For some powders, such as Panadyne SiC F240/F600, it was noted that after blending the bulk volume of the powder in its jar had increased and the powder moved more easily during sampling, or if the jar was slightly tilted. The increased volume and flowability eventually subsided as time passed. This would be a possible cause for increasing/decreasing flow energy measurements across consecutive tests if not for three reasons. The first being that the powders of Panadyne B₄C F240 and WC FWC 300 (both exhibited increasing values), and SiC F240 (decreasing values) did not show any visible changes in bulk volume or flowability after having been blended. Secondly, some powders did not have increasing/decreasing flow energy values through consecutive tests, despite them being noted to have increased bulk volume and flowability after blending. Lastly, if over time measured energy values changed due to relaxation of powder in its load jar, one would expect to see changing flow energy values throughout the stability region of any given SVFR test, as the powder sample undergoes a conditioning cycle per run and tip speed is kept constant. This phenomenon of incrementally changing measurement values through consecutive tests was not noted for any other FT4 test type. Further data collection, and analysis, is necessary to determine if something causes this behavior, if behavior is inherent to certain powders, or if the phenomenon is statistically significant in the first place.

The last SVFR data of some note were those of silicon nitride. Excluding the Panadyne Si₃N₄ grade SiN-B ($\sim$ F1200), the other two grades, SiN-6 (≤ 9 μ m, $\sim$ F600) and SiN-9.5 (average size of 0.6–0.8 μ m), had SVFR data with greater instability and/or uncertainty. [Fig. 5.6](#) shows plots of these data. Both grades exhibited inconsistency in flow energy values through their respective stability regions. This could indicate that these two grades were particularly friable and that measured flow energy values were susceptible to the degree of attrition that may have occurred. Of note, the SiN-B grade, which has a general particle size between those of the two grades shown in [Fig. 5.6](#), did not exhibit such instability.



(a) Panadyne Si₃N₄ SiN-6



(b) Panadyne Si₃N₄ SiN-9.5

Figure 5.6: (a) FT4 Stability and Variable data for Panadyne silicon nitride SiN-6 and (b) SiN-9.5.

Considering that prior comparison of SVFR data for like grades from different vendors implied source could affect SVFR results, it is a possibility that the three Panadyne Si_3N_4 grades were not produced in the same manner, or from the same stock. However, this cannot be said for certain without further testing and analysis.

5.1.2 Compressibility Results and Discussion

The Compressibility test measures the percent change in volume, relative to initial conditioned volume, after consecutively applied stresses of 1, 2, 4, 6, 8, 10, 12, and 15 kPa. An example plot of compressibility data for Panadyne Al_2O_3 F1200 is shown in Fig. 5.7. Error bars represent the standard deviation of six repeated compressibility tests of virgin powder. The dotted line is for visual ease in reading data across the compression cycles. Excluding scale, compressibility data for the majority of powders tested behaved similar to that of the example plot. Error was typically consistent across all applied stresses and did not significantly increase for higher applied stresses. When plotted, data exhibited similar curvature to that seen in the example plot.

Shown in Fig. 5.8 is a plot of compressibility data for Al_2O_3 F1200 grades from Panadyne, Atlantic Equipment Engineers (A.E.E.), and Metallurgical Supplies (M.S.). The compressibility data for the Panadyne and A.E.E. F1200 grades were near in value while the M.S. F1200 data values were distinctly separate; this is similar to the behavior of the SVFR data of these three grades. However, while the SVFR data of M.S. were higher in value than those of the other two grades, the reverse is true for the compressibility data.

Fig. 5.9 and Fig. 5.10 show compressibility data of Panadyne Al_2O_3 F240, F600, and F1200 grades along with 70/30% F240/F600 and F600/F1200 grades mixed in-house. Plots of identical grades for B_4C and SiC may be found in Fig. C.5 and Fig. C.6. All mixed grades, excluding Al_2O_3 F240/F600, had compressibility values that were greater than the values of their larger constituent grade and less than the values of their smaller constituent grade.

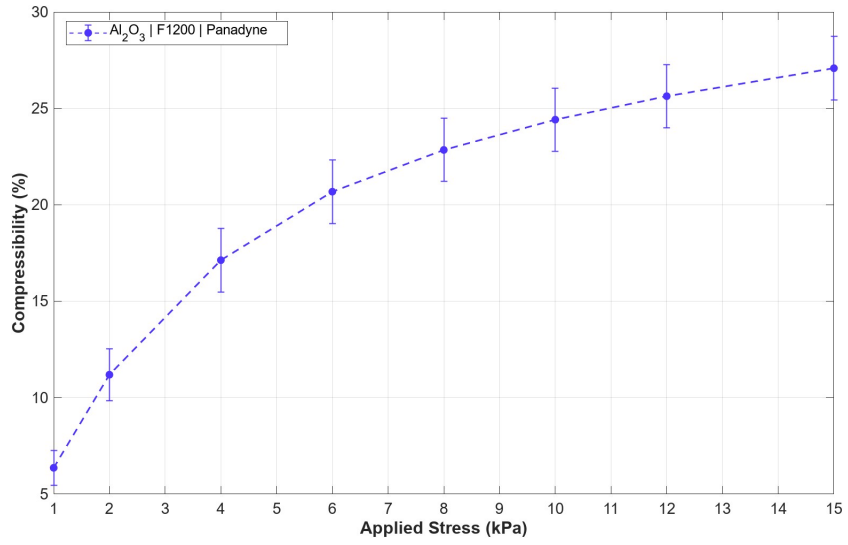


Figure 5.7: FT4 Compressibility data for Panadyne aluminum oxide F1200.

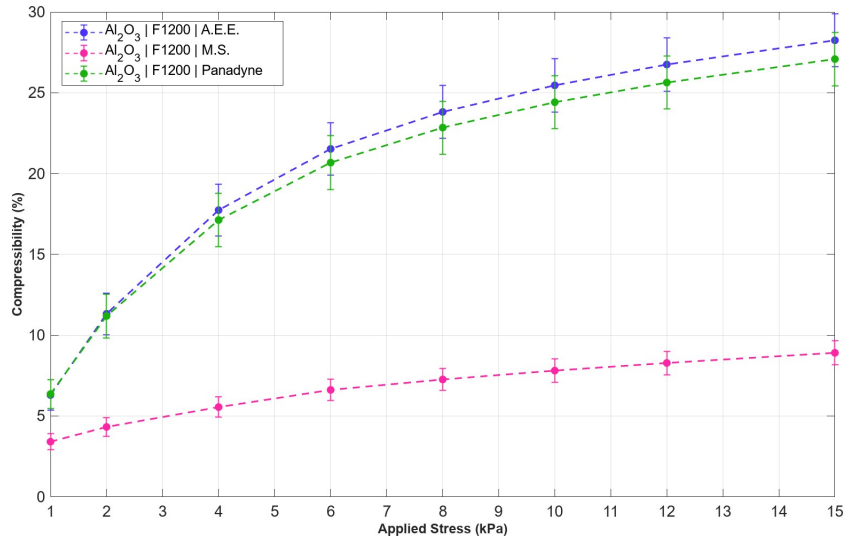


Figure 5.8: FT4 Compressibility data for aluminum oxide F1200 grades sourced from Panadyne, Atlantic Equipment Engineers (A.E.E.), and Metallurgical Supplies (M.S.).

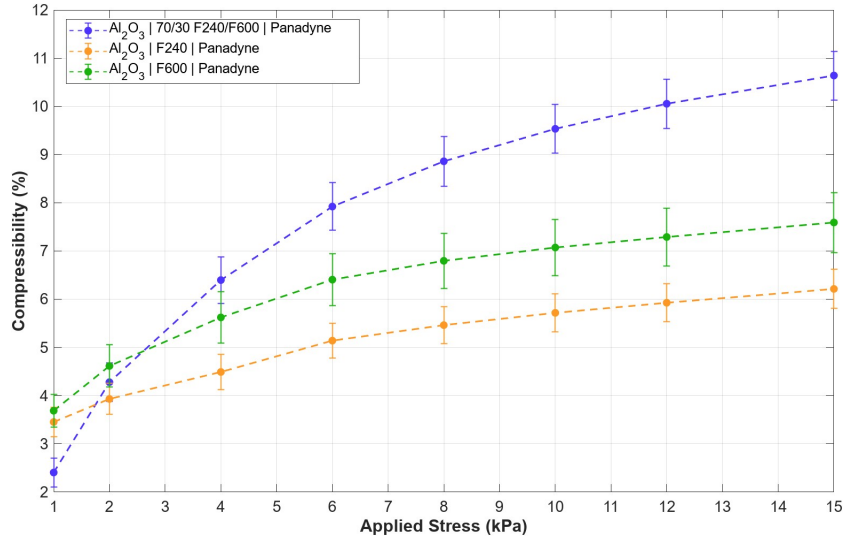


Figure 5.9: FT4 Compressibility data for Panadyne aluminum oxide F240, 70/30% mixed F240/F600, and F600 grades.

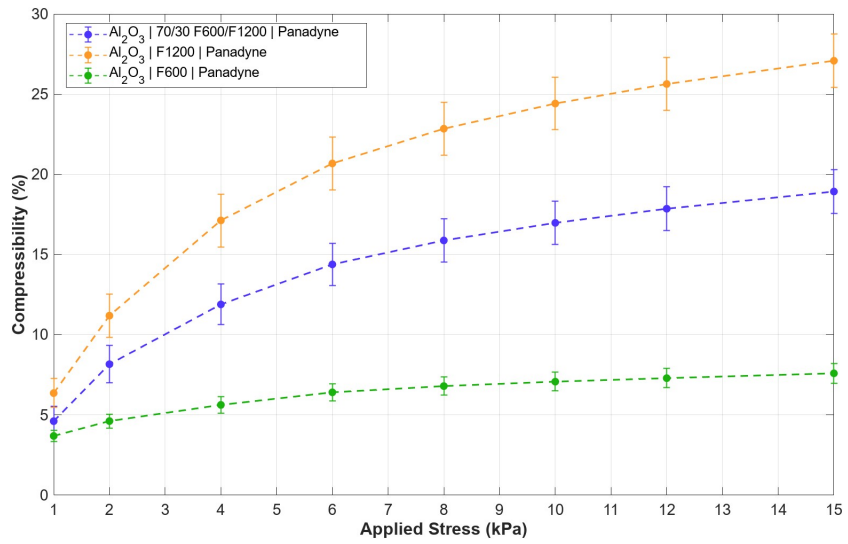


Figure 5.10: FT4 Compressibility data for Panadyne aluminum oxide F600, 70/30% mixed F600/F1200, and F1200 grades.

The increase in overall compressibility of a mixed grade relative to its larger component was expected. The surpassing of base grade compressibilities for Al_2O_3 F240/F600 was not expected. However, this is not an unreasonable result once one considers that mixing coarse and fine powder grades with appropriate ratio can yield greater green and sintered densities than either constituent grade.

Notably though, the relative increases in compressibility values from F240 to F240/F600 to F600 were not the same across the three materials. For most applied stress values, Al_2O_3 F240/F600 exhibited greater percent compressibilities than its base grades. The percent compressibilities of B_4C F240/F600 had values that were roughly halfway between the corresponding values of the F240 and F600 base grades. Lastly, the compressibility values of SiC F240/F600 aligned more closely with those of the F600 base grade. Both Al_2O_3 F600/F1200 and B_4C F600/F1200 had percent compressibility values that were mostly in-between the values of their constituent grades. The F600/F1200 grade of SiC had percent compressibilities closer in value to its larger constituent grade of F600. This was unexpected given that the F240/F600 grade of SiC was more biased towards its smaller grade. The cause for the odd behavior of the compressibility data for the mixed grades of SiC compared to the mixed grades of the other two materials is unclear.

Fig. 5.11 shows compressibility data for all three grades of Si_3N_4 , sourced from Panadyne. Exact grades of F240, F600, and F1200 for Si_3N_4 could not be acquired. Further available information on particle size distributions of the grades shown in Fig. 5.11 may be found in Table B.7. The key takeaway from this plot is that overall compressibility values increased as particle size decreased. For all other powders that had multiple grades tested, the inverse was true, compressibility decreased as particle size increased.

Given that the SVFR data for grades of SiN-6 and SiN-9.5 indicated those powders may be friable, it is a possibility this was reflected in their compressibility data. However, this would not explain the compressibility values of SiN-B as its SVFR data did not indicate friability.

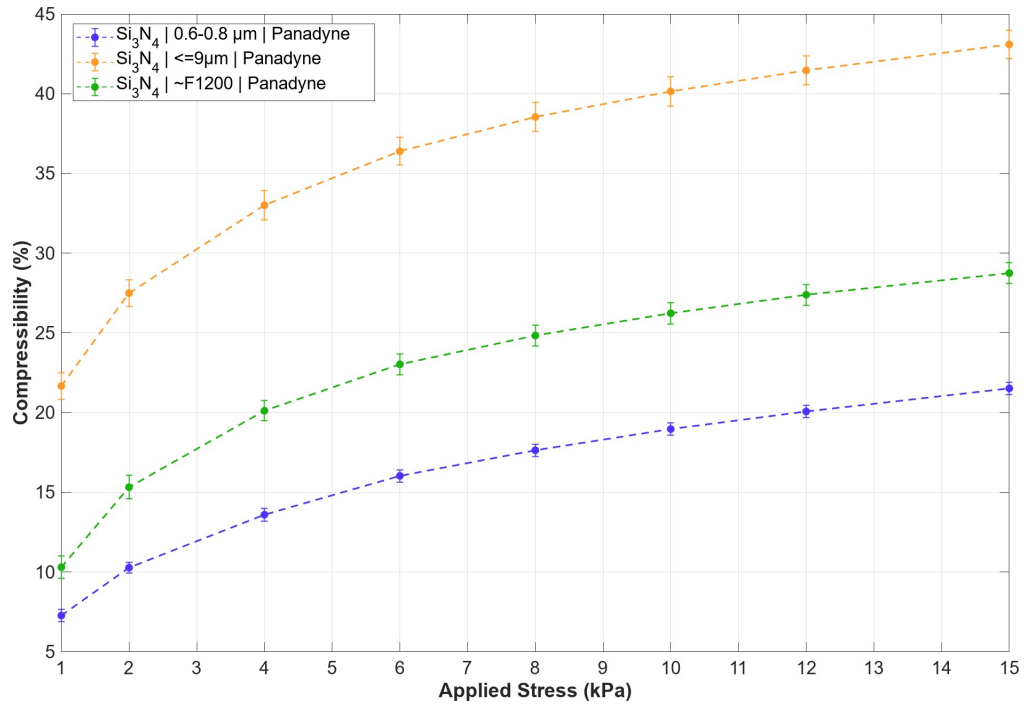


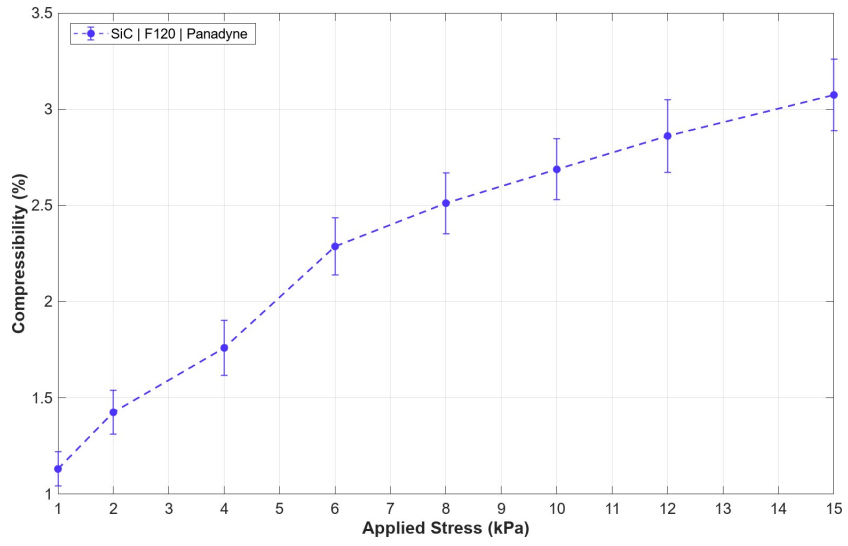
Figure 5.11: FT4 Compressibility data for Panadyne silicon nitride grades of SiN-6 ($\leq 9 \mu\text{m}$), SiN-B ($\sim\text{F1200}$), and SiN-9.5 ($0.6\text{--}0.8 \mu\text{m}$).

Another possible cause could be differences in the span of the particle size distributions of each grade. A larger span would allow for greater compaction as smaller particles could fit in-between larger ones. As exact particle size distribution data could not be collected, this remains a conjecture.

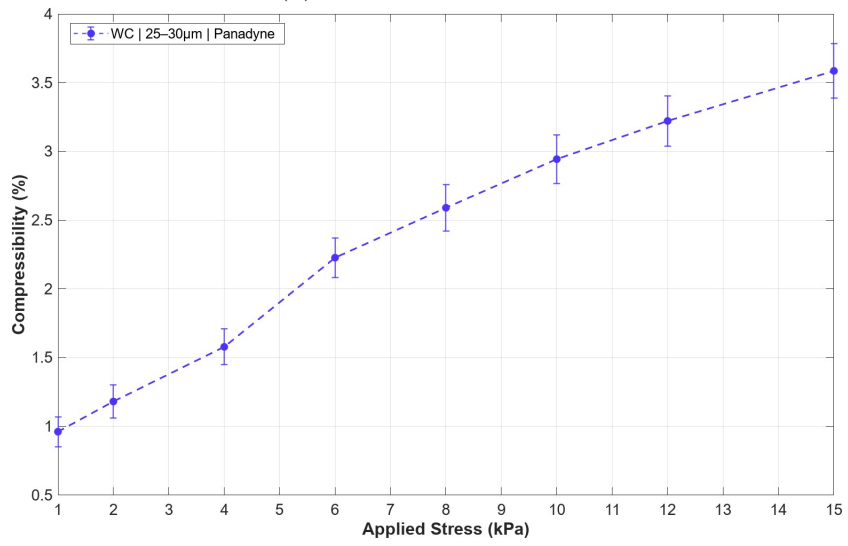
For coarser grades of material, the lack of compressibility and curvature was much more pronounced. Fig. 5.12 shows plots of compressibility data for Panadyne SiC F120 and WC FWC 300. While not shown, the F180 grade of SiC displayed similar behavior to that of the F120 grade. The FWC 300 grade of WC had compressibility data not that different than that of SiC F120. As the general particle size of each grade is not too dissimilar, it is reasonable that the compressibility data of each would be similar, despite coming from different materials with significantly different particle densities.

5.1.3 Shear Cell Results and Discussion

The Shear Cell test measures the shear stress required to induce flow in an initially pre-consolidated powder sample under an applied normal stress. For all shear testing conducted, an initial pre-shear consolidation stress of 15 kPa was used and shear stresses required to induce flow were measured under consecutive normal stresses of 9, 8, 7, 6, and 5 kPa. An example plot of shear cell data for Panadyne Al_2O_3 F1200 is shown in Fig. 5.13. The error bars represent the standard deviation of six repeat tests using virgin powder. Dotted lines are for visual ease in finding data points. Typically, Mohr circle analysis is overlaid on a plot of shear cell data. First, a yield locus is constructed by applying a best fit line to the shear points (5-9 kPa) extrapolated to intercept the y-axis. Then, two Mohr circles are constructed using the yield locus, intercept of the yield locus, and the pre-shear point (15 kPa). Neither a yield locus or Mohr circles are present in the example plot, nor any of the shear cell data plots moving forward as they make reading plots of data from multiple powders difficult. Furthermore, as with other FT4 test data discussed so far, a broad scope is taken.



(a) Panadyne SiC F120



(b) Panadyne WC FWC 300

Figure 5.12: (a) FT4 Compressibility data for Panadyne silicon carbide F120 and (b) tungsten carbide FWC 300.

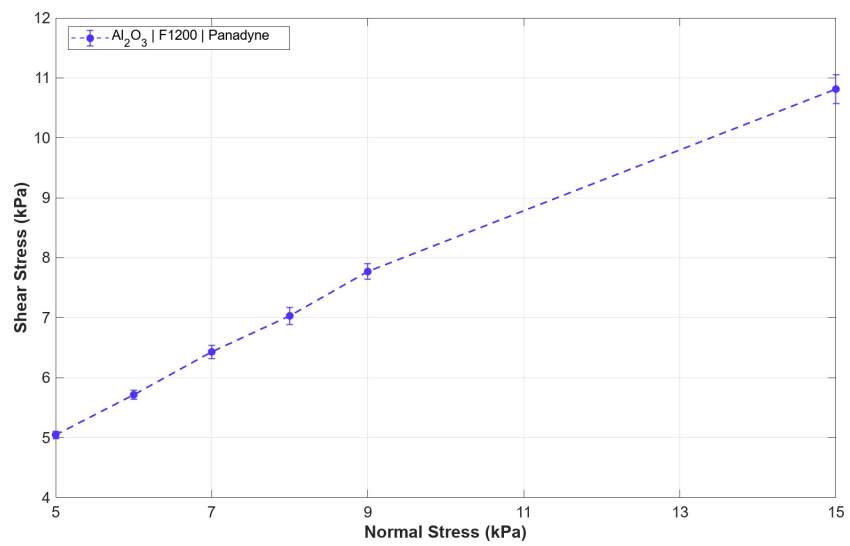


Figure 5.13: FT4 Shear Cell data for Panadyne aluminum oxide F1200.

All rheology tests utilized in this work provide a litany of parameters; Mohr circle analysis itself provides nine parameters. To discuss every parameter for all 25 tested powders in detail would provide little information that could not be better covered more generally in data analysis.

Before the shear cell data collected in this work can be examined, a critical aspect of the FT4 Shear Cell test must be discussed. Not evident in any of the shear cell data plots shown in this work is that shear stress values are normalized and x-axis values of data points are set equal to the values selected during test setup in the FT4 software, i.e., at the 9 kPa normal stress 8.89 kPa may actually be applied, but would be reported as 9 kPa in the raw data and plot. The forcing of measured normal stress values to their selected, integer values is not necessarily problematic as Mohr circle analysis and parameter calculation conducted by the FT4 appeared to use the actual normal stresses measured. For visual clarity in comparing shear cell data, plots herein retain this “forcing” of normal stress values.

As for the normalization, the FT4 scales every measured shear stress value by the average of all five pre-shear stress values divided by each one’s pre-shear stress value. This normalization does affect Mohr circle analysis and calculated parameters. Without this normalization, data typically have much larger spread and parameters are often undefined, unable to be calculated. As such, this scaling was kept on for all shear cell data collected.

What makes these two aspects concerning is that the scaling of data and forcing of normal stress values are done by default. While the scaling of data is discussed in a supplementary document for the FT4 on how to analyze shear cell data, neither aspect is prominently noted anywhere in the FT4 software or operating manuals. In the literature containing FT4 Rheometer shear cell data, one will almost always see normal stress values reported as exact integers. Whether or not other workers are aware that these are not true measured values, and also that measured shear stresses are scaled by default, is unknown.

Shown in Fig. 5.14 is a plot of shear cell data for Al_2O_3 F1200 grades from Panadyne, Atlantic Equipment Engineers (A.E.E.), and Metallurgical Supplies (M.S.). Unlike their SVFR and Compressibility test results, the shear cell data of the Panadyne and A.E.E. grades were not tightly grouped together nor notably offset from the M.S. shear cell values. From this data alone, it would be difficult to determine which of the other two grades that the A.E.E. grade more closely resembled. However, it is readily apparent from these data that three statistically different powders were tested. Overlapping error in SVFR and Compressibility test results of the A.E.E. and Panadyne grades made statistical differentiation of the two difficult.

Shear cell data plots of Panadyne Al_2O_3 F240, F600, and F1200 grades in addition to 70/30% F240/F600 and F600/F1200 grades mixed in-house are given in Fig. 5.15 and Fig. 5.16. Plots of identical grades for B_4C and SiC may be found in Fig. C.7 and Fig. C.8. Excluding Al_2O_3 F240/F600, both mixed grades of all three materials had shear stress values that were greater than the stress values of their larger constituent grade and less than those of their smaller constituent grade.

Overall, there were fewer general trends, or notable outliers, in the shear cell data of tested powders that deserve detailed discussion compared to the SVFR or compressibility data. The WC FWC 300 powder shear cell data did not exhibit high relative error, unlike its SVFR and compressibility counterparts. As for the Si_3N_4 grades, the grade with the lowest shear stress values was SiN-B ($\sim$ F1200), followed by SiN-6 ($\leq 9 \mu\text{m}$, $\sim$ F600), and lastly SiN-9.5 (average size of $0.6\text{--}0.8 \mu\text{m}$) with the highest values. Compared to the trend generally found with grades of differing size of other tested powders, it is interesting that SiN-B had the lowest shear stress values despite it being the middle-sized Si_3N_4 grade.

5.1.4 Direct Pressure Consolidation Results and Discussion

The Direct Pressure Consolidation (DPC) test measures the energy needed to induce flow in a powder sample which has been compacted under an applied stress a set

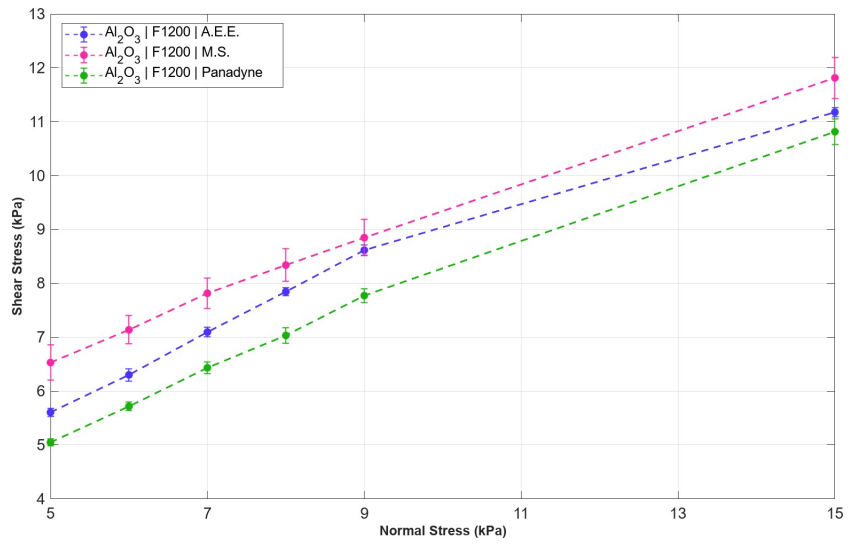


Figure 5.14: FT4 Shear Cell data for aluminum oxide F1200 grades sourced from Panadyne, Atlantic Equipment Engineers (A.E.E.), and Metallurgical Supplies (M.S.).

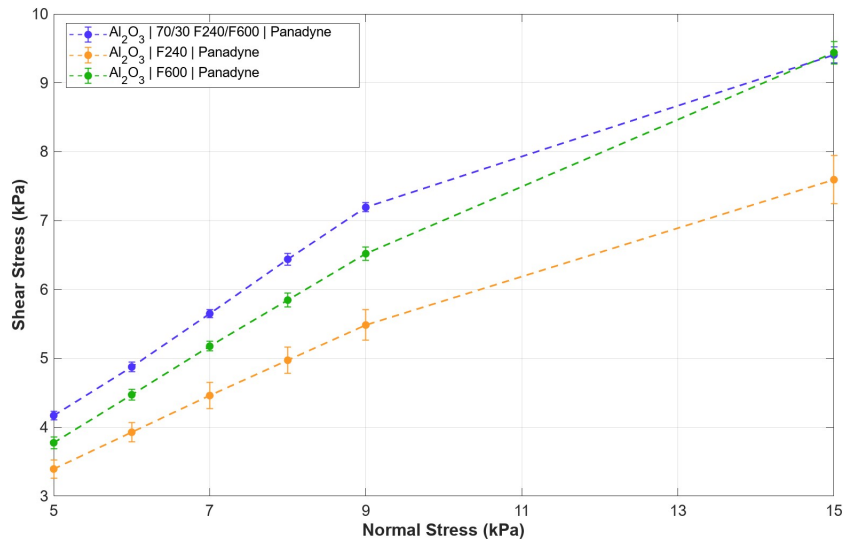


Figure 5.15: FT4 Shear Cell data for Panadyne aluminum oxide F240, 70/30% mixed F240/F600, and F600 grades.

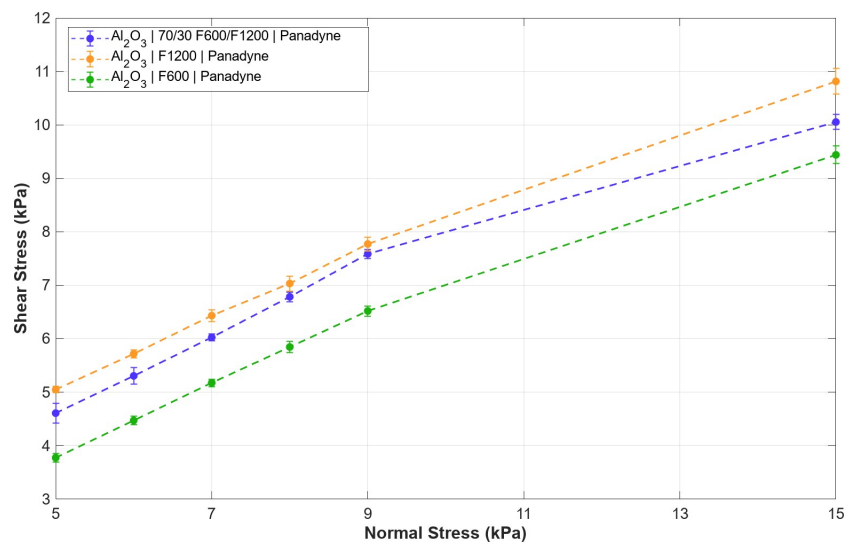


Figure 5.16: FT4 Shear Cell data for Panadyne aluminum oxide F600, 70/30% mixed F600/F1200, and F1200 grades.

number of increments. A detailed description of the testing process, including the same pressure/increment combinations used for every powder and how the number of samples to measure per combination were determined, may be found in [Methodology](#). To reiterate what has been said previously, DPC testing demanded much time. Typically, the time required to collect all SVFR, shear cell, and compressibility data for a powder was equivalent to the time needed to collect its DPC data. Furthermore, no prior work with DPC testing could be found in the literature. Consequently, a broad, exploratory approach was taken with DPC testing. This is reflected in the number of pressure/increment combinations utilized and the number of samples measured.

As DPC data is three-dimensional, all figures herein of plotted DPC data show data of only one powder to reduce visual clutter. An example DPC plot of Panadyne Al₂O₃ F600 DPC data is shown in [Fig. 5.17](#). All DPC plots in this work have identical format to this example plot. Error bars are the standard deviation of, at minimum, two, and at maximum, five repeat measurements of virgin powder. When error bars are not visible, it is because they are visually smaller than the data point (not present in example plot). A 3D surface fit, described in the following chapter, was applied to the data. It allows for quicker comparing of DPC data of different powders. The y-axis, loading fraction, is the reciprocal of the number of increments used for a testing combination. Loading fraction was used as it provides set bounds that were useful in data analysis. Thin, black residual lines were drawn from the surface fit to each data point; a clear example is the data point at a loading fraction of 0.2 and 5 kPa normal stress (leftmost point). Residual line visibility may be obfuscated slightly by error bars for some data points. Data points and parts of error bars that include flow energy values which were greater than surface fit values were opaque relative to it, i.e., they visually appear in front of the fit two-dimensionally. The reverse is true for values less than surface fit values.

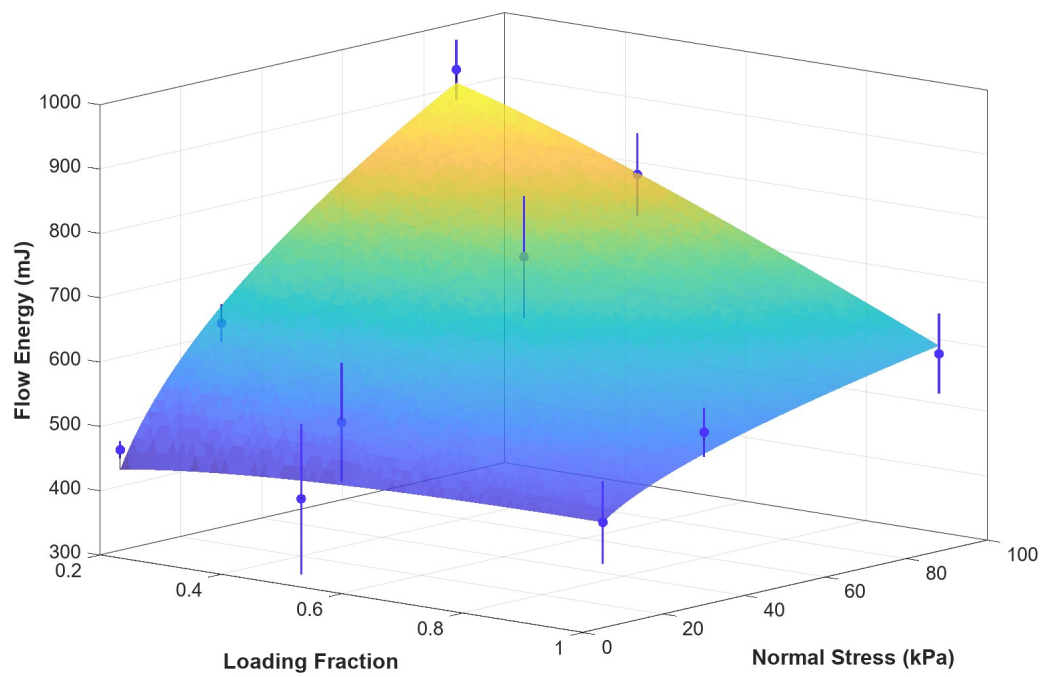
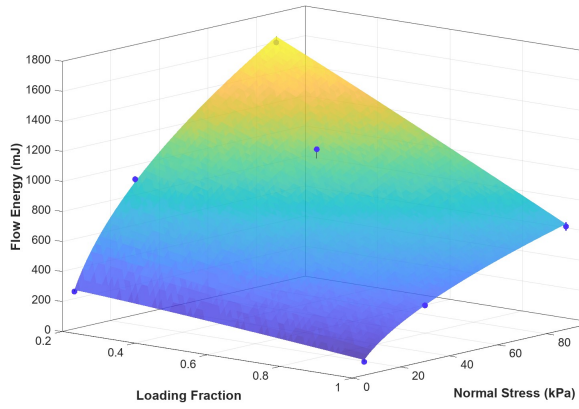


Figure 5.17: FT4 Direct Pressure Consolidation data for Panadyne aluminum oxide F600.

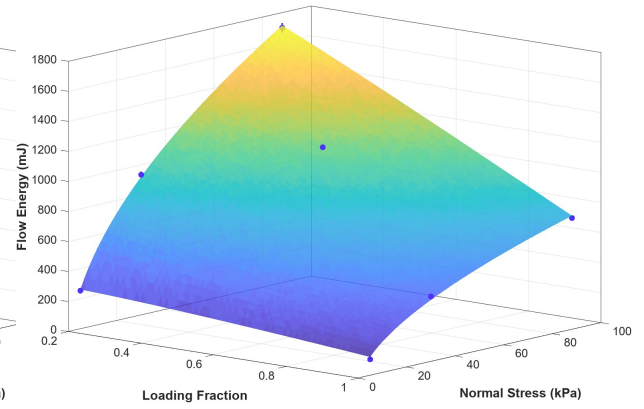
Fig. 5.18 contains DPC data plots of three Al_2O_3 F1200 grades from A.E.E., Panadyne, and M.S. (top left, clockwise). As with the SVFR and compressibility data, DPC data of the A.E.E. and Panadyne grades were similar, while those of the M.S. grade were not. The error on M.S. data points was also larger. Curvature of the surface fit was also different. In fact, the surface fit curvature exhibited in the DPC data plots of the A.E.E. and Panadyne grades was what was generally seen in the surface fits of all powders, excluding a few exceptions. At a loading fraction of 1, corresponding to one increment, flow energies of the M.S. grade did not increase as a function of normal stress, which the flow energies of the other two Al_2O_3 F1200 grades, and almost all other powders, did increase.

One other exception to the increase in flow energy values at a loading fraction of 1 as a function of normal stress were the DPC data of Panadyne Al_2O_3 F240. Plots of its data, and the DPC data of Panadyne Al_2O_3 70/30% F240/F600 mixed grade and F600 grade are given in Fig. 5.19. A trend in these plots found in the DPC data for mixed grades of all materials (plots not provided) is that the flow energy values of a mixed grade were higher than those of its larger constituent grade, and lower than those of its smaller constituent grade. The same general trend was present in the majority of the SVFR, compressibility, and shear cell data of the mixed grades.

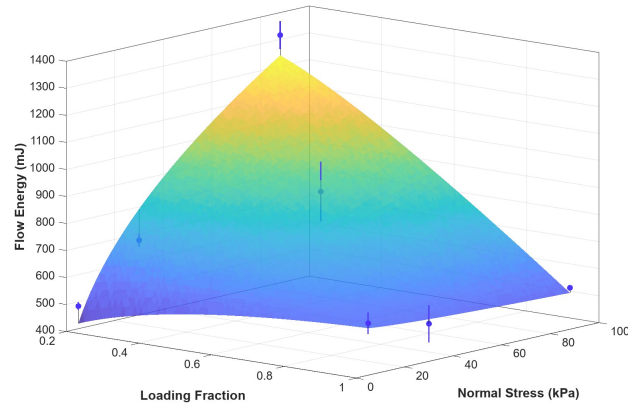
Beyond the powders of Panadyne Al_2O_3 F240 and M.S. Al_2O_3 F1200, the only powders having DPC data which did not strictly follow the general trends common to all other powders were Panadyne B_4C F240 and SiC F120. Fig. 5.20 contains plots of DPC data for each grade. For the B_4C F240 grade, the data point at a loading fraction of 0.2 and normal stress of 20 kPa had a much lower flow energy value than would be expected. Inversely, the flow energy value of the point at a loading fraction of 0.5 and normal stress of 60 kPa was greatly higher than one would expect based on all other DPC data. As for the SiC F120 grade, its testing required the greatest number of samples to be taken, reflected in error bars of its data and the bad surface fit. To note, error generally improved as average particle size decreased across the SiC



(a) Al_2O_3 F1200 A.E.E.



(b) Al_2O_3 F1200 Panadyne



(c) Al_2O_3 F1200 M.S.

Figure 5.18: FT4 Direct Pressure Consolidation data for aluminum oxide F1200 grades sourced from (a) Atlantic Equipment Engineers (A.E.E.), (b) Panadyne, (c) and Metallurgical Supplies (M.S.).

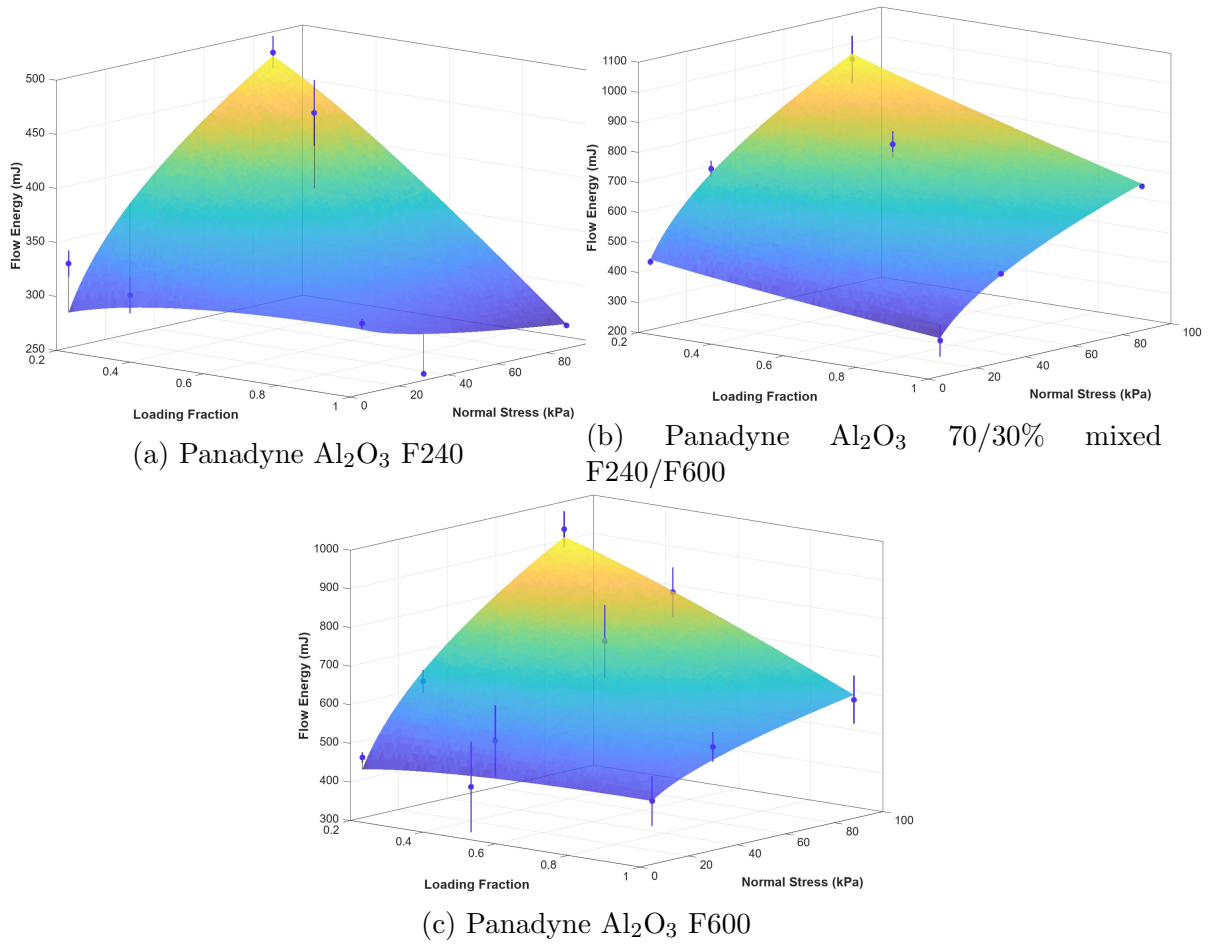
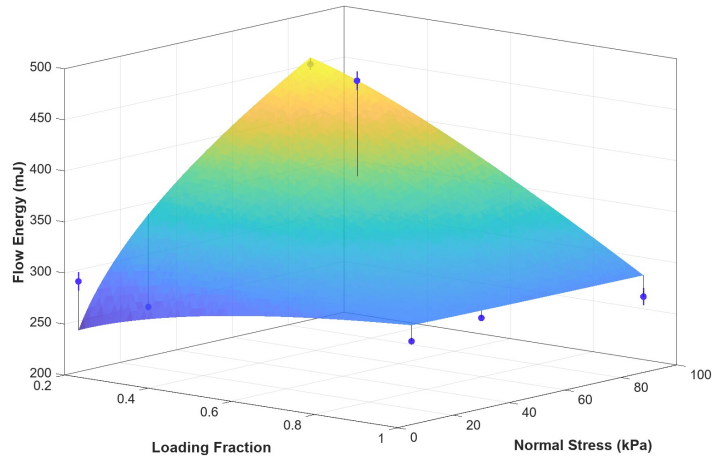
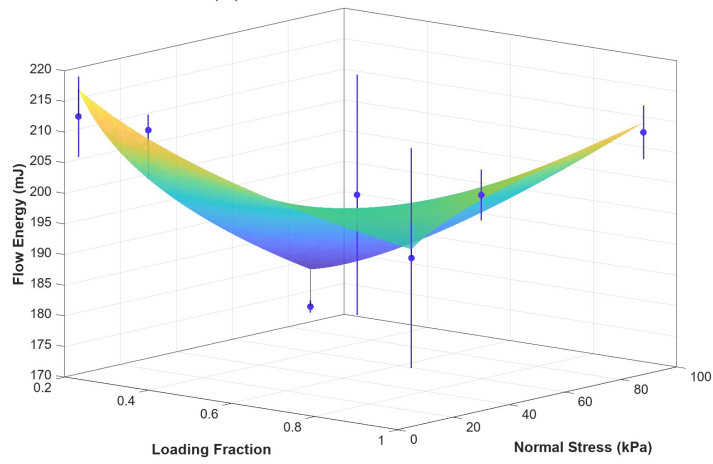


Figure 5.19: FT4 Direct Pressure Consolidation data for (a) Panadyne aluminum oxide F240, (b) 70/30% mixed F240/F600, (c) and F600 grades.



(a) Panadyne B₄C F240



(b) Panadyne SiC F120

Figure 5.20: (a) FT4 Direct Pressure Consolidation data for Panadyne boron carbide F240 and (b) silicon carbide F120.

grades. The F120 grade had an average size of 107.5 μm , the largest of any powder tested, which may be a reason for its anomalous data.

The trend of flow energy values increasing as average particle size decreased did not apply to the three Panadyne Si_3N_4 grades. Plots of their DPC data are not given as they all had similar surface fit curvature and error, the only differences being offsets in overall flow energy values between each grade. Notably, of the three, the SiN-B ($\sim$ F1200) grade had the lowest flow energy values, followed by the larger SiN-6 (≤ 9 μm , $\sim$ F600) grade, and then the smallest grade, SiN-9.5 (average size of 0.6–0.8 μm), with the highest values. This trend for the Si_3N_4 grades was also observed in their compressibility and shear cell data. Just as with those data, it is not clear as to why the Si_3N_4 grades did not follow the general trend of increasing measurement values as particle size decreases observed in the other powders which had multiple grades tested.

5.2 GranuTools Results and Discussion

5.2.1 GranuPack Results and Discussion

The GranuPack provides tapped density values. In addition to many others, the classical parameters of the Hausner Ratio and Carr Index are calculated from tapped density data. An example plot of results from one GranuPack test of Panadyne Al_2O_3 F1200 is shown in Fig. 5.21 below. For every powder tested, three repeated GranuPack tests were conducted using virgin powder. Values and parameters taken/calculated from the data were averaged before use in any analysis. However, as the GranuPack does not condition powder samples into a reproducible state at the start of the test, as the FT4 claims to achieve for its tests, averaging tapped densities across the three tests of a material would not be entirely appropriate. Plotting averaged tapped density data of multiple grades against each other, as has been done for the four previously discussed FT4 tests, is not feasible.

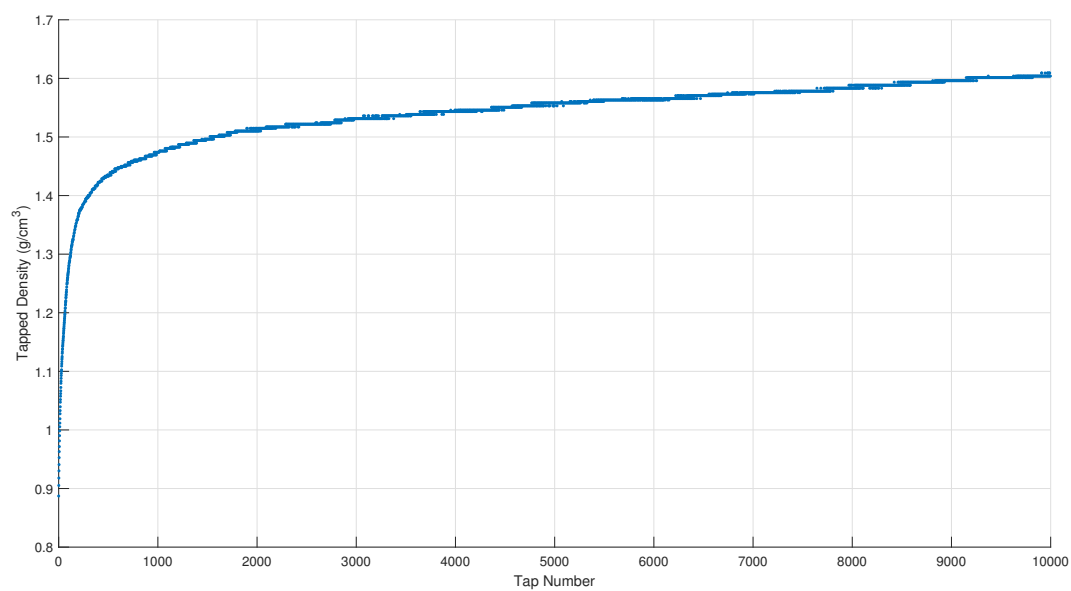


Figure 5.21: GranuPack tapped density data for Panadyne aluminum oxide F1200.

As exemplified in Fig. 5.21, all GranuPack tests were allowed to run for 9999 taps, the maximum number possible in the settings. Traditionally, though, tapped density testing uses 500 taps. However, the ceramic powders tested in this work were unlike those that have the most tapped density information available in the literature, e.g., pharmaceutical and food industry powders. Additionally, the GranuPack test does not need any further interaction once started, allowing for concurrent testing with other equipment. These facts motivated the decision to use 9999 taps, to gain more data which may prove useful.

Throughout GranuPack testing, it was repeatedly observed that 9999 taps did appear to provide more useful data. Fig. 5.22 demonstrates this. It is a close-up of the first 500 taps of tapped density data for Panadyne Al₂O₃ F1200, which was shown with all 9999 taps in the previous figure. From this plot, it appeared that tapped density values would plateau, at least within 1000 further taps. It is not evident from the plot that tapped density values would continuously increase as tap number approached 9999 taps. Yet, this was the case. Every powder tested had an average 9999th tapped density ($\rho_{tap,9999}$) greater than its average 500th tapped density ($\rho_{tap,500}$).

This trend was observed in the ρ_{∞} values at 500 and 9999 taps for the majority of powders. These are the extrapolated tapped densities found from fitting data to Eqn. 5.1, where n is the number of taps, $\rho(n)$ the tapped density of the n th tap, ρ_0 the initial bulk density, and τ a fitting constant. This trend was also noted in the Hausner Ratio and Carr Index values for all powders; however, as each parameter is proportional to final tapped density ($\rho_{tap,9999}$ or $\rho_{tap,500}$) over initial bulk density, this was expected as all $\rho_{tap,500}$ values were less than their $\rho_{tap,9999}$ counterpart.

$$\rho(n) = \rho_{\infty} - \frac{\rho_{\infty} - \rho_0}{1 + \ln\left(1 + \frac{n}{\tau}\right)} \quad (5.1)$$

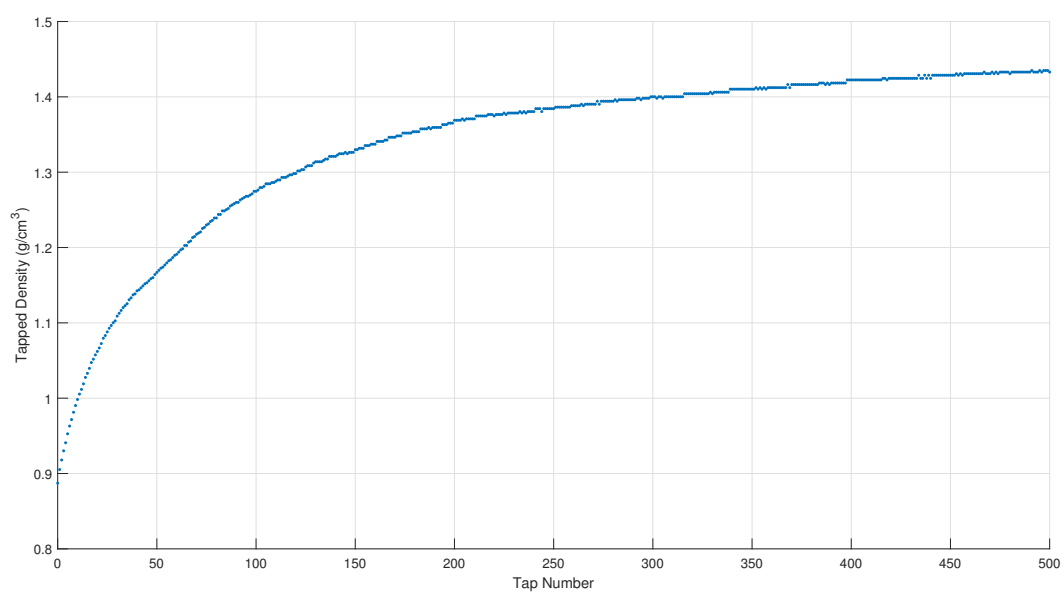


Figure 5.22: First 500 taps of GranuPack tapped density data for Panadyne aluminum oxide F1200.

The remaining parameters provided by the GranuPack not discussed so far are the fitting constant τ , the characteristic tap number $n_{1/2}$ (tap number at which tapped density is one half the final tapped density), and the slope index α (the slope of line passing through the origin and tangent to the curve of the first 10 data points). As with any parameters of an instrument mentioned, analysis of overall data is more prudent than to discuss each parameter in detail on a powder-by-powder basis. However, τ and $n_{1/2}$ must be discussed now as they were removed from future analysis.

Fig. 5.23 below shows the percent relative standard deviations of τ , fitted to 9999 taps, for all 25 materials tested. Overall error across τ values was significant. For τ values fitted using only 500 taps, error was marginally better, but not enough to be reliable for use in analysis. Interestingly, though, error on ρ_∞ values were all reasonable, despite the value having been calculated from the same fit that τ is determined from. This likely arises from the fact that, while the 500th tapped density values of a powder were very close across multiple tests, the rates at which these tapped density values were approached were not always consistent across tests. In Fig. 5.24 is a bar graph of percent relative standard deviations of $n_{1/2}$, calculated from 500 taps, for all materials tested. The error on $n_{1/2}$ values calculated from 9999 taps were slightly better, but still not acceptable for use in analysis. The error in these values may also stem from the same reason of high error prevalence in τ values, the rate of change in tapped density values was not always consistent across tests. In one test, half the final tapped density may have been quickly reached, resulting in a low $n_{1/2}$, and vice versa for the next test.

5.2.2 GranuFlow Results and Discussion

The GranuFlow provides mass flow rate measurements as a function of aperture size. Data are fitted to a modified form of the Beverloo Equation by the instrument software to extract further parameters. A plot of mass flow rate data for Panadyne SiC F120 is

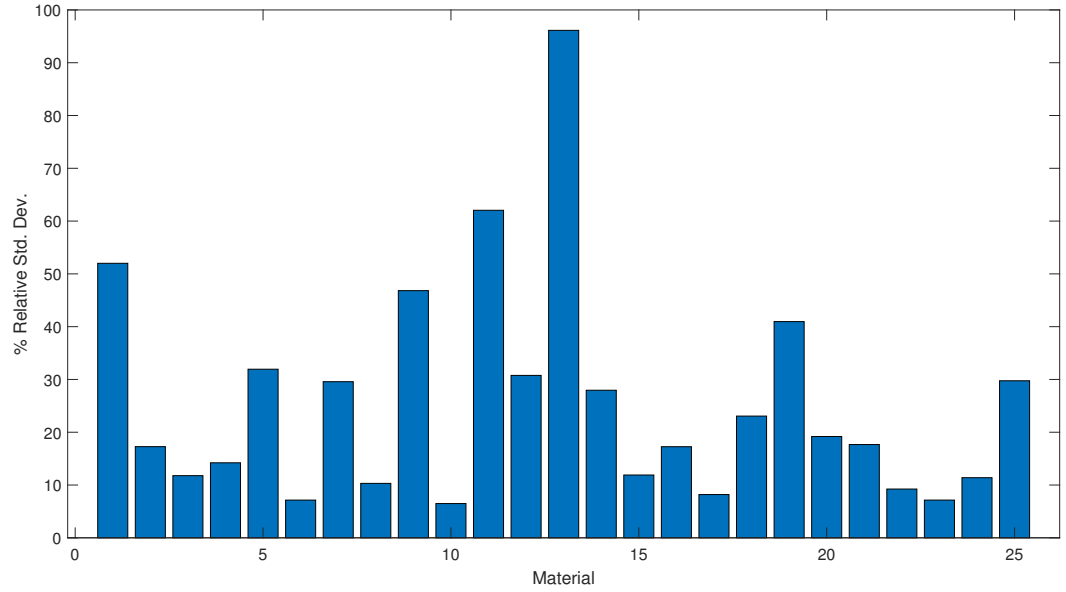


Figure 5.23: Percent relative standard deviations of GranuPack fitting constant τ , fitted to 9999 taps, for all powders tested.

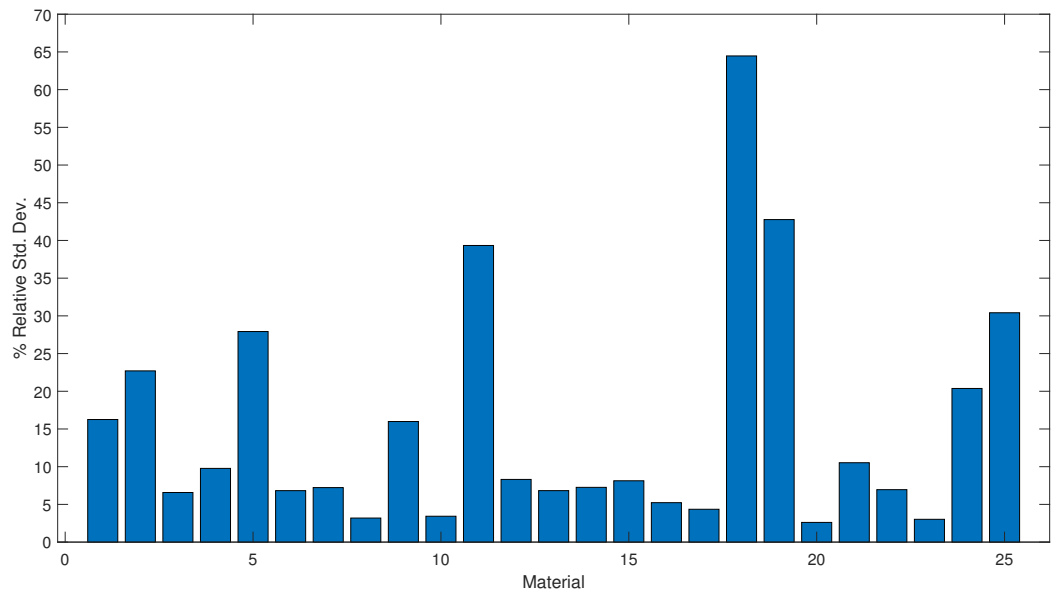


Figure 5.24: Percent relative standard deviations of GranuPack characteristic tap number $n_{1/2}$, calculated from 500 taps, for all powders tested.

shown in Fig. 5.25, exemplifying what fairly well-behaved GranuFlow data looks like. While data were not fitted to the modified Beverloo Equation used by the GranuFlow software, curvature in the data were clearly present, which is expected of mass flow rate data. As can be seen in the plot, no mass flow rate data could be collected for the 30 mm aperture. This issue was not isolated to the Panadyne SiC F120 powder. The cause of this is that the GranuFlow has difficulty collecting data for a fast-flowing powder.

The GranuFlow takes a mass measurement every 0.5 ± 0.1 seconds. This was determined from looking at raw data, it is not mentioned in the manual. For slower flowing powders, this is less of an issue as many data points can be collected. However, if, for example, a powder fully empties into the beaker on the mass scale in two seconds, only four data points may be collected. The time measurement of each data point has a 20% relative uncertainty. Fitting these four points in order to calculate the mass flow rate for the given aperture diameter will not provide a reliable value. This was particularly noticeable with powders which only flowed through larger aperture sizes, as the respective flow rates were inherently high. To be clear, the limiting factor is flow rate, not mass flow rate. Data for highly dense powders may still be possible to collect as long as flow occurs over a sufficient length of time. Although less obvious curvature is present in the data, mass flow rate data of Panadyne WC FWC 300 are shown in Fig. 5.26. This was the only material in which mostly reliable data could be collected for every aperture size. Unfortunately, the inability of the instrument to sufficiently record data for powders which flowed too fast was the smaller of two problems. Frequently, powder would not flow for smaller apertures, or would intermittently in a fashion that prevented accurate measurement, i.e., flow, stop, flow briefly, then fully stop. Combining the limitations imposed by both these issues, the end result was that mass flow rate data were collected for only 7 of the 25 powders used in this work. Mass flow rate data for every aperture diameter could be collected for only one of these powders.

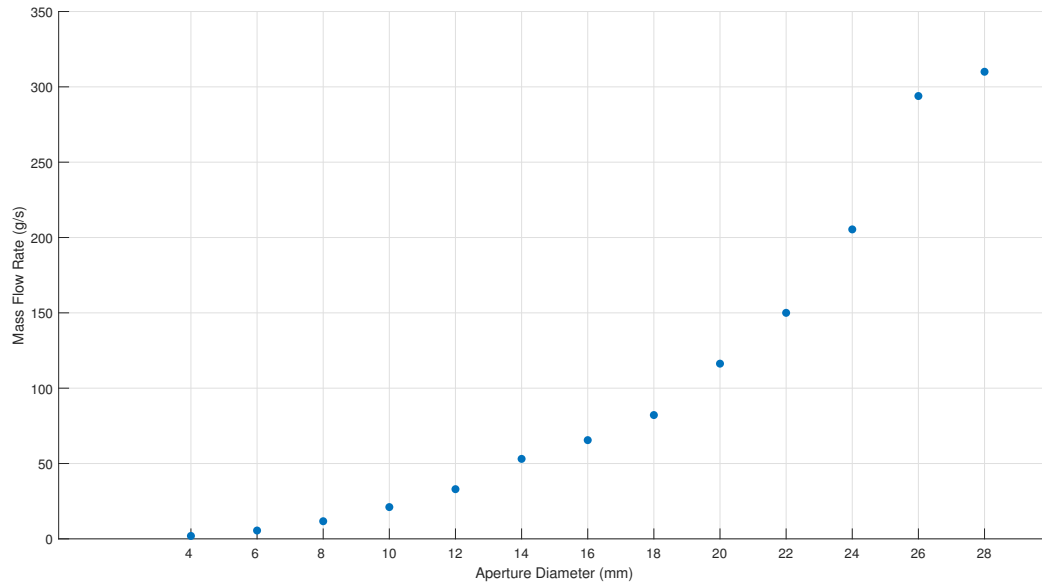


Figure 5.25: GranuFlow mass flow rate data for Panadyne silicon carbide F120.

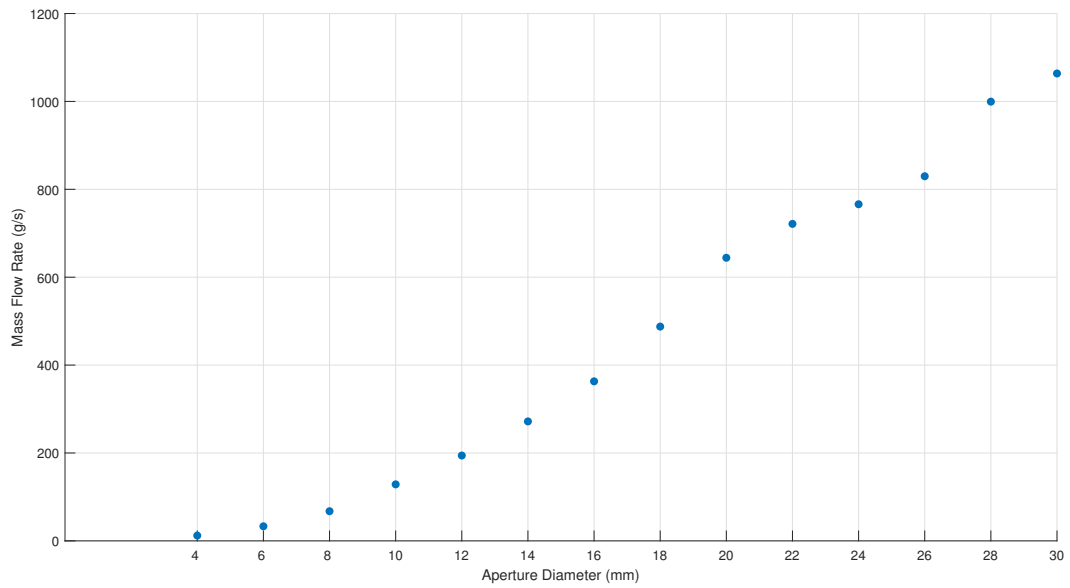


Figure 5.26: GranuFlow mass flow rate data for Panadyne tungsten carbide FWC 300.

Most often, only data for apertures 6-16 or 18-28 could be collected. Due to the lack of data, no GranuFlow data were used in future analysis.

The last topic of note is one of safety. Many powders would aerosolize during flow, often visibly. Simple face PPE (mask, goggles) sufficed in reducing potential hazards. However, this holds true for the micron-sized powders tested in this work, which also were refractory ceramics, having a key attribute of being relatively inert. Regardless of the data collection issues of the instrument, if one wishes to take flowmeter measurements of nano-sized and/or more reactive ceramic powders, an enclosed flowmeter may prove safer than the GranuFlow, at least without the addition of further protective measures like a glovebox.

5.2.3 GranuHeap Results and Discussion

The GranuHeap takes images of a powder heap and uses a computational algorithm to measure various parameters, such as angle of repose and powder height. In a single test, 16 images were taken at incremental angles. The exact testing methodology has been provided in [Methodology](#). Data from nine tests were averaged to calculate parameters for each tested powder. The data for any given powder includes at least 144 images. This limits discourse to discussing only measured/calculated parameters. Which, as argued previously, is far less useful than broad analysis of specific test measurements. Unlike the data generated by the GranuPack, there were no overarching trends in the GranuHeap data to discuss. Lastly, unlike the GranuFlow, there were no prominent issues which affected data collection.

Chapter 6

Analysis of Results

6.1 Creation of New Parameters

In the process of testing, it was often noticed that creating new variables calculated from data, and fits applied to data, could prove to be useful in analysis as additional parameters; or, perhaps, serve as better metrics than some of the variables provided by the FT4 Powder Rheometer. Ultimately, three parameters have been created from FT4 Stability and Variable Flow Rate (SVFR) test data and three parameters associated with a fit to SVFR data, three parameters from fitting FT4 Compressibility test data, and four parameters from fitting FT4 Direct Pressure Consolidation (DPC) test data. Additionally, the seven pressure/increment combinations used in DPC testing, and their respective measurement values, could not be found in any other work in the literature at the time of writing; in fact, no discussion of DPC testing could be found. The mentioned parameters, fits, and novel measurements are discussed in this section before analysis of results is presented. Lastly, [Appendix C](#) contains tables listing all parameters used in analysis for ease of reference.

6.1.1 Stability and Variable Flow Rate Parameters

For the SVFR test, three parameters were created using the base data provided by the test and three associated with a fit of data. The shortened names of these parameters as used in figures in this chapter, their descriptions, and shortened names and descriptions of the parameters provided by the FT4 are listed in [Table C.1](#) in [Appendix C](#) for referencing convenience. To note, the first entry in this table is d_{50} ,

the 50th percentile particle size in microns. Due to lab restraints, no particle size distribution data could be collected, only data (d_{50}) from Certificates of Analysis were available. For lack of a better category, these data were grouped with SVFR data in all figures.

The first of the three SVFR parameters is normalized basic flowability energy (NBFE). It is given by basic flowability energy divided by split mass. This parameter accounts for density and bulk density of materials. NBFE has been used in other works focused on powder rheology and has been shown to provide some use for comparing powders. However, its utility relative to BFE has not been explored for the types of ceramic powders used in this work.

The second parameter is an adjusted stability index (SI_{adj}). The Stability Index (SI) as provided by the FT4 is calculated by dividing flow energy of cycle 7 by the cycle 1 flow energy. Slightly shifted, cycles 8 and 2 are instead used for SI_{adj}. To note, cycles 1-8 are all conducted at a tip speed of 100 mm/s. The FT4 likely uses cycle 7 instead of 8 as the Stability test it offers uses only seven measurement cycles. The separate Variable Flow Rate test uses four cycles. It is likely in the combined SVFR test that the calculation for SI relies on the code used for the Stability test. However, it is reasonable to think that using flow energy of the highest cycle at a 100 mm/s tip speed would lend more weight to calculating how stable a powder is. Lastly, as mentioned in [Results and Discussion](#), it was noted that flow energies of cycle 1 often were not near in value of the average flow energy of cycles 2-8 and also exhibited higher standard deviations than those of the other cycles. This is despite the fact that conditioning occurred before every cycle. It is possible that this is not reflective of overall stability, but simply that a powder is not always "truly conditioned" until at least one cycle has occurred. For these reasons, it was felt that using cycle 2 instead of cycle 1 may be better.

In fact, excluding the first cycle, one would expect a powder to display similar flow energy values for all cycles done at a tip speed of 100 mm/s, not just two of them. An ideal stable powder would not have its measured flow energy rely on the number of

cycles conducted (for a given tip speed). The third parameter, named Stability, is an attempt to better reflect this. It is the percent relative uncertainty of flow energies of cycles 2-8, the first cycle excluded for the reasons given above. An additional benefit of this calculation is that it is less biased by a single flow energy deviation. Unlike SI and SI_{adj}, if one cycle has an abnormally high standard deviation, the overall calculation is less influenced by it.

The other three parameters originate from applying a weighted least-squares power fit, given in Eqn. 6.1 below, to SVFR data.

$$ax^b \tag{6.1}$$

When applying this fit, data of cycles 1-8 (tip speed of 100 mm/s) were averaged together as one point, and remaining data points of flow energy measured at 70, 40, and finally 10 mm/s were used. Data were fitted as a function of increasing tip speed, correspondingly decreasing measured flow energy. Fit parameters a and b were taken from fits applied to every SVFR dataset to use as parameters for further analysis. The motivation for this was to explore if a smaller number of parameters could accurately reflect all information provided by SVFR data for a powder, instead of using BFE, SI, Specific Energy, Friability, and/or other calculated parameters not natively provided by the FT4. Along these lines, the R-squared values of fits were also included as a parameter with the intent to hopefully capture the same information that stability-related variables might capture. This does assume that SVFR data inherently abide by a power law relationship. However, there is some credence to this assumption as well-behaved SVFR data appear to abide by this law, be it of powders in this work, of tested powders found in the literature, or of the powders presented in FT4 manuals.

6.1.2 Compressibility Parameters

Relative to the SVFR test, the Compressibility test offers far fewer parameters to explore. Respectively, this makes comparison of compressibility data of different

powders more difficult as there are no simple parameters to quickly compare. However, the test does provide percent compressibility data points for multiple applied normal stresses. While looking at these data of tested powders, it was noticed that the percent compressibility measured at the final applied normal stress, 15 kPa, might be a useful metric to use as it sufficiently varied across different powders. This parameter is designated as "CPS.15kPa" in all figures presented in this chapter.

Beyond this, a fit was applied to compressibility data. A weighted least-squares log fit, shown in Eqn. 6.2 below, was used.

$$a + b \log x \tag{6.2}$$

Similar to the fit applied to SVFR data, the fitting parameters a and b were taken from fits for use as variables in analysis. Unlike SVFR fitting, the intent was an attempt to condense information provided by all data of a Compressibility test into singular parameters, not to reduce the total number of parameters. The R-squared values of fits were also included as a parameter. This assumes compressibility data are accurately described by a weighted logarithmic fit, regardless of powder tested. All of the parameters described in this subsection are listed in Table C.2 in [Appendix C](#)) for reference.

6.1.3 Direct Pressure Consolidation Parameters

At the time of writing, other works using DPC testing could not be found. How important any of the measurements provided by it were unknown. While the FT4 does have a manual associated with the test, it does not provide any recommendations as to which pressure/increment combinations to use. Given the overwhelming lack of information on utility, and even use, of DPC testing, all pressure/increment combination values were included as parameters in analysis. There were seven combinations, ranging from 1 increment with 5 kPa applied normal stress to 5

increments compressed under 88 kPa. Specific details on DPC testing methodology have been given in [Methodology](#).

As was seen in DPC plots in the previous chapter, [Results and Discussion](#), 3D least-squares surface fits were applied to DPC data. The exact fitting equation used for all DPC flow energy data is given in Eqn.6.3 below.

$$a\sqrt{x} + b\sqrt{y} + cx\sqrt{y} + d \quad (6.3)$$

In the above equation, a - d are fitting parameters, loading fraction (reciprocal of number of increments) is given by x , and y is the applied normal stress in kPa. Fit coefficients were used in analysis as parameters just like the fit coefficients used in SVFR or compressibility data fitting. Similarly, the R-squared values of DPC fits were also used. Why, specifically, the fitting equation shown above was used to fit DPC data is argued below.

To begin, loading fraction was used instead of number of increments for modelling purposes. It provided set bounds ($0 < x \leq 1$), whereas the upper bound for number of increments is not limited. The utility of loading fraction extends beyond modelling purposes too. By having normalized boundaries, future DPC data which could include data points at increments not used can be more easily compared to existing data.

The DPC test is similar to the SVFR test in that it measures energy required to induce flow. It is therefore reasonable to expect that in the hypothetical DPC test of a powder using one increment and no applied normal stress, the measured flow energy would be proportional to the flow energies that would be measured in an SVFR test of the same material. This could be captured in a term which is a function of loading fraction only. However, doing so would couple together the rate at which flow energy increases as a function of loading fraction and any inherent differences between powders. To elaborate, in the prior discussion of SVFR results, in [Results and Discussion](#), it was noted that flow energy values of grades of identical material were proportional to average particle size of the grade. The same could be

said for compressibility data. Based on this, it was believed that using a single fitting constant (d) to describe DPC flow energy when a single increment was used without compression would be most appropriate.

As for the first term in the fit equation, taking the loading fraction value to a power greater than one did not seem appropriate. From the DPC data collected for the 25 powders tested in this work, flow energy was noted to increase as number of increments used increased, or respectively as loading fraction decreased. Because curvature was also exhibited, there was no reason to think that a simple term of $a \cdot x$ could sufficiently describe observed behavior. Similarly, taking the reciprocal of loading fraction, or taking it to a negative power, also did not seem like it would accurately reflect behavior. While flow energy does increase as loading fraction decreases, one would not expect this to occur indefinitely. For an infinitely small loading fraction, it is illogical to think an infinitely large flow energy would result. Self-limiting linear terms, like $a \cdot \log(x)$ or $a \cdot x^n$ where $0 < n \leq 1$, were left as the primary contenders.

A self-limiting term for normal stress also made sense. As normal stress increases, so will particle rearrangement and elastic deformation. Eventually, these two effects will plateau as plastic deformation increasingly occurs. Yet, this too, will ultimately plateau. From this it was reasoned that a self-limiting term for normal stress should be used, e.g., log, reciprocal, or roots. However, as applied normal stress could theoretically be zero, as it is for SVFR testing, the use of a root was thought to be the most appropriate of possible terms.

Two-way Analysis of Variation, ANOVA, was used to determine if an interaction effect between number of increments (inversely loading fraction) and applied normal stress might exist, therefore determining if an interaction term would be appropriate to include in the fit. Overwhelmingly, p-values of DPC data of tested powders were consistently less than 0.05, signifying an interaction effect was likely to exist. Based on this, an interaction term was added to the fit. Of the possible forms to use, it was decided that a term of the form $x \cdot f(y)$ would be best as applied normal stress

appeared to influence flow energy more than loading fraction based on collected data. Furthermore, the range of normal stress values is unbounded, whereas loading fraction is bounded. For the same reasons argued in the previous paragraph, a self-limiting function, specifically a root, was thought to be the most appropriate function to apply to normal stress in the interaction term.

Common to all of the fit terms, excluding the constant, is that they were determined to require a function of the form of a logarithm or root. Because only one term could have a logarithmic form, it made most sense to use a sum of roots for consistency across all terms. A square root was used for every term, for lack of any specific root values to use for each term. This final fit was applied to the DPC datasets of all 25 tested powders. R-squared values of fits were 0.99 for 12 of the 25 powders, less than 0.95 for 6 of the powders, and less than 0.90 for only 3 of the tested powders.

Finally, it must be directly stressed that the fitting equation applied to DPC data was empirically and deductively determined. There is no known theoretical basis, or derivation from first principals, to it. However, it did accurately represent DPC data of the powders used in this work, which contained five ceramic materials of differing chemical composition and multiple grades of varying size. Whether this would extend to any ceramic powder of similar material and size to those used herein, ceramic powders of differing chemical composition or size, or to non-ceramic powders, can only be determined with further testing and analysis.

6.1.4 GranuTools Parameters

Covered in [Results and Discussion](#), data from the GranuTools GranuFlow were not included in analysis as a sufficient amount could not be collected. Enough data to conduct analysis were collected for the GranuPack and GranuHeap. Unlike the tests discussed previously, no truly novel parameters were created from GranuPack

or GranuHeap data. However, some parameters were included in analysis which were not found to have been used in relevant literature.

In the discussion of GranuPack data it was noted that 9999 taps of tapped density data appeared to capture more information than 500 taps did. That is, plots of 500 taps for powders often appeared as if tapped density would plateau, at least within another 1000 taps; however, plots of 9999 taps worth of data demonstrated this was frequently not the case. To further explore this, additional parameters were added that were extended versions of traditional parameters, e.g., the Hausner Ratio for 9999 taps, in addition to the same parameter for the traditional number of 500 taps. These, and all other GranuPack parameters included in analysis, are listed in Table C.5 in [Appendix C](#) for reference.

The three primary parameters provided by the GranuHeap are Angle of Repose (AOR), height of the powder heap, and the Cohesive Index (CI), also called static cohesive index in some GranuHeap documents. One other parameter is directly provided by the GranuHeap software the static angle of repose. This parameter was excluded; consistently the average static angle of repose value had a relative standard deviation within the span of 50-100%, regardless of powder tested. However, other values are measured/calculated in the GranuHeap test, but can only be found in raw data files. They are not shown in the data viewer software associated with the instrument. It was clear that some of the values would provide no analytical use.

However, some values notably varied across tested powders, indicating they might capture information on a powder that was not fully captured by the three primary parameters. These values found in raw data files were "isoh", "AreaAbove", and "AreaBelow." The first is the height of the isosceles triangle projected onto the powder heap. For any given powder, "AreaAbove" and "AreaBelow" were near in value, but would vary across different tested powders. What each value corresponds to, though, is unclear. Nonetheless, they were included in analysis as their data were collected and there was some indication that they could provide analytical utility. All GranuHeap parameters used in analysis are listed in Table C.6 in [Appendix C](#) for reference.

6.2 Correlative Analysis

One primary objective of this work was to elucidate how rheological measurements of ceramic powders may relate to one another. Specifically, for ceramic powders used for grinding media and crucibles, not those often used in the pharmaceutical and food sciences which have received considerably more study on their rheological characteristics. Consequently, a broad study like this, having used a wide range of ceramic powders and rheology tests, is not conducive to seeking causal relationships. Instead, examination of correlative relationships is more appropriate, which also has the benefit of providing a foundation for which future workers could expand upon.

This section explores correlations between parameters originating from one test and correlations between parameters originating from different tests. Parameters shown in correlation heatmaps have been provided in [Appendix C](#) with short descriptions for reference, if needed. All data from all materials/grades of powder were used for calculating correlation values. In presented correlation heatmaps, a significance cut-off level of 95% was used. Only correlations which had a p-value less than or equal to 0.05 are shown. Insignificant correlations were whited-out and their calculated values not provided.

6.2.1 Single Test Correlations

Fig. [6.1](#) is a correlation heatmap of the parameters provided by the FT4 SVFR test, along with d_{50} , the 50th percentile particle size. The largest positive correlation, with a value of 0.90, was between BFE and CBD_SVFR. This was the only base SVFR parameter that CBD_SVFR correlated with. Notably, SI and FRI are calculated by dividing two flow energy measurements, and calculation of SE requires division by split mass. Assuming powder density was a factor in measured flow energy, these three values would be independent from said factor. However, BFE, which is the flow energy measured during the seventh cycle, would not be expected to be independent of powder density. Considering that NBFEE did not significantly correlate

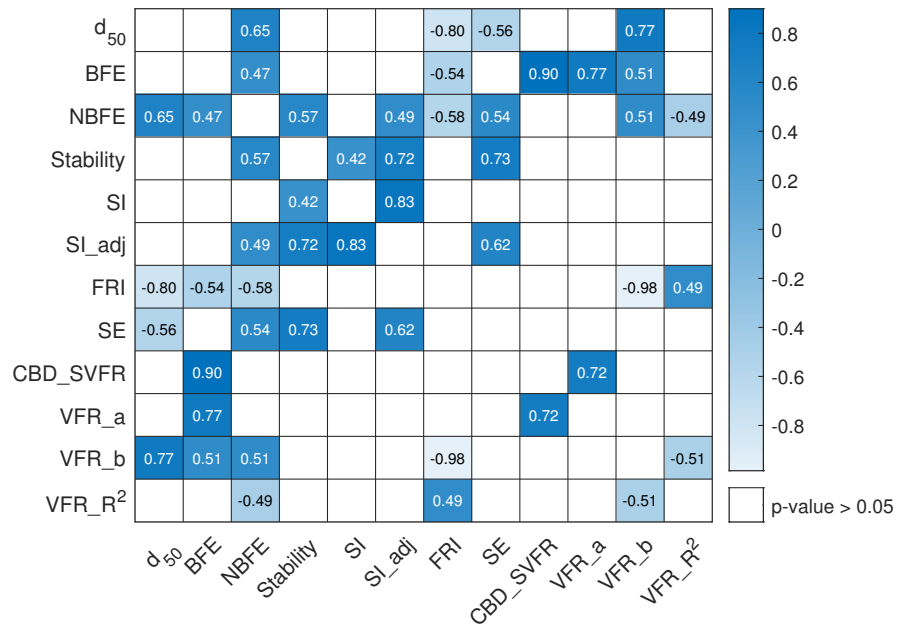


Figure 6.1: Correlation heatmap of FT4 Stability and Variable Flow Rate test and associated parameters. All parameters described in Table C.1.

with CBD_SVFR, it is likely that the correlation between CBD_SVFR and BFE could stem from the fact that BFE is not independent of mass/conditioned density. The fitting parameter VFR_a may capture some information related to powder density, as it only correlated with BFE and CBD_SVFR.

The largest negative correlations were -0.98 between VFR_b and FRI and -0.80 between d_{50} and FRI. Correspondingly, d_{50} had a positive correlation with VFR_b, as would be expected. The relationship between FRI and VFR_b was not a surprise. Higher values of FRI indicate a powder requires exponentially more energy to induce flow as a function of decreasing tip speed. Inversely, as data were fitted as a function of increasing tip speed (correspondingly decreasing measured flow energy), VFR_b should decrease. This does not help determine what power, or if a constant value regardless of powder tested, should be used for fitting, but does give evidence towards a non-linear function being appropriate for fitting data.

SI and SI_adj had a strong positive correlation. However, SI_adj correlated with Stability more strongly than SI did. This was anticipated based on prior observations. Of all measurement cycles conducted at a tip speed of 100 m/s, the first cycle typically exhibited greater uncertainty on its measurement relative to those of the other cycles. Because Stability and SI_adj did not include measurements of a first cycle in their calculations, they were subjected to less variation. Along these lines, Stability and SI_adj shared the same correlations, i.e., if Stability positively correlated with another variable, so did SI.

Notably, VFR_R^2 did not correlate with Stability, SI, or SI_adj. Neither it, or VFR_a or VFR_b, significantly correlated with SE. These four variables, Stability, SI, SI_adj, and SE, are all taken/calculated from measurements collected in the stability regime: cycles 1-8 of the SVFR test. Between all three VFR fit parameters, correlations with all dynamic test variables (BFE, NBFE, and FRI) were found. From these data and analysis, it would appear that the VFR fit captures information relating to the bulk density, particle size, and propensity to require further energy at slower tip speeds of a powder, but fails to describe the inherent stability of a powder.

Shown in Fig. 6.2 is a correlation heatmap of the parameters provided by the FT4 Compressibility test. The two fit parameters, C_a and C_b, were taken from a fit applied to all compressibility data. Interestingly, the single data point of compressibility measured at 15 kPa, CPS_15kPa, correlated very strongly with both fit parameters. Seemingly, a single measurement point captured as much information as multiple points. While the Compressibility test does not take long to run (and is mostly hands-off), reducing the number of measurements taken would save time when multiple tests of one or more powders are needed. Furthermore, conditioned bulk density, CBD_C, was strongly correlated negatively to C_R². Giving further credence to the thought that all information captured by the fit may be able to be described by a single measurement point, since calculation of CPS_15kPa requires measurement of CBD_C.

Despite how it is calculated, the fact that CPS_15kPa did not strongly correlate with CBD_C is not abnormal. This just implies that overall compressibility is not tied to bulk density. A highly dense powder is not inherently less compressible than a less dense powder. For example, the grade of tungsten carbide tested, which had the highest bulk density of all powders, exhibited similar compressibility values to those of the F120 and F180 grades of silicon carbide, which had bulk densities around six times less than that of the tungsten carbide powder.

Fig. 6.3 is a correlation heatmap of the parameters provided by the FT4 Shear Cell test. The most obvious feature is the number of strong correlations. This heavily implies some parameters are redundant in the information they carry. For example, AIF_E and AIF_SS strongly correlated with one another and shared similar values in their correlations with other variables. This also extended slightly to the correlations of AIF. From this analysis, there does not appear much use in calculating AIF or AIF_E, or using either in addition to AIF_SS in other analyses.

FF and Rel demonstrated similar behavior, having had considerable overlap in their correlations with other parameters. This was expected, though, as both values are proportional to MPS divided by UYS, as noted by their correlation of 1.00 with

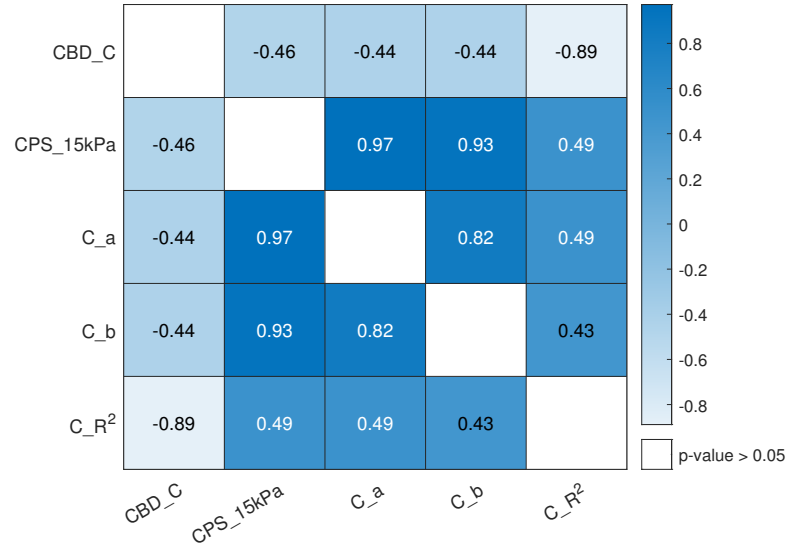


Figure 6.2: Correlation heatmap of FT4 Compressibility test and associated parameters. All parameters described in Table C.2.

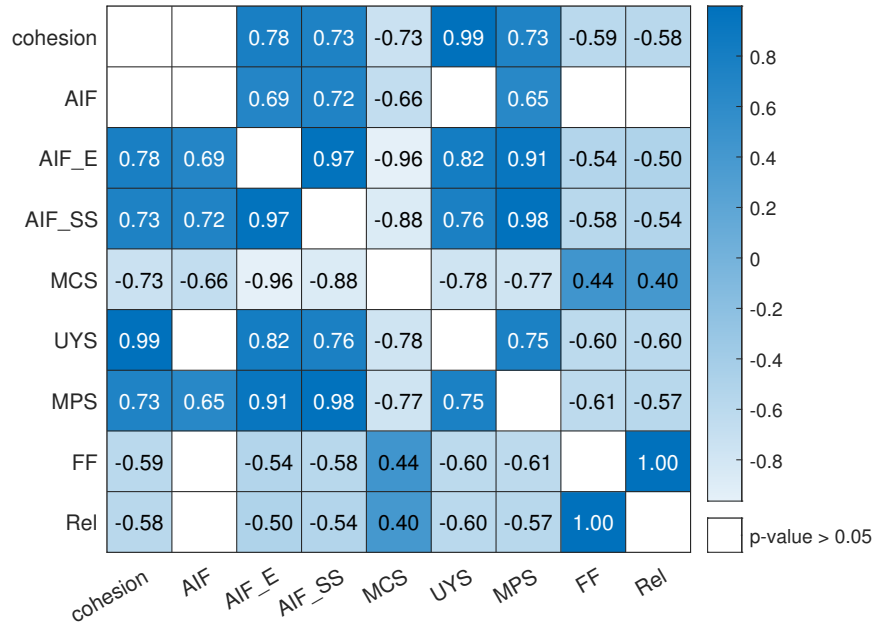


Figure 6.3: Correlation heatmap of FT4 Shear Cell test and associated parameters. All parameters described in Table C.3.

one another. The same phenomenon was found with cohesion and UYS, they had a strong correlation (0.99) with one another and overlapped in the correlations they had with other parameters. Excluding the correlations with AIF_SS and FF (or Rel), the absolute correlative values of MCS and MPS with other parameters were near in value.

Unlike the SVFR and Compressibility tests, measuring specific parameters, instead of all, from the Shear Cell test does not reduce the amount of data or time needed. All parameters of the test require a full dataset and Mohr circle analysis. However, this analysis indicates a smaller selection of parameters may be able to be used in other analyses without much loss in information captured. The combined set of four variables of AIF_SS, MCS or MPS, cohesion or UYS, and FF or Rel described data approximately as well as the combined set of all nine variables did.

A correlation heatmap of parameters provided by the FT4 Direct Pressure Consolidation test is presented in Fig. 6.4 on the following page. As DPC testing could not be found in the literature, one objective is to refine which increment/pressure combinations may not be necessary for future testing. Of the increment/pressure combinations, DPC_(2,60) had the most significant correlations greater than 0.90, with three of the six other combinations. All other combinations had significant correlations greater than 0.90 with only one or two other combinations. Overall, it does not appear that any of the combinations were clearly redundant.

Extending this examination to correlations between combinations and fitting parameters, there were no noticeable trends. If, hypothetically, DPC_b (coefficient of the square root of applied pressure) correlated strongly with DPC_(1,5) through DPC_(1,88) and DPC_(5,5) through DPC_(5,88), then it could indicate that just six measurement points, potentially less, suffice for determining the fit parameter DPC_b. Thus, reducing the need to use a large number of testing combinations in future testing, at least to some extent. However, neither this hypothetical trend, nor any other similar trend, were found between measurement combinations and fit parameters.

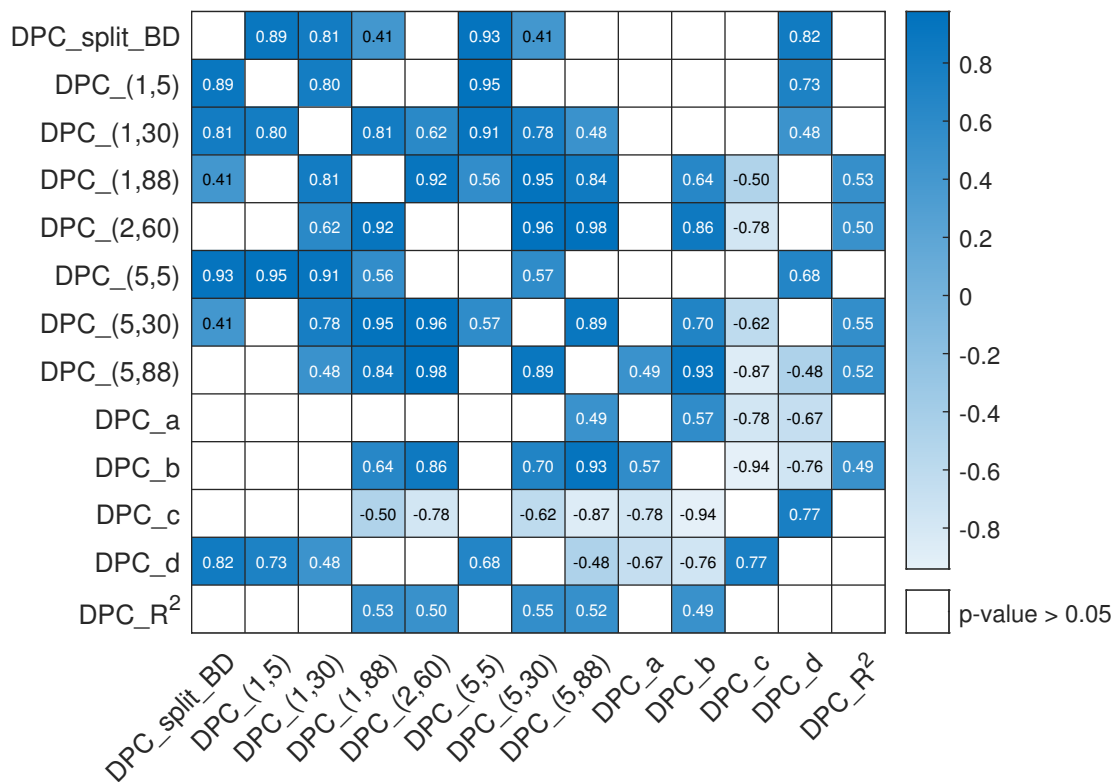


Figure 6.4: Correlation heatmap of FT4 Direct Pressure Consolidation test and associated parameters. All parameters described in Table C.4.

Focusing on just correlations between DPC fit parameters, the interaction term DPC_c strongly correlated negatively with DPC_b. Furthermore, both terms had significant correlations with the same variables, excluding DPC_R². This could simply be an artefact of applied pressure having a greater range of values than loading fraction (inverse of number of increments). Both DPC_b and DPC_c were proportional to applied pressure, whereas DPC_a and DPC_c were both proportional to loading fraction. Values of DPC_c are influenced more greatly by applied pressure than loading fraction; consequently, DPC_c is more likely to correlate with DPC_b than DPC_a. However, this is assuming the greater variation in pressure values is the cause of this correlation. It cannot be ruled out that either term, DPC_b or DPC_c, is truly necessary for appropriate fitting of DPC data.

The last note of interest is that DPC_d mostly correlated with variables that none of the other three fit parameters significantly correlated with, specifically DPC_split_BD, DPC_(1,5), DPC_(1,30), DPC_(5,5), and DPC_(5,88). Intriguingly, values were not similar across the correlations. For example, the correlation with DPC_(5,5) was positive but negative with DPC_(5,88). Why this occurred is unknown, but the overall correlations of DPC_d relative to other fit parameters does indicate that DPC_d may have captured information that the other fit parameters failed to describe.

In Fig. 6.5 a correlation heatmap of the parameters provided by the GranuTools GranuPack test is given. A key feature observed in GranuPack data, discussed in [Results and Discussion](#), was that plots of 500 taps seemed to imply little could be gained by collecting further tap data and that tapped density would quickly plateau. Yet, plots of 9999 taps demonstrated that tapped density curves of many powders took many more taps before convergence occurred, and that running the test for 9999 appeared to capture more information on a powder. From the correlation heatmap, it is made clear that running a test for 9999 taps does not provide additional comparative power. Every parameter measured/calculated with 9999 taps had a correlation of 0.98 or greater with its 500 taps counterpart.

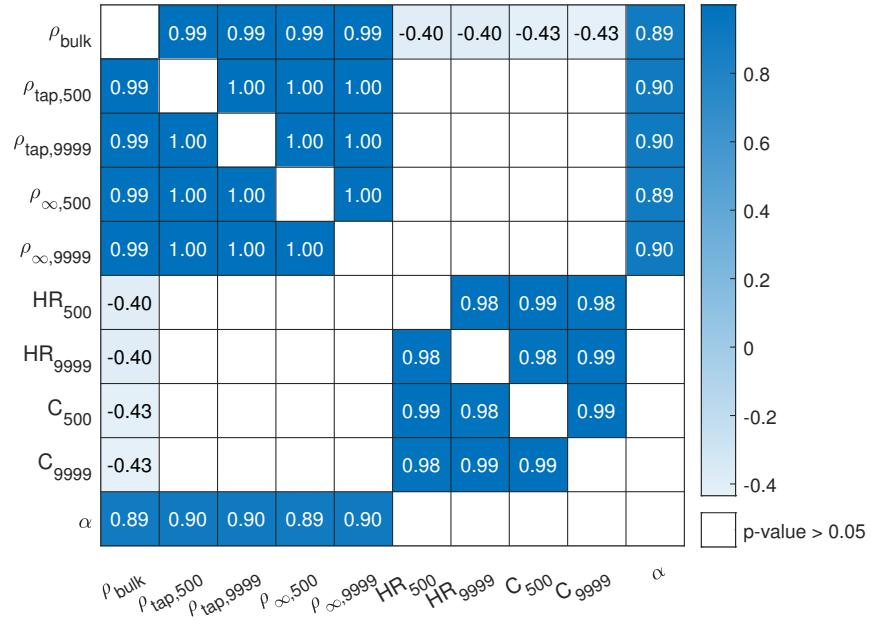


Figure 6.5: Correlation heatmap of GranuTools GranuPack test parameters. All parameters described in Table C.5.

Furthermore, correlative values that 9999 taps parameters had with ρ_{bulk} and α were nearly identical to the correlative values of the 500 taps parameters. Using less taps than 500 may still sufficiently characterize a powder, but would not considerably reduce time required for testing. Using 500 taps instead of 9999 taps reduces time required by around 2.5 hours, whereas using, for example, 100 taps instead of 500 taps would reduce time needed by roughly 6.5 minutes. Altogether, there does not appear to be any utility in using more than 500 taps.

Other notable correlations were those between ρ_{bulk} , $\rho_{tap,500}$, and $\rho_{\infty,500}$. The last parameter is automatically calculated by the GranuPack using the data of 500 taps. Based on its correlations with other parameters, particularly ρ_{bulk} and $\rho_{tap,500}$, analysis suggests it did not describe a feature not already described through another parameter. This premise is then extended further in that ρ_{bulk} and $\rho_{tap,500}$ very strongly correlated with one another and had near-identical correlative values with other parameters. Overall, ρ_{bulk} , $\rho_{tap,500}$, and $\rho_{\infty,500}$ do not appear to be unique from one another. If effectively indistinguishable, this raises the question if data beyond just ρ_{bulk} are useful. Although, bulk density can be measured by other tests, thereby inducing uncertainty as to if measuring tapped density would even be necessary for sufficiently characterizing a ceramic powder.

However, Hausner Ratio and Carr Index parameters did not significantly correlate with ρ_{bulk} ; and α had a correlation of 0.89 with ρ_{bulk} , not quite completely proportional. Additionally, Hauser Ratio and Carr Index parameters strongly correlated with one another, which was expected given how each are calculated. All these parameters require tap data. Although, the Hausner Ratio and Carr Index can theoretically be calculated using less than 500 taps, and α only requires 10 taps worth of data. Nonetheless, these analyses imply that, while tapped density values may not be as useful as expected, parameters calculated from those values may still provide some characterization utility.

Fig. 6.6 is a correlation heatmap of parameters provided by the GranuTools GranuHeap test. Unfortunately, there is little to be taken away from the found correlations. One observation is that `area_abv` and `isoh` had a correlation of 1.00 with each other and shared identical correlative values with all other parameters. This makes it clear that only one of these two parameters are necessary, despite it not having been clear what `area_abv` represented in the raw data files. Although `area_blw` and `CI` had a strong correlation with one another, their lack of near-identical correlative values with other parameters makes it hard to determine if both parameters are necessary. A similar situation was present between `AOR` and `height`.

6.2.2 Multi-Test Correlations

In Fig. 6.7 is a correlation heatmap of FT4 SVFR parameters with all other FT4 test parameters. From examining self-correlations of SVFR parameters, it was noted that `VFR_a` correlated only with parameters which were dependent on bulk density: `CBD_SVFR` and `BFE`. Of the other non-fit related, FT4 parameters, `VFR_a` correlated with `CBD_C`, `DPC_split_BD`, and `DPC` increment/pressure combinations at and below 30 kPa. Significant correlations between `BFE` and other non-SVFR test parameters were similar. If one assumes that measured flow energy in DPC testing depends partially on bulk density, then as higher pressures are applied, this influence would be reduced. Under this context, these correlations would be expected. In fact, this was partially noted in the self-correlations of DPC parameters in Fig. 6.4, `DPC_split_BD` correlated strongly with low pressure combinations and was not found to significantly correlate with high pressure combinations. As such, it is likely that a better fitting equation to apply to SVFR data would be one which incorporates bulk density.

The 50th percentile particle size, d_{50} , did not overwhelmingly correlate with any other FT4 parameter; although, it had the highest number of significant correlations

of the SVFR parameters. This is not surprising, as the importance of particle size to

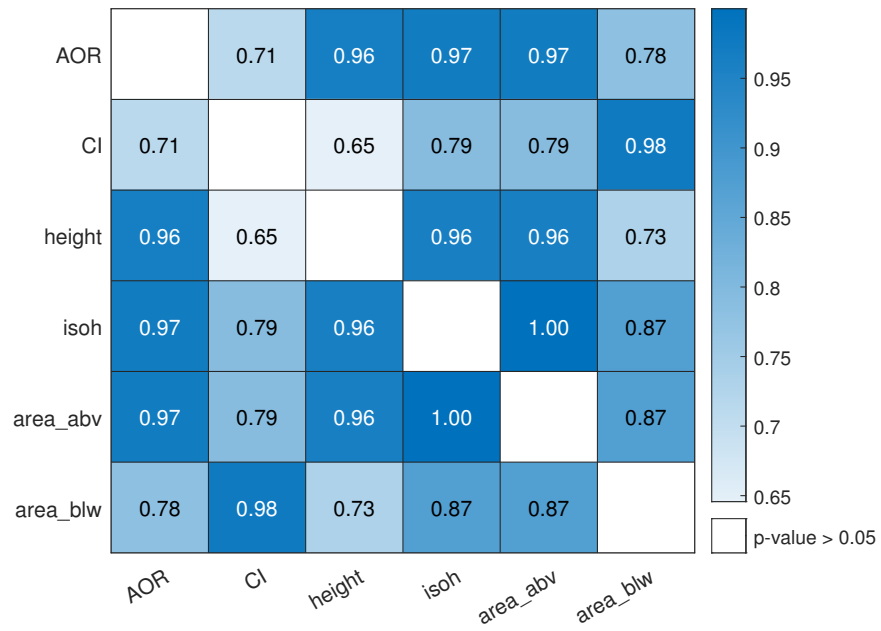


Figure 6.6: Correlation heatmap of GranuTools GranuHeap test parameters. All parameters described in Table C.6.

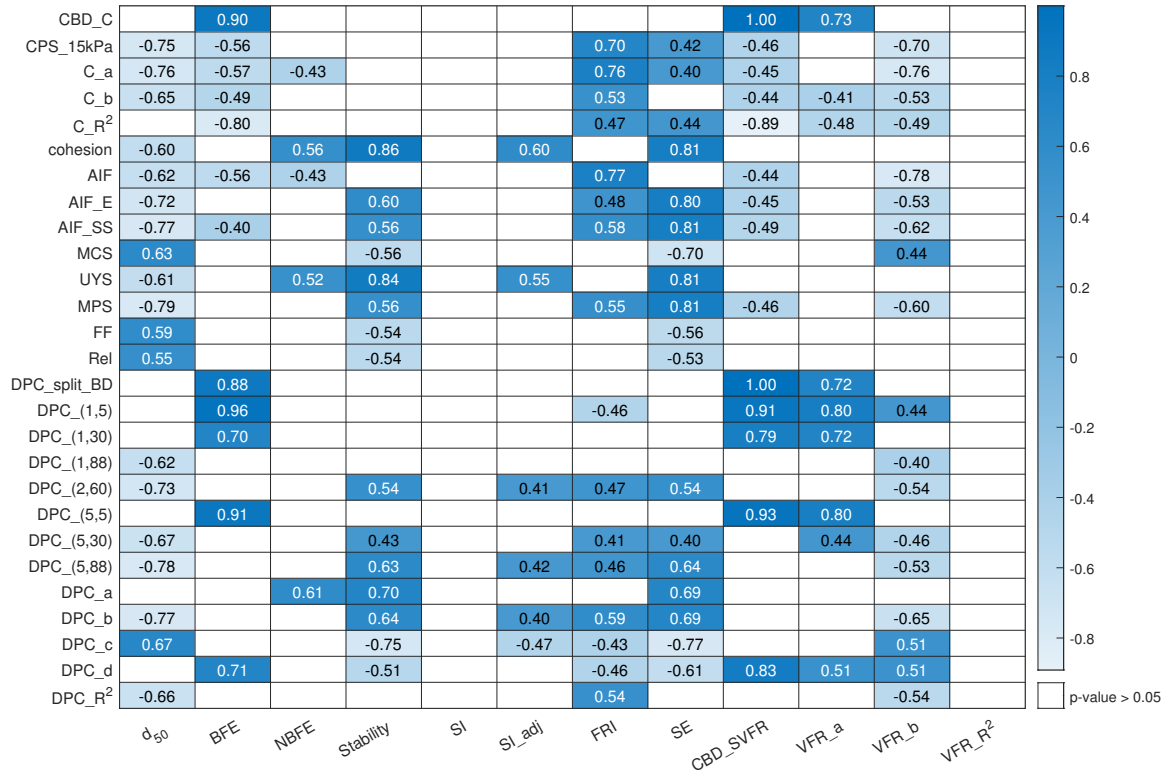


Figure 6.7: Correlation heatmap of FT4 Stability and Variable Flow Rate test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.

rheological properties is well-known. On the other end of the spectrum, VFR_R^2 did not significantly correlate with any other parameter.

Similarly, SI did not significantly correlate with any parameter. However, Fig. 6.1 showed that SI had a correlation of 0.83 with SI_adj. It would be expected for SI and SI_adj to share some common correlations, but this was not the case. It is possible the uncertainty on SI values, due to it being calculated with the first SVFR cycle, reduced its correlative power with other parameters. Stability correlated with multiple parameters, most notably cohesion and UYS from the Shear Cell test.

Shown in Fig. 6.8 is a correlation heatmap of FT4 Compressibility test parameters with all other FT4 test parameters. It was observed in the self-correlation analysis of Compressibility parameters that CPS_15kPa strongly correlated positively with Compressibility fit parameters C_a and C_b, and CBD_C strongly correlated negatively with C_R². Based on this, it was thought that a single measurement point (CPS_15kPa, which also requires measurement of CBD_C) might describe a powder nearly as well as multiple measurement points summarized through a fit. From Fig. 6.8, it is evident that CPS_15kPa, C_a, and C_b all had similar correlative values with other FT4 parameters. The same was true for CBD_C and C_R², but with opposite sign. While not one-to-one correlations, this does suggest that one measurement point would suffice in describing the compressibility of a powder, at a potentially small loss in information captured.

Shown in Fig. 6.9 below is a correlation heatmap of FT4 Shear Cell test parameters with all other FT4 parameters. From the self-correlation analysis of Shear Cell parameters, it was noted that AIF, AIF_E, and AIF_SS appeared to be redundant with one another, and that using only AIF_SS would suffice for characterizing. The same behavior was observed in FF vs. Rel and cohesion vs. UYS, due to redundancy in the pairings, only one parameter from each set appeared to be useful. The redundancy across the AIF-related parameters did extend to correlations with other FT4 test parameters. Given the overlap, there does not generally appear to be much use in using AIF and/or AIF_E in addition to AIF_SS.

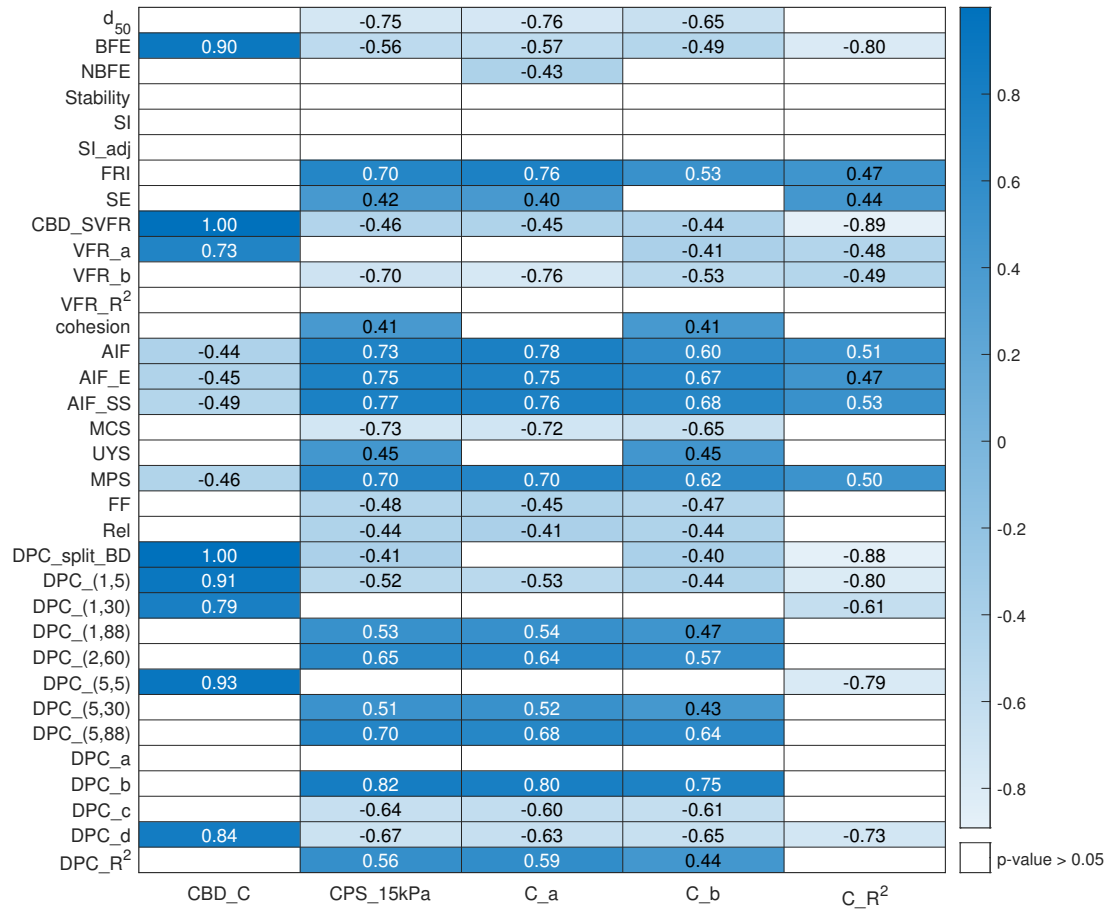


Figure 6.8: Correlation heatmap of FT4 Compressibility test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.

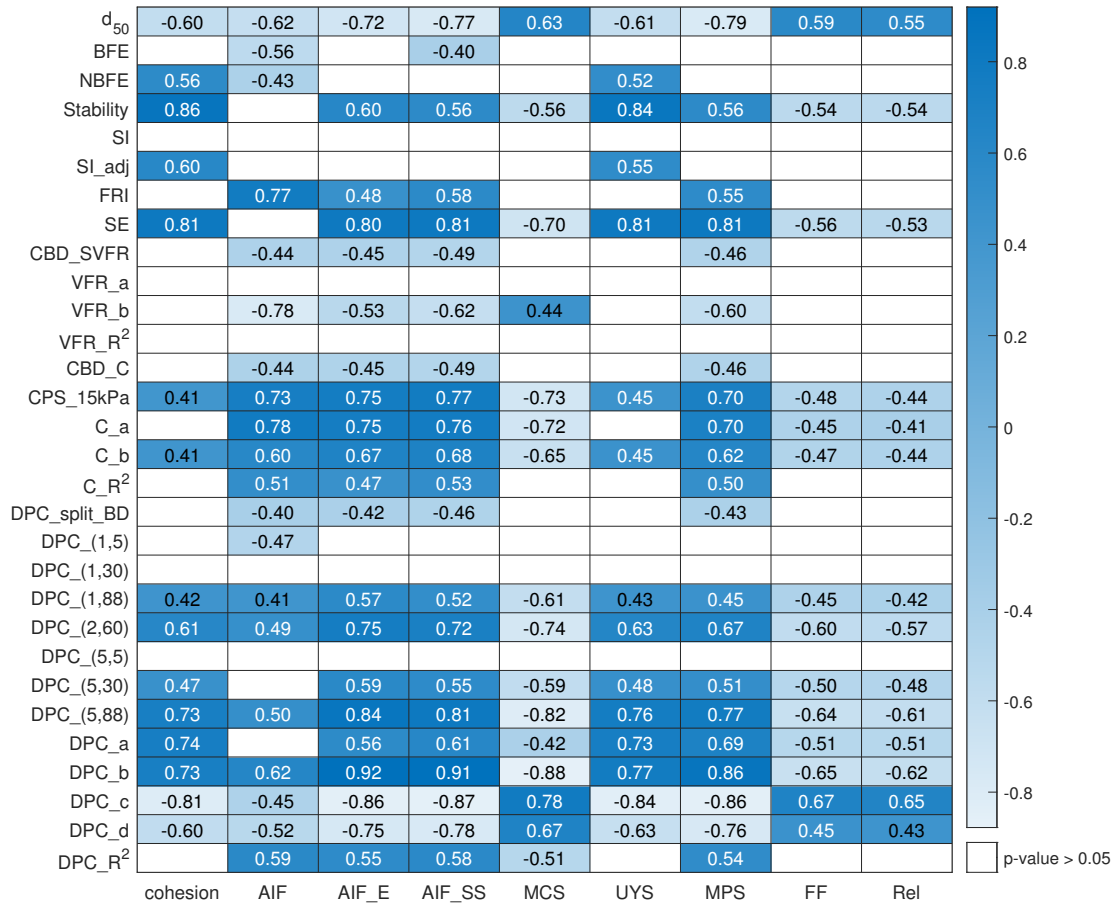


Figure 6.9: Correlation heatmap of FT4 Shear Cell test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.

The same can be said for FF and Rel, and cohesion and UYS, even more so as their correlations with other parameters were closer in value. Which parameter of each pair would be more fruitful to use in other analyses, though, is not clear, only that just one would likely be necessary.

Fig. 6.10 is a correlation heatmap of FT4 DPC test parameters with parameters from all other FT4 tests. In Fig. 6.4, it was shown that DPC_b and DPC_c could be redundant with one another, and that a DPC fitting equation may not need both terms. It can be seen in Fig. 6.10 that, while they did correlate significantly with the same set of parameters, their absolute values were not overwhelmingly similar. Based on these analyses, neither DPC_b or DPC_c can be said to be fully redundant.

Other large correlations between select DPC parameters and other FT4 test parameters were found, but no general trend could be noticed. For example, in the discussion of multicorrelation analysis focused on Shear Cell test parameters, it was argued that shear cell data could be effectively described by just AIF_SS, FF or Rel, and cohesion or UYS. DPC_b had a correlation of 0.91 with AIF_SS and DPC_c had a correlation of -0.84 with UYS, but no strong correlation was found with FF or Rel and a DPC parameter. Otherwise, one could argue that in some circumstances DPC testing alone would suffice, and the loss of information one could potentially gain by also conducting Shear Cell testing would be negligible.

Fig. 6.11 shows a correlation heatmap of GranuTools GranuPack parameters with all FT4 test parameters. The discourse for the self-correlation analyses of GranuPack parameters centered upon the necessity of individual variables, and the test as a whole. The first question of necessity was for 500 taps parameters and their 9999 taps counterparts, e.g., $\rho_{tap,500}$ versus $\rho_{tap,9999}$, HR_{500} versus HR_{9999} , etc. Across all pairs, the difference in correlative value between a 500 taps parameter and its 9999 taps counterpart was minimal, and in some cases shared an identical correlative value. From these analyses, and the self-correlation analyses provided previously, it is evident that there is likely nothing gained in way of characterization by measuring tapped density for 9999 taps instead of the traditional 500 taps.

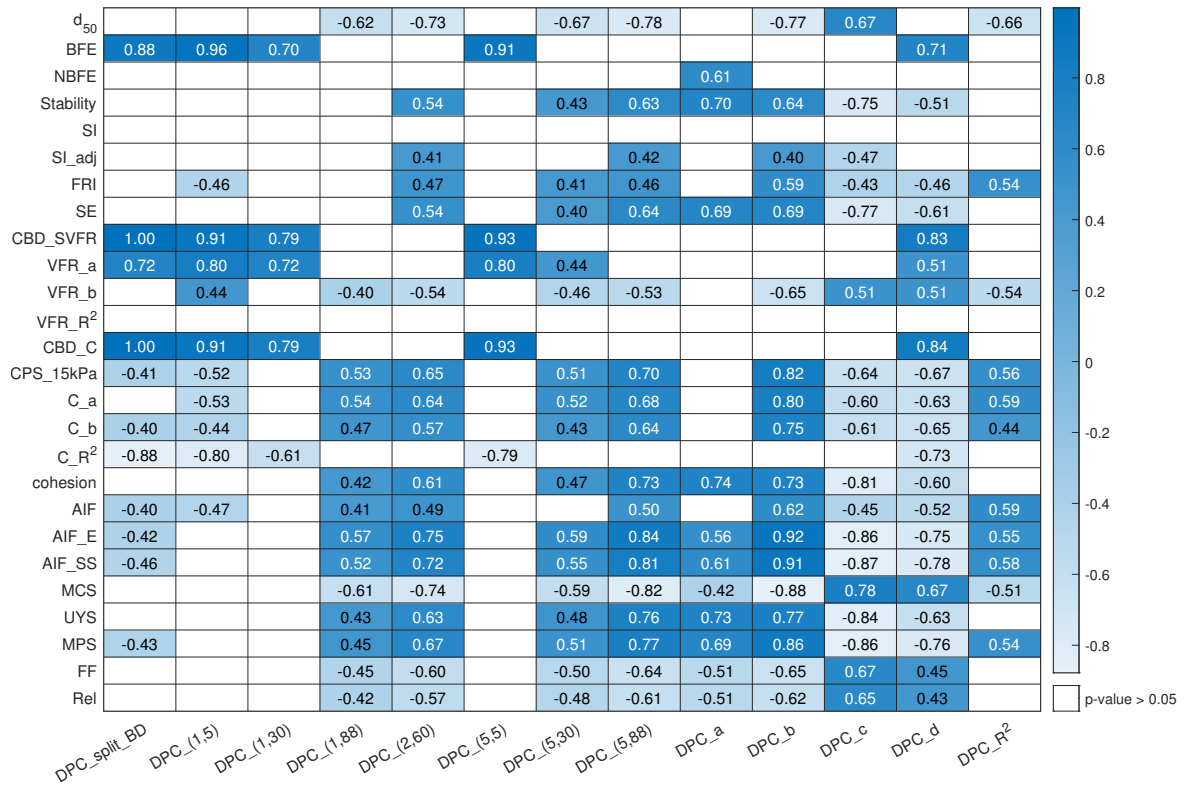


Figure 6.10: Correlation heatmap of FT4 Direct Pressure Consolidation test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4.

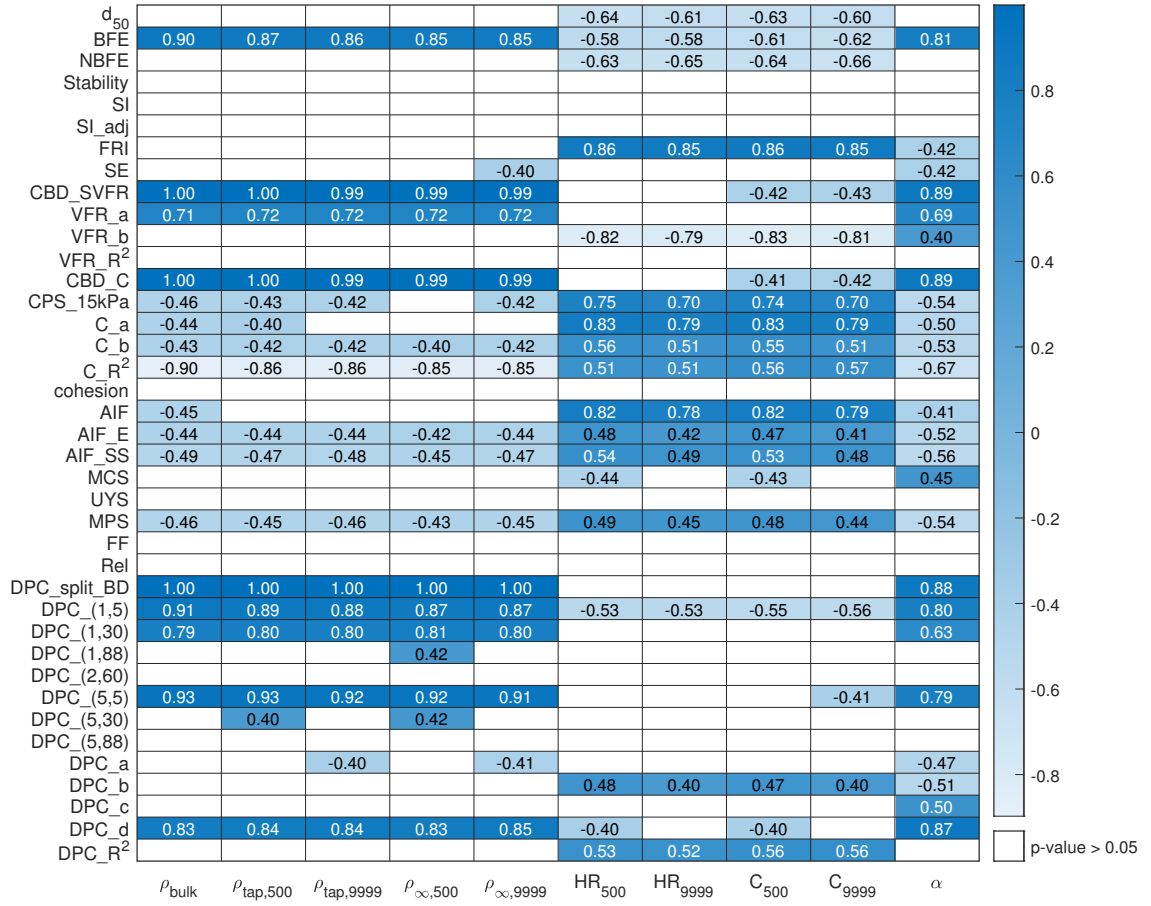


Figure 6.11: Correlation heatmap of GranuTools GranuPack test parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.5.

Consequently, all 9999 taps parameters were removed from principal component analysis, which is presented in the following section.

The second question of necessity was for $\rho_{tap,500}$ and $\rho_{\infty,500}$. While they did not share the same number of significant correlations, they had similar values for the significant correlations they did share. In fact, this behavior was also present with ρ_{bulk} , which was expected as $\rho_{tap,500}$ and $\rho_{\infty,500}$ each had a correlation of 0.99 with it. These correlations make it unsurprising that all three parameters had correlations of 1.00 with other bulk density parameters (CBD_SVFR, CBD_C, and DPC_split_BD). However, the implication this imposed was unexpected. Excluding α , all other parameters of the Hausner Ratio, and Carr Index, the bulk and tapped density data provided by the GranuPack test appeared to yield little use, as bulk densities measured in multiple other tests greatly correlated with these data.

Fig. 6.12 shows a correlation heatmap of GranuTools GranuHeap parameters with all FT4 parameters. In the self-correlation analyses of GranuHeap parameters it was found that *isoh* and *area_abv* had a correlation of 1.00 with one another and shared near-identical correlative values with other GranuHeap parameters. This behavior extended to the correlations with all FT4 parameters, thus providing further confirmation to the 1.00 correlation found between the two. From this, there does not appear to be any utility in including both parameters in other types of analyses.

Similarly, CI had a correlation of 0.98 with *area_blw*, and AOR had a correlation of 0.96 with *height* in Fig. 6.6. Each pair had similar correlative values to each other with all FT4 parameters, excluding a select few where significance was found for only one member in a pair. This implies that in addition to *area_abv*, *area_blw* did not appear to capture information not already described by another GranuHeap parameter. The same can be said of AOR and *height*. The analyses suggest that only one of the two parameters is necessary for characterization.

The final correlative heatmap, given in Fig. 6.13, is of the GranuTools GranuPack and GranuHeap parameters. There is little to be said regarding this heatmap which has not already been discussed for other heatmaps.

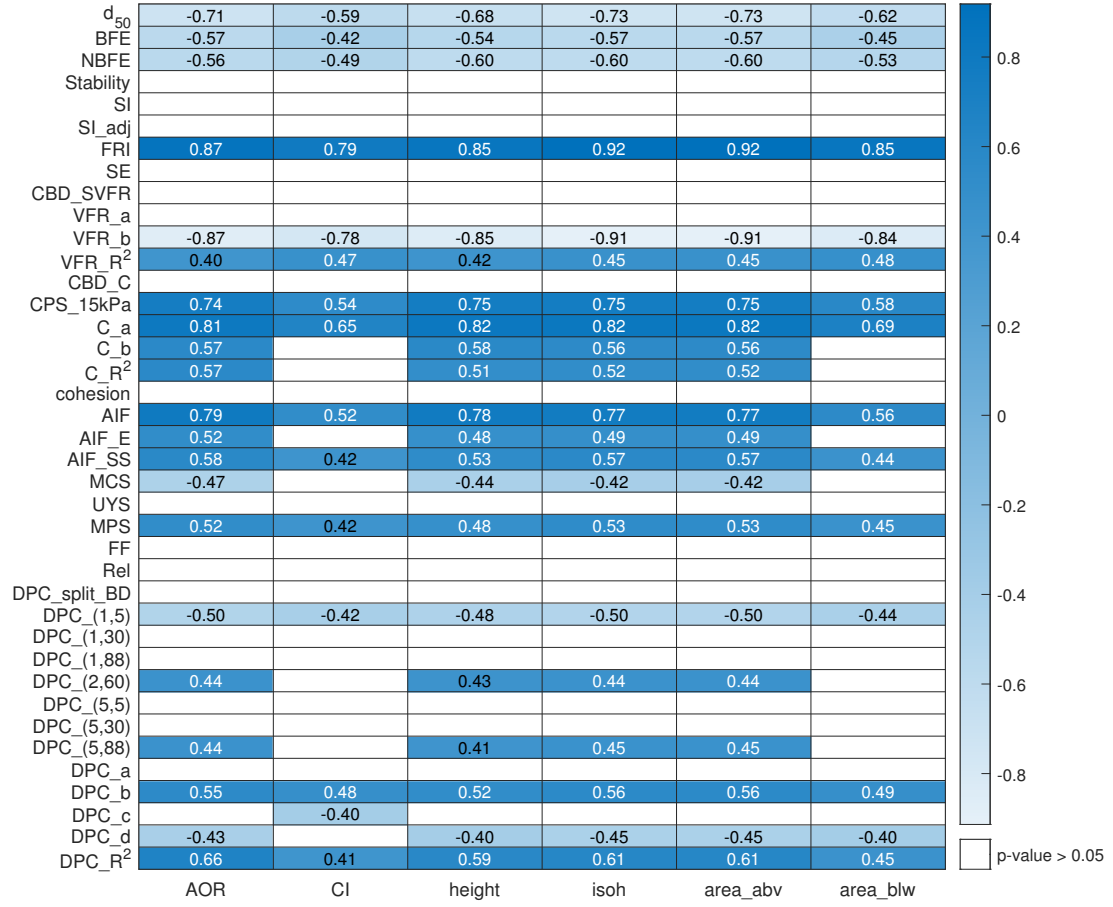


Figure 6.12: Correlation heatmap of GranuTools GranuHeap parameters with all other FT4 parameters. All listed parameters are described in Tables C.1-C.4 and Table C.6.



Figure 6.13: Correlation heatmap of parameters from GranuTools GranuPack and GranuHeap tests. All listed parameters are described in Tables C.5-C.6.

GranuHeap parameters of `isoh` and `area_abv` had identical correlative values, just as they did for all FT4 parameters. Similar behavior was present for `CI` and `area_blv`, and `AOR` and `height`, although the latter parameters of each pair had slightly stronger correlations than their counterparts.

As for the GranuPack parameters, bulk and tapped density-based parameters, and α , did not significantly correlate with any GranuHeap parameter, excluding a weak correlation between ρ_{bulk} and `AOR`. Hausner Ratio and Carr Index parameters shared similar correlative values. This was expected given how they are calculated and the fact that 500 taps parameters and their 9999 taps were previously shown to not significantly differ.

6.3 Principal Component Analysis

While correlative analysis helps to determine where relationships between parameters may lie, it does not necessarily determine which parameters capture the most information of a tested powder. For multi-collinear data, which was present in many of the parameters discussed in the previous section, interpretation of said data can be difficult. It is not readily clear the "importance" of any given parameter. This is compounded further when input dimensionality is high, such as what was present in this work, which had 51 parameters once select GranuPack variables were removed.

Principal Component Analysis (PCA) is a common method used in situations like these. PCA reduces dimensionality by orthogonally transforming data into a smaller, uncorrelated variable space. The transformed data are linear combinations of the original data that capture the most variance. These linear combinations are called principal components (PCs). Subsequent PCs describe less and less variation in the data. All of this is mathematically described in Eqn. 6.4 below. The original data set, X , is modeled by the product of T , a set of scores, and P , a matrix of loadings.

$$X = TP^T \tag{6.4}$$

To determine scores and loadings, a covariance/correlation matrix of the original data is decomposed into eigenvectors and eigenvalues. The eigenvalues are sorted from largest to smallest, i.e., ranked by decreasing variance in the original data. PCs are then constructed by taking the dot product of the original, normalized data with the eigenvectors, ranked by the sorted eigenvalues. The coordinates of the original variables in the projected space are given by the scores. The loadings represent the weights of each variable for every dimension, or component. The total number of PCs constructed is equal to the total number of observations in the original dataset minus one. Not all PCs need to be used for sufficient representation of transformed data, the specific number to use is situational.

For this work, PCA was conducted with MATLAB by applying an alternating least squares algorithm on data that were centered and standardized, thereby using the correlation matrix. The alternating least squares algorithm was used instead of the singular value decomposition method as it is capable of handling a small number of missing entries, i.e., the few powders which did not have a d_{50} value available from their certificate of analysis. All parameters were included, except for those whose removal was argued for in previous sections.

As previously mentioned, the number of PCs to keep is circumstantial. One method to determine the number to keep is by looking at cumulative explained variance. Fig. 6.14, a scree plot, provides a visualization of this. The dashed red line is the cumulative percent variance described by additional PCs. Typically, a threshold such as 90% or 95% is used to determine the number of PCs to retain. The former would require the first six components, and the latter would require the first eight components. For this work, focus is on determining which parameters carry the most information, not using PCs as predictors in other modeling. Consequently, using the first three PCs, which had a cumulative explained variance of 82%, is sufficient.

Conveniently, three PCs can be visualized at once. Fig. 6.15 is a plot of the loadings of the first three PCs. Residual lines, drawn from the light blue plane, for loadings of the first PC are shown. The percent variance explained by each PC

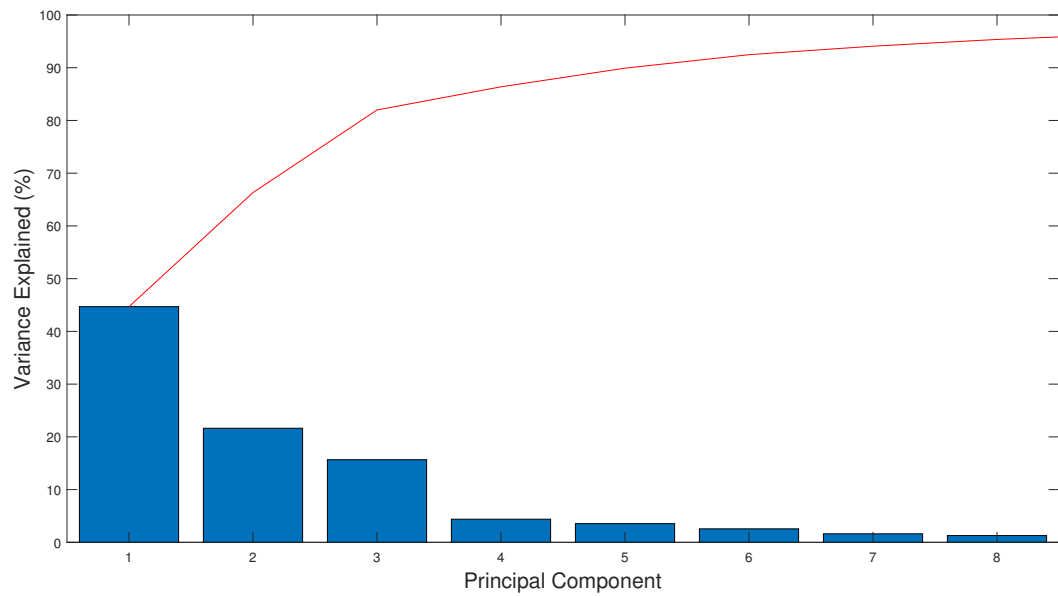


Figure 6.14: Scree plot of first eight components of the principal component analysis.

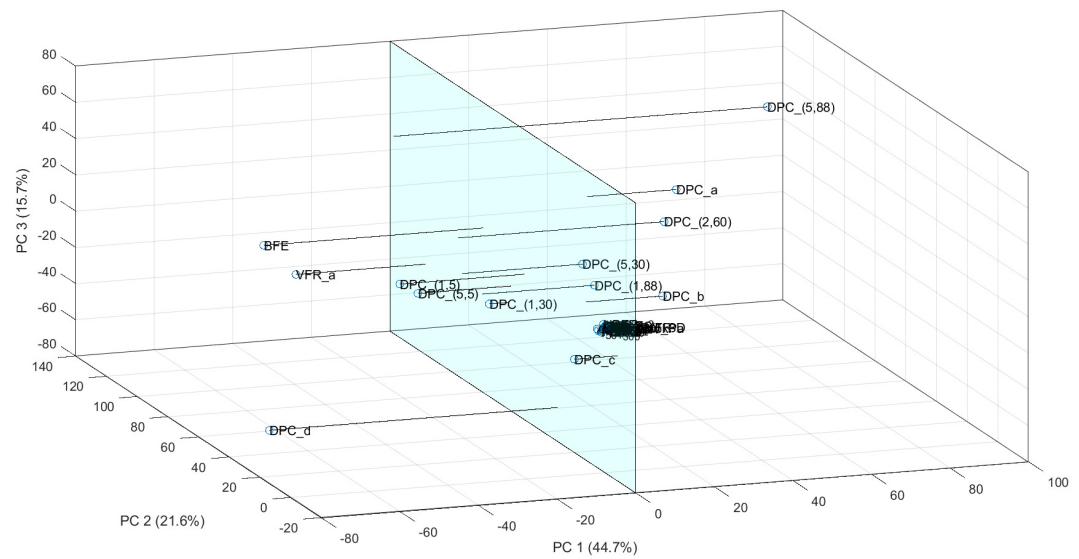


Figure 6.15: Plot of loadings of first three principal components (PCs). Residuals along PC 1 are drawn for each loading from the light blue plane that intersects PC 1.

is given in parentheses. Two similar plots with residuals drawn for PCs two and three are given in Fig. C.9 and Fig. C.10 in Appendix C. Perhaps the most obvious feature in Fig. 6.15, a large cluster of variables may be seen clumped around the origin. On the contrary, the variables of BFE, VFR_a, DPC fit parameters a-d, and all DPC increment/pressure combinations are noticeably outside of the cluster. These variables captured the most variance along PC 1, with those further away from the plane explaining greater amounts. Residuals for PCs 2 and 3 were similar- the same set of variables captured the most variance for each PC.

Excluding BFE, the results of this analysis were entirely unexpected. In other works which have utilized PCA for powder rheology data in a similar manner, the parameters which explained the most variance typically were BFE, particle size parameters like d_{50} , and parameters from Shear Cell, Compressibility, and tapped density tests. In fact, if one hides BFE, VFR_a, and all DPC parameters except for DPC_split.BD and DPC_R² in plotting, the resulting plot of the first three PCs, shown in Fig. 6.16, is similar to what one might find in other works.

The degree to which the highest-ranking loadings in Fig. 6.15 surpass the loadings shown in Fig. 6.16, those commonly found to be the most important in the literature, is significant. This suggests that out of the Freeman Technology FT4 Powder Rheometer tests of SVFR, Compressibility, Shear Cell, and DPC and the GranuTools' GranuPack and GranuHeap tests, just two tests, SVFR and DPC, are necessary to explain most variance. Furthermore, as only BFE and VFR_a from the SVFR test were found to have high loadings, the full SVFR test may not be necessary. BFE is seventh cycle of the SVFR test, conducted at a tip speed of 100 mm/s and measured during the "stability" portion of the SVFR test. However, the separate Variable Flow Rate test also measures flow energy at a tip speed of 100 mm/s. The same measurement points used for finding VFR_a (and other fit parameters) are present in the separate VFR test.

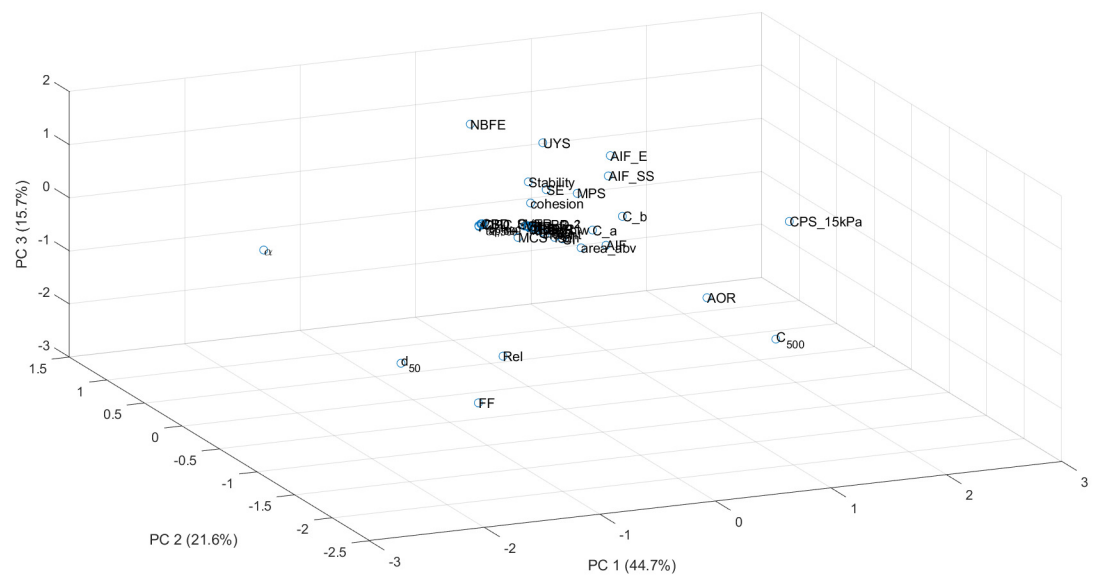


Figure 6.16: Plot of loadings of first three principal components with select loadings visually removed from plot.

Beyond these general trends, more specific details may be found by examining two-dimensional plots of loadings. Fig. 6.17 is a 2D scatter plot of the loadings of the first two PCs. Along these PCs, DPC_a and DPC_b had similar loadings. These two parameters sharing similar loadings for at least one PC is not surprising considering they were previously shown to correlate strongly with one another. As can be seen in Fig. 6.18, these two parameters were not closely grouped together along the third PC.

Loadings along PC 1 seem to be grouped by measured flow energy. BFE, with a large negative loading, was typically the lowest measured flow energy of a powder. On the other end of PC 1 is DPC_(5,88), which was always the highest measured flow energy of a powder. Notably, DPC_d has a PC 1 loading similar to that of BFE. This is not abnormal once one recalls that DPC_d is a fitting constant in the full DPC equation. In the situation where no pressure is ever applied to a powder, the predicted flow energy of a powder would be its calculated constant DPC_d. Similarly, no direct pressure is ever applied in the SVFR test.

As pointed out with Fig. 6.16, the 3D reduced loadings scatter plot, in relevant works in the literature, explained variance is typically spread across parameters from multiple test types. Such parameters usually originate from a range of tests that correspond to the three general states of a powder: static, when a powder is compacted, such as what occurs in Compressibility or tapped density tests; quasistatic, when powder begins to flow, like that measured in the Shear Cell test; and dynamic, when a powder is free-flowing, as is measured in the SVFR test. Correspondingly, parameters often group together in accordance with powder state. For example, the parameters of CBD_C, CBD_SVFR, DPC_split_BD, ρ_{bulk} , $\rho_{tap,500}$, and $\rho_{\infty,500}$ were all grouped together and visibly overlapped in Fig. 6.16. All of those parameters correspond to a static state of powder. However, their loadings on the PCs were so small relative to the loadings of BFE, VFR_a, and DPC parameters that they insignificantly contributed to total explained variance. Considering the DPC test measures the energy to induce steady-state flow in a compacted powder, it is

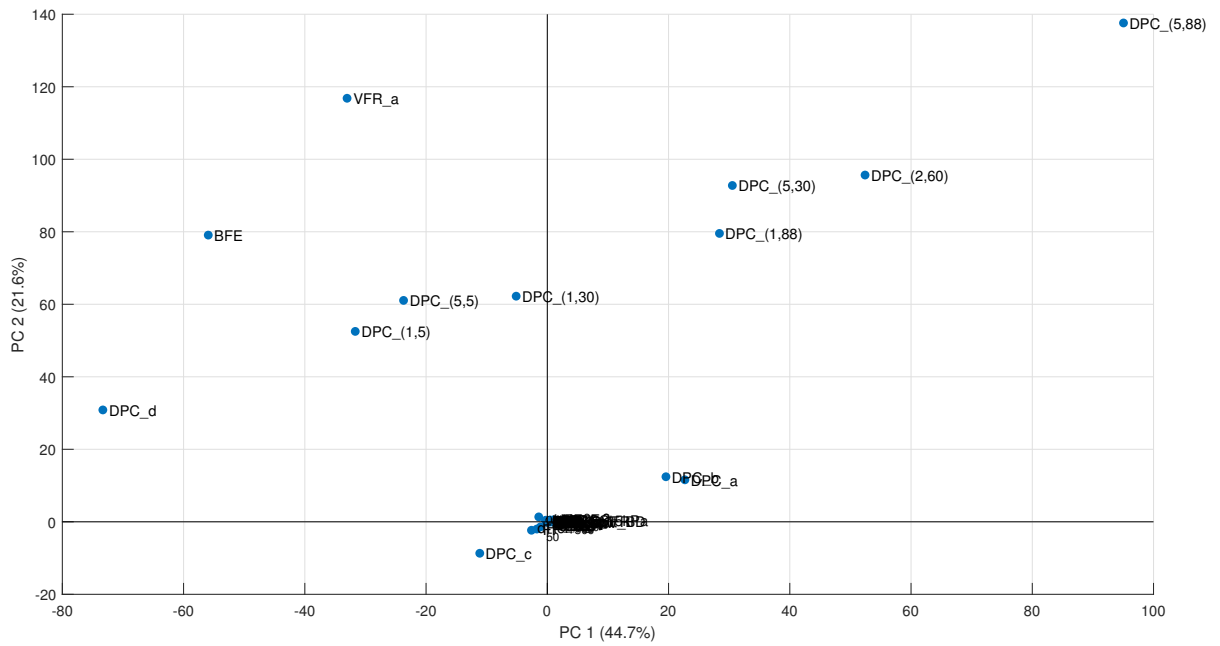


Figure 6.17: 2D scatter plot of loadings from the first and second principal components.

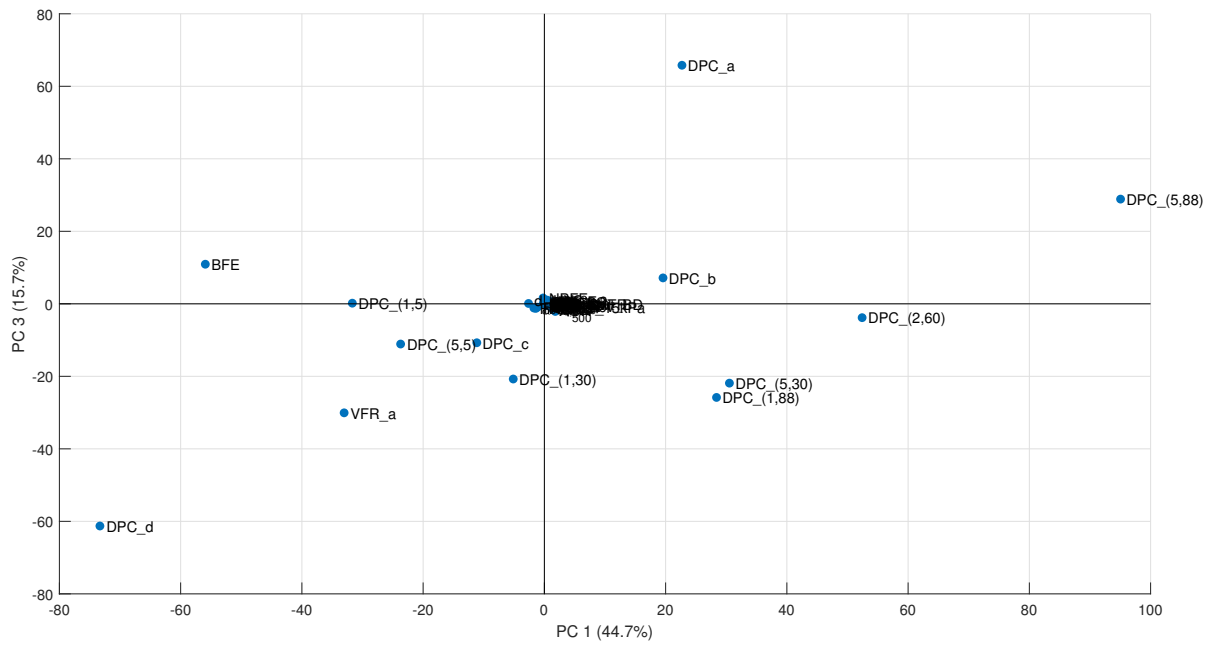


Figure 6.18: 2D scatter plot of loadings from the first and third principal components.

possible that aspects of all three powder conditions are probed by the test. If true, this could explain the lack of groupings of high-value loadings one would otherwise expect to find.

The dominance of BFE, VFR_a, and DPC parameters was not restricted to just the first three PCs. This can be seen in Fig. 6.19 on the following page. It is a bar chart of the weighted sum of squares of loadings for every parameter across all 24 PCs. For every parameter ($i=1:51$), the weighted sum of squares was found by multiplying its loading on each PC ($j=1:24$), $w_{i,j}$, by the explained variance, σ_j , of each PC. Only parameters which had a weighted sum of squares value equal to or greater than 100 were plotted.

As can be seen in the figure, across all PCs, BFE, VFR_a, and DPC parameters explained the majority of all variance. Right at the cutoff of 100 was DPC_c (rounded up), the subsequent parameter (not shown) having had a weighted sum of squares value of 5.04 was d_{50} . All subsequent parameters had continuously decreasing values.

The overarching implication from the PCA results was that tested ceramic powders could be sufficiently characterized with just two types of tests, the Stability and Variable Flow Rate test and Direct Pressure Consolidation test offered by the Freeman Technology FT4 Powder Rheometer. Ideally, these novel PCA results stem from the fact that parameters from fitting Stability and Variable Flow Rate test data (e.g., VFR_a) have not been used before; and, perhaps more significantly, because the Direct Pressure Consolidation test and its associated parameters have not been previously explored in any capacity. It should be noted, though, that similar works which conducted PCA on ceramic powders generally used finer powders, particularly types often used in food and pharmaceutical industries. However, results herein are similar to what may be typically found in other works if one visually removes select parameters from a loadings plot, as was demonstrated in Fig. 6.16. This gives some credence to the notion that PCA results for these other types of ceramic powders could be similar to those found herein if DPC testing had been included.

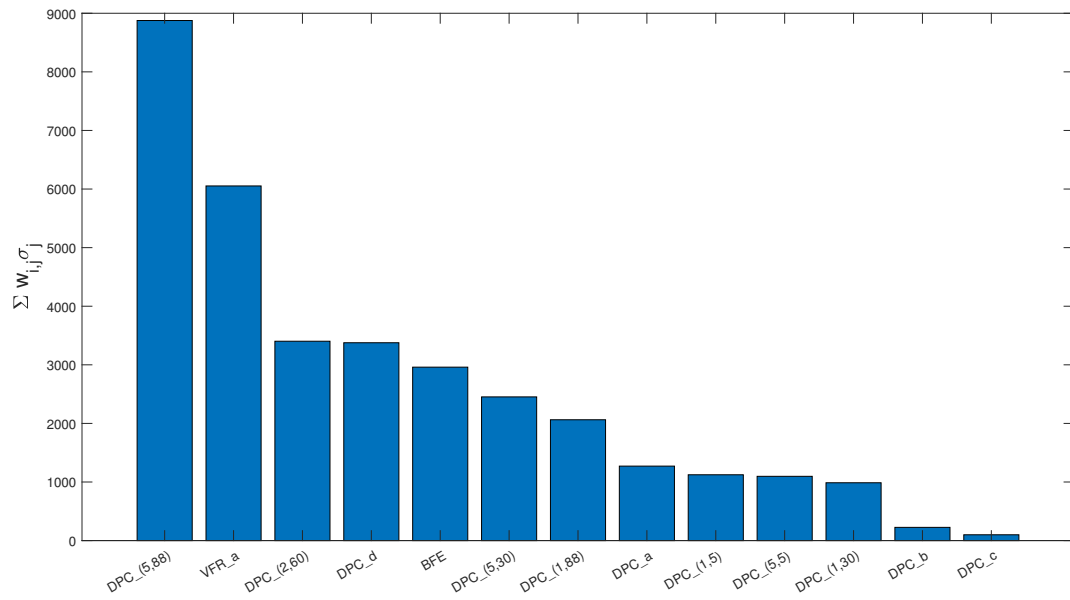


Figure 6.19: Weighted sum of squares of every parameter across all principal components. Only parameters with a sum value equal to or greater than 100 are shown.

Lastly, a linear PCA method was used, as opposed to the less commonly-used non-linear kernel PCA method. As such, non-linear relationships were not looked for. The possibility that some of the DPC and SVFR parameters had non-linear relationships with one another, which could in theory reduce the variance each parameter captured, cannot be discarded. Nonetheless, what can be said with absolute certainty is that Direct Pressure Consolidation testing should be explored further as a characterization technique for ceramic powders, and potentially for other powders in general.

Chapter 7

Conclusion and Recommendations

7.1 Conclusion

This work investigated relationships among rheological parameters, and the general importance of each parameter towards powder characterization, originating from a wide selection of static, quasi-static, and dynamic rheological tests for 25 ceramic powders. Tests included the Freeman Technology FT4 Powder Rheometer Stability and Variable Flow Rate (SVFR), Compressibility, Shear Cell, and Direct Pressure Consolidation (DPC) tests and tests using the GranuTools GranuPack, GranuFlow, and GranuHeap equipment. At time of writing, the DPC test was not found to have been used in any other work. Tests were conducted on various-sized powders of aluminum oxide (Al_2O_3), boron carbide (B_4C), silicon carbide (SiC), silicon nitride (Si_3N_4), and tungsten carbide (WC). Three F1200 grades of Al_2O_3 were acquired from different vendors to ascertain how origin source may affect rheological properties. Mixed grades of Al_2O_3 , B_4C , and SiC were made by mixing smaller and larger grades of constituent materials together.

In [Chapter 5](#), which covers general results, it was observed in the SVFR data that powder may not have been conditioned into a reproducible state before the first test cycle. This was contrary to the claims made in the manual of the instrument, which are often found repeated in the literature. Furthermore, it was noted that how tight the FT4 powder vessel was clamped down (manually done by knob) affected energy measurements. This could be particularly important for cross-lab reproducibility. Large grades, like SiC F120 and WC 25-30 μm , showed much

smaller changes in volume when compressed compared to other tested powders. Compressibility decreased as particle size increased for grades of like material, except for Si_3N_4 , which had increasing percent compressibilities as a function of increasing particle size. From FT4 Shear Cell testing, it was discovered that the instrument automatically normalized measured data, but did not make the fact it did so clear. While normalizing is not inherently an issue, it could be problematic in that some published works may have unknowingly used processed, instead of raw, data. For DPC data, flow energy generally increased as particle size decreased for like material, except for Si_3N_4 , which had no general trend. Of the results from the GranuTools instruments, the most notable observation was the ineffectiveness of the GranuFlow for the ceramic powders tested. Insufficient data could be collected due to either inability of a powder to flow, or the inability of the GranuFlow to precisely record change in measured mass fast enough.

One of the three Al_2O_3 grades, of like size sourced from three different vendors, could be differentiated from the others by the SVFR or Compressibility tests. All three grades could be differentiated by use of the Shear Cell test, and all three could be differentiated for 5 of the 7 increment/pressure combinations used for DPC testing. This was despite all three grades having similar particle size distribution and chemical composition, thus giving further credence to the notion that particle size distribution and chemical composition are insufficient to fully characterize a ceramic powder. The mixed grades typically had SVFR flow energy values between the values of their constituent grades. The same trend was generally true for mixed grade results from all other tests, excluding the GranuPack and GranuFlow tests. Tapped densities of mixed grades measured by the GranuPack test were generally higher than either tapped density of the constituent grades.

In [Chapter 6](#), novel parameters calculated from rheology data and from fitting data were created. These parameters and all base parameters provided by used tests were explored using correlative analysis and principal component analysis. From [correlative analysis](#) it was observed that parameters from the dynamic regime of the

SVFR test correlated with one another and parameters from the stability regime correlated with each other. No significant correlations among variables between both regimes were found. Parameters from fitting Compressibility test data significantly correlated strongly with the compressibility measurement taken at 15 kPa, implying that a single measurement point may describe a powder as well as multiple points. Correlative analysis showed that there did not appear any use in calculating the parameters of Angle of Internal Friction (AIF) or Effective AIF (AIF_E) in addition to Steady State AIF (AIF_SS) due to significant correlations found. Furthermore, it was observed that the combined set of parameters of AIF_SS, MCS or MPS, cohesion or UYS, and FF or Rel captured approximately the same information as all nine Shear Cell test parameters did. Analysis of GranuPack data showed that collecting data beyond 500 taps did not capture additional information. Excluding a few calculated parameters taken from raw data, there did not appear to be much use for raw data due to found significant correlations with density-related parameters from other tests.

Most significantly, the section on [principal component analysis](#) showed that tested ceramic powders could be sufficiently characterized with just the Direct Pressure Consolidation (DPC) test and the Stability and Variable Flow Rate (SVFR) test. The most significant contributors to captured information were all DPC measurement points, DPC fit parameters, Basic Flowability Energy measured by the SVFR test, and a parameter (VFR_a) from fitting SVFR data. Removal of DPC parameters yielded results similar to what has been observed in other works- sufficient characterization of ceramic powders, typically those used in pharmaceutical/food industries, requires parameters from a multitude of tests. Notably, the DPC test and its fits used in this work have not been previously used in any other found work. For ceramic powders often used as grinding media and crucibles, this work demonstrated that such powders may be adequately characterized rheologically using just two tests, the SVFR test and the DPC test.

7.2 Recommendations for Future Work

A novel aspect of this work was the implementation of, and fitting data thereof, Direct Pressure Consolidation (DPC) testing. Herein, DPC testing was shown to capture a significant portion of information on tested powders and greatly outweigh other rheology tests in overall importance. As DPC testing has not been conducted in any other work, it would be fruitful to investigate it further for ceramic powders like those tested here, and potentially for powders in general. Similarly, exploring other increment/pressure combinations to use in the DPC test could increase information captured.

A limitation of this work was the lack of full particle size distribution measurements for tested powders. It has been frequently shown that many rheological properties are influenced by particle size distribution, not just the 50th percentile size, as was used in this work. It is possible that the ranking in information captured of parameters used herein could be different if other particle size distribution measurements, such as span, were included in analysis. Likewise, DPC results found herein may not be similar for powders with non-unimodal particle size distributions. Such powders can be compacted more than their unimodal counterparts, which could affect DPC measurements given the consolidating nature of the test.

Lastly, investigation into the relationships between rheological parameters and consolidated properties of ceramics should be considered. Other works have shown that chemical composition and particle size distribution measurements are insufficient to characterize a ceramic powder and that rheological techniques can greatly supplement characterization. This work has better elucidated relationships, and general importance, of rheological tests and parameters for ceramic powders. Applying this learned knowledge could yield a framework for predicting consolidated properties of ceramics using a combination of physical and chemical properties, like chemical composition and particle size distribution, and rheological measurements,

such as results from Direct Pressure Consolidation testing and Stability and Variable Flow Rate testing.

Bibliography

- [1] M. Rios, “Developments in powder flow testing,” *Pharmaceutical technology (2003)*, vol. 30, no. 2, 2006.
- [2] J. K. Prescott and R. A. Barnum, “On powder flowability,” *Pharmaceutical technology*, vol. 24, no. 10, pp. 60–85, 2000.
- [3] G. MiDi, “On dense granular flows,” *The European Physical Journal E*, vol. 14, no. 4, pp. 341–365, Aug. 2004, ISSN: 1292-8941, 1292-895X. DOI: [10.1140/epje/i2003-10153-0](https://doi.org/10.1140/epje/i2003-10153-0).
- [4] M. Leturia, M. Benali, S. Lagarde, I. Ronga, and K. Saleh, “Characterization of flow properties of cohesive powders: A comparative study of traditional and new testing methods,” *Powder Technology*, vol. 253, pp. 406–423, Feb. 2014, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2013.11.045](https://doi.org/10.1016/j.powtec.2013.11.045).
- [5] J. Schwedes, “Review on testers for measuring flow properties of bulk solids,” *Granular matter*, vol. 5, no. 1, pp. 1–43, 2003.
- [6] D. Schulze, *Powders and bulk solids: behavior, characterization, storage and flow*. Springer, 2008, ISBN: 978-3-540-73767-4.
- [7] M. Krantz, H. Zhang, and J. Zhu, “Characterization of powder flow: Static and dynamic testing,” *Powder Technology*, vol. 194, no. 3, pp. 239–245, Sep. 2009, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2009.05.001](https://doi.org/10.1016/j.powtec.2009.05.001).
- [8] M. S. Escotet-Espinoza *et al.*, “Using a material property library to find surrogate materials for pharmaceutical process development,” *Powder technology*, vol. 339, pp. 659–676, 2018.
- [9] A. Vasilenko, S. Koynov, B. J. Glasser, and F. J. Muzzio, “Role of consolidation state in the measurement of bulk density and cohesion,” *Powder Technology*,

- vol. 239, pp. 366–373, May 2013, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2013.02.011](https://doi.org/10.1016/j.powtec.2013.02.011).
- [10] B. Van Snick *et al.*, “A multivariate raw material property database to facilitate drug product development and enable in-silico design of pharmaceutical dry powder processes,” *International journal of pharmaceuticals*, vol. 549, no. 1-2, pp. 415–435, 2018.
 - [11] Y. Wang, S. Koynov, B. J. Glasser, and F. J. Muzzio, “A method to analyze shear cell data of powders measured under different initial consolidation stresses,” *Powder technology*, vol. 294, pp. 105–112, 2016.
 - [12] Y. Wang, T. Li, F. J. Muzzio, and B. J. Glasser, “Predicting feeder performance based on material flow properties,” *Powder Technology*, vol. 308, pp. 135–148, Feb. 2017, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2016.12.010](https://doi.org/10.1016/j.powtec.2016.12.010).
 - [13] F. J. Muzzio, T. Shinbrot, and B. J. Glasser, “Powder technology in the pharmaceutical industry: The need to catch up fast,” *Powder Technology*, vol. 124, no. 1, pp. 1–7, Apr. 2002, ISSN: 0032-5910. DOI: [10.1016/S0032-5910\(01\)00482-X](https://doi.org/10.1016/S0032-5910(01)00482-X).
 - [14] S. Banerjee, “Properties of refractories,” in *Refractories Handbook*, G. Schacht, Ed. Marcel Dekker, 2004, pp. 1–10.
 - [15] M. N. Rahaman, *Ceramic Processing and Sintering*, 2nd ed. Boca Raton: CRC Press, Jan. 2017, ISBN: 978-1-315-27412-6. DOI: [10.1201/9781315274126](https://doi.org/10.1201/9781315274126).
 - [16] B. J. Kellett and F. F. Lange, “Thermodynamics of densification: I, sintering of simple particle arrays, equilibrium configurations, pore stability, and shrinkage,” *Journal of the American Ceramic Society*, vol. 72, no. 5, pp. 725–734, 1989, ISSN: 1551-2916. DOI: [10.1111/j.1151-2916.1989.tb06208.x](https://doi.org/10.1111/j.1151-2916.1989.tb06208.x).

- [17] X. Kuang, G. Carotenuto, and L. Nicolais, “A review of ceramic sintering and suggestions on reducing sintering temperatures,” *Advanced Performance Materials*, vol. 4, no. 3, pp. 257–274, 1997.
- [18] J. Chappell, T. A. Ring, and J. D. Birchall, “Particle size distribution effects on sintering rates,” *Journal of Applied Physics*, vol. 60, no. 1, pp. 383–391, 1986.
- [19] R. M. German, “Prediction of sintered density for bimodal powder mixtures,” *Metallurgical Transactions A*, vol. 23, no. 5, pp. 1455–1465, May 1992, ISSN: 0360-2133, 1543-1940. DOI: [10.1007/BF02647329](https://doi.org/10.1007/BF02647329).
- [20] L. Martin, D. Nagle, and M. Rosen, “Effect of particle size distribution upon specific surface area and ultrasonic velocity in sintered ceramic powders,” *Materials Science and Engineering: A*, vol. 246, no. 1-2, pp. 151–160, May 1998, ISSN: 09215093. DOI: [10.1016/S0921-5093\(97\)00757-0](https://doi.org/10.1016/S0921-5093(97)00757-0).
- [21] C. L. Martin and D. Bouvard, “Isostatic compaction of bimodal powder mixtures and composites,” *International Journal of Mechanical Sciences*, vol. 46, no. 6, pp. 907–927, 2004, ISSN: 0020-7403. DOI: [10.1016/j.ijmecsci.2004.05.012](https://doi.org/10.1016/j.ijmecsci.2004.05.012).
- [22] C. W. Park and D. Y. Yoon, “Effects of SiO_2 , CaO , and MgO additions on the grain growth of alumina,” *Journal of the American Ceramic Society*, vol. 83, no. 10, pp. 2605–2609, 2000, ISSN: 1551-2916. DOI: [10.1111/j.1151-2916.2000.tb01596.x](https://doi.org/10.1111/j.1151-2916.2000.tb01596.x).
- [23] K. Maca, V. Pouchly, K. Bodišová, P. Švančárek, and D. Galusek, “Densification of fine-grained alumina ceramics doped by magnesia, yttria and zirconia evaluated by two different sintering models,” *Journal of the European Ceramic Society*, vol. 34, no. 16, pp. 4363–4372, Dec. 2014, ISSN: 0955-2219. DOI: [10.1016/j.jeurceramsoc.2014.06.030](https://doi.org/10.1016/j.jeurceramsoc.2014.06.030).

- [24] F. Thevenot, "Boron carbide - a comprehensive review," *Journal of the European Ceramic Society*, vol. 6, no. 4, pp. 205–225, Jan. 1990, ISSN: 0955-2219. DOI: [10.1016/0955-2219\(90\)90048-K](https://doi.org/10.1016/0955-2219(90)90048-K).
- [25] T. K. Roy, C. Subramanian, and A. K. Suri, "Pressureless sintering of boron carbide," *Ceramics International*, vol. 32, no. 3, pp. 227–233, Jan. 2006, ISSN: 0272-8842. DOI: [10.1016/j.ceramint.2005.02.008](https://doi.org/10.1016/j.ceramint.2005.02.008).
- [26] V. D. Krstic, "Optimization of mechanical properties in sic control of the microstructure," *MRS Bulletin*, vol. 20, no. 2, pp. 46–48, Feb. 1995, ISSN: 0883-7694, 1938-1425. DOI: [10.1557/S0883769400049228](https://doi.org/10.1557/S0883769400049228).
- [27] F. F. Lange, "Hot-pressing behaviour of silicon carbide powders with additions of aluminium oxide," *Journal of Materials Science*, vol. 10, no. 2, pp. 314–320, Feb. 1975, ISSN: 0022-2461, 1573-4803. DOI: [10.1007/BF00540356](https://doi.org/10.1007/BF00540356).
- [28] S. Hampshire, "Silicon nitride ceramics - review of structure, processing and properties," *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 24, no. 1, p. 8, 2007.
- [29] W. Han, Y. Li, G. Chen, and Q. Yang, "Effect of sintering additive composition on microstructure and mechanical properties of silicon nitride," *Materials Science and Engineering: A*, vol. 700, pp. 19–24, Jul. 2017, ISSN: 09215093. DOI: [10.1016/j.msea.2017.05.100](https://doi.org/10.1016/j.msea.2017.05.100).
- [30] A. Gubernat, P. Rutkowski, G. Grabowski, and D. Zientara, "Hot pressing of tungsten carbide with and without sintering additives," *International Journal of refractory metals and hard materials*, vol. 43, pp. 193–199, 2014.
- [31] K. Kornaus, M. Raczka, A. Gubernat, and D. Zientara, "Pressureless sintering of binderless tungsten carbide," *Journal of the European Ceramic Society*, vol. 37, no. 15, pp. 4567–4576, Dec. 2017, ISSN: 0955-2219. DOI: [10.1016/j.jeurceramsoc.2017.06.008](https://doi.org/10.1016/j.jeurceramsoc.2017.06.008).

- [32] R. M. Spriggs, "Expression for effect of porosity on elastic modulus of polycrystalline refractory materials, particularly aluminum oxide," *Journal of the American Ceramic Society*, vol. 44, no. 12, 628-629, Dec. 1961, ISSN: 0002-7820, 1551-2916. DOI: [10.1111/j.1151-2916.1961.tb11671.x](https://doi.org/10.1111/j.1151-2916.1961.tb11671.x).
- [33] K. K. Phani and S. K. Niyogi, "Young's modulus of porous brittle solids," *Journal of Materials Science*, vol. 22, no. 1, pp. 257-263, Jan. 1987, ISSN: 0022-2461, 1573-4803. DOI: [10.1007/BF01160581](https://doi.org/10.1007/BF01160581).
- [34] R. W. Rice, C. C. Wu, and F. Boichelt, "Hardness-grain-size relations in ceramics," *Journal of the American Ceramic Society*, vol. 77, no. 10, pp. 2539-2553, 1994, ISSN: 1551-2916. DOI: [10.1111/j.1151-2916.1994.tb04641.x](https://doi.org/10.1111/j.1151-2916.1994.tb04641.x).
- [35] R. W. Rice, "The porosity dependence of physical properties of materials: A summary review," *Key Engineering Materials*, vol. 115, pp. 1-20, 1996, ISSN: 1662-9795. DOI: [10.4028/www.scientific.net/KEM.115.1](https://doi.org/10.4028/www.scientific.net/KEM.115.1).
- [36] K. K. Phani and D. Sanyal, "The relations between the shear modulus, the bulk modulus and young's modulus for porous isotropic ceramic materials," *Materials Science and Engineering: A*, vol. 490, no. 1, pp. 305-312, Aug. 2008, ISSN: 0921-5093. DOI: [10.1016/j.msea.2008.01.030](https://doi.org/10.1016/j.msea.2008.01.030).
- [37] S. J. Glass and K. G. Ewsuk, "Ceramic powder compaction," *Mrs Bulletin*, vol. 22, no. 12, pp. 24-28, 1997.
- [38] R. Freeman and X. Fu, "Characterisation of powder bulk, dynamic flow and shear properties in relation to die filling," *Powder Metallurgy*, vol. 51, no. 3, pp. 196-201, 2008, ISSN: 0032-5899, 1743-2901. DOI: [10.1179/174329008X324115](https://doi.org/10.1179/174329008X324115).
- [39] E. Beaunac, M. Leturia, A. -. Robisson, C. Ablitzer, and K. Saleh, "Comparison of two powder conditioning methods to improve uo2 powder flowability

- for press die filling,” *Powder Technology*, vol. 395, pp. 1–13, Jan. 2022, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2021.09.003](https://doi.org/10.1016/j.powtec.2021.09.003).
- [40] J. Halloran, “Role of powder agglomerates in ceramic processing,” *Forming of Ceramics. Advances in Ceramics*, no. 9, p. 67, 1983.
- [41] C.-Y. Wu, O. Ruddy, A. Bentham, B. Hancock, S. Best, and J. Elliott, “Modelling the mechanical behaviour of pharmaceutical powders during compaction,” *Powder Technology*, vol. 152, no. 1-3, pp. 107–117, Apr. 2005, ISSN: 00325910. DOI: [10.1016/j.powtec.2005.01.010](https://doi.org/10.1016/j.powtec.2005.01.010).
- [42] R. M. German, *Sintering Theory and Practice*. Jan. 1996.
- [43] F. Klocke, “Modern approaches for the production of ceramic components,” *Journal of the European Ceramic Society*, vol. 17, no. 2-3, 457–465, Jan. 1997, ISSN: 09552219. DOI: [10.1016/S0955-2219\(96\)00163-X](https://doi.org/10.1016/S0955-2219(96)00163-X).
- [44] J. Zheng and J. S. Reed, “Particle and Granule Parameters Affecting Compaction Efficiency in Dry Pressing,” *Journal of the American Ceramic Society*, vol. 71, no. 11, pp. C456–C458, 1988, ISSN: 1551-2916. DOI: [10.1111/j.1151-2916.1988.tb07546.x](https://doi.org/10.1111/j.1151-2916.1988.tb07546.x).
- [45] K. Kendall, “Influence of powder structure on processing and properties of advanced ceramics,” *Powder Technology*, vol. 58, no. 3, pp. 151–161, Jul. 1989, ISSN: 00325910. DOI: [10.1016/0032-5910\(89\)80109-3](https://doi.org/10.1016/0032-5910(89)80109-3).
- [46] J. J. Lannutti, “Characterization and control of compact microstructure,” *MRS Bulletin*, vol. 22, no. 12, pp. 38–44, Dec. 1997, ISSN: 0883-7694, 1938-1425. DOI: [10.1557/S0883769400034734](https://doi.org/10.1557/S0883769400034734).
- [47] P. Lu, J. J. Lannutti, P. Klobes, and K. Meyer, “X-ray Computed Tomography and Mercury Porosimetry for Evaluation of Density Evolution and Porosity Distribution,” *Journal of the American Ceramic Society*, vol. 83, no. 3, pp. 518–522, 2000, ISSN: 1551-2916. DOI: [10.1111/j.1151-2916.2000.tb01227.x](https://doi.org/10.1111/j.1151-2916.2000.tb01227.x).

- [48] P. Chen, G.-Y. Kim, and J. Ni, “Investigations in the compaction and sintering of large ceramic parts,” *Journal of Materials Processing Technology*, vol. 190, no. 1-3, pp. 243–250, Jul. 2007, ISSN: 09240136. DOI: [10.1016/j.jmatprotec.2007.02.039](https://doi.org/10.1016/j.jmatprotec.2007.02.039).
- [49] J. Boehmler, F. Moitrier, T. Bourré, J. Rossit, F. Delorme, and S. Lemonnier, “Influence of powder state and rheology on sintering behaviour of sic,” *Open Ceramics*, vol. 8, Dec. 2021, ISSN: 2666-5395. DOI: [10.1016/j.oceram.2021.100192](https://doi.org/10.1016/j.oceram.2021.100192).
- [50] H. G. Merkus, *Particle size measurements: fundamentals, practice, quality*, ser. Particle technology series. Springer, 2009, ISBN: 978-1-4020-9015-8.
- [51] E. C. Abdullah and D. Geldart, “The use of bulk density measurements as flowability indicators,” *Powder Technology*, vol. 102, no. 2, pp. 151–165, 1999, ISSN: 0032-5910. DOI: [10.1016/S0032-5910\(98\)00208-3](https://doi.org/10.1016/S0032-5910(98)00208-3).
- [52] ASTM Standard D6393-21, “Standard test method for bulk solids characterization by carr indices,” 2008. DOI: [10.1520/D6393_D6393M-21](https://doi.org/10.1520/D6393_D6393M-21).
- [53] R. O. Grey and J. K. Beddow, “On the hausner ratio and its relationship to some properties of metal powders,” *Powder Technology*, vol. 2, no. 6, pp. 323–326, 1969, ISSN: 0032-5910. DOI: [10.1016/0032-5910\(69\)80024-0](https://doi.org/10.1016/0032-5910(69)80024-0).
- [54] H. H. Hausner, “Friction conditions in a mass of metal powder,” Polytechnic Inst. of Brooklyn. Univ. of California, Los Angeles, Tech. Rep., 1967.
- [55] A. Dutta and L. Dullea, “A comparative evaluation of negatively and positively charged submicron particles as flow conditioners for a cohesive powder,” in *AIChE Symposium Series*, vol. 86, 1990, pp. 26–40.
- [56] R. L. Carr, “Evaluating flow properties of solids,” *Chem. Eng.*, vol. 18, pp. 163–168, 1965.

- [57] N. Harnby, A. Hawkins, and D. Vandame, “The use of bulk density determination as a means of typifying the flow characteristics of loosely compacted powders under conditions of variable relative humidity,” *Chemical engineering science*, vol. 42, no. 4, pp. 879–888, 1987.
- [58] G. E. Amidon, P. J. Secreast, and D. Mudie, “Particle, powder, and compact characterization,” in *Developing solid oral dosage forms*, Elsevier, 2009, pp. 163–186.
- [59] ASTM Standard B213-20, “Standard test methods for flow rate of metal powders using the hall flowmeter funnel,” 2020. DOI: [10.1520/B0213-20](https://doi.org/10.1520/B0213-20).
- [60] ISO 4490, *Metallic powders — Determination of flow rate by means of a calibrated funnel (Hall flowmeter)*, 2018.
- [61] MPIF 03, “Method for determination of flow rate of free-flowing metal powders using hall apparatus,” *Standard Test Methods for Metal Powders and Powder Metallurgy Products*, 2022.
- [62] G. Hagen, *Bericht über die zur Bekanntmachung geeigneten Verhandlungen der Königl. Preuss. Akademie der Wissenschaften zu Berlin. der Wissenschaften, Königliche Akademie*, 1855.
- [63] B. P. Tighe and M. Sperl, “Pressure and motion of dry sand: Translation of hagen’s paper from 1852,” *Granular Matter*, vol. 9, no. 3, pp. 141–144, Jun. 2007, ISSN: 1434-7636. DOI: [10.1007/s10035-006-0027-x](https://doi.org/10.1007/s10035-006-0027-x).
- [64] W. A. Beverloo, H. A. Leniger, and J. van de Velde, “The flow of granular solids through orifices,” *Chemical Engineering Science*, vol. 15, no. 3, pp. 260–269, Sep. 1961, ISSN: 0009-2509. DOI: [10.1016/0009-2509\(61\)85030-6](https://doi.org/10.1016/0009-2509(61)85030-6).
- [65] J. R. Darias, M. A. Madrid, and L. A. Pagnaloni, “Differential equation for the flow rate of discharging silos based on energy balance,” *Physical Review E*, vol. 101, no. 5, p. 052905, May 2020, ISSN: 2470-0045, 2470-0053. DOI: [10.1103/PhysRevE.101.052905](https://doi.org/10.1103/PhysRevE.101.052905).

- [66] R. M. Nedderman, *Statics and kinematics of granular materials*. Cambridge University Press Cambridge, 1992, vol. 352.
- [67] A. W. Jenike, “Storage and flow of solids,” *Bulletin No. 123, Utah State University*, 1964.
- [68] ASTM Standard D6773-16, “Standard shear test method for bulk solids using the schulze ring shear tester,” 2002. DOI: [10.1520/D6773-16](https://doi.org/10.1520/D6773-16).
- [69] ASTM Standard D6128-16, “Test method for shear testing of bulk solids using the jenike shear cell,” 2000. DOI: [10.1520/D6128-16](https://doi.org/10.1520/D6128-16).
- [70] ASTM Standard D7891-15, “Standard test method for shear testing of powders using the freeman technology ft4 powder rheometer shear cell,” 2015. DOI: [10.1520/D7891-15](https://doi.org/10.1520/D7891-15).
- [71] J. W. Carson and H. Wilms, “Development of an international standard for shear testing,” *Powder Technology*, vol. 167, no. 1, pp. 1–9, 2006, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2006.04.005](https://doi.org/10.1016/j.powtec.2006.04.005).
- [72] S. Koynov, B. Glasser, and F. Muzzio, “Comparison of three rotational shear cell testers: Powder flowability and bulk density,” *Powder Technology*, vol. 283, pp. 103–112, Oct. 2015, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2015.04.027](https://doi.org/10.1016/j.powtec.2015.04.027).
- [73] V. Ganesan, K. Muthukumarappan, and K. A. Rosentrater, “Flow properties of DDGS with varying soluble and moisture contents using jenike shear testing,” in *2007 ASAE Annual Meeting*, American Society of Agricultural and Biological Engineers, 2007, p. 1.
- [74] R. J. Berry and M. S. A. Bradley, “Investigation of the effect of test procedure factors on the failure loci and derived failure functions obtained from annular shear cells,” *Powder Technology*, Special Edition from the PSA2005 Conference, vol. 174, no. 1, pp. 60–63, 2007, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2006.10.023](https://doi.org/10.1016/j.powtec.2006.10.023).

- [75] J. F. Carr and D. M. Walker, "An annular shear cell for granular materials," *Powder Technology*, vol. 1, no. 6, pp. 369–373, 1968, ISSN: 0032-5910. DOI: [10.1016/0032-5910\(68\)80019-1](https://doi.org/10.1016/0032-5910(68)80019-1).
- [76] R. E. Freeman, J. R. Cooke, and L. C. R. Schneider, "Measuring shear properties and normal stresses generated within a rotational shear cell for consolidated and non-consolidated powders," *Powder Technology*, Selection of Papers from the Symposium Powder Science and Technology - Powders and Sintered Material STP-PMF 2007, vol. 190, no. 1, pp. 65–69, 2009, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2008.04.084](https://doi.org/10.1016/j.powtec.2008.04.084).
- [77] D. Schulze, "Flowability and time consolidation measurements using a ring shear tester," *Powder handling and processing*, vol. 8, no. 3, pp. 221–226, 1996.
- [78] J. Schwedes, "Flow properties of bulk solids and their use in solving industrial problems," in *Handbook of conveying and handling of particulate solids*, A. Levy and H. Kalman, Eds., ser. Handbook of powder technology. Elsevier Science B.V., 2001, vol. 10, pp. 137–152. DOI: [https://doi.org/10.1016/S0167-3785\(01\)80016-6](https://doi.org/10.1016/S0167-3785(01)80016-6). [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0167378501800166>.
- [79] A. W. Jenike, "Gravity flow of bulk solids," *Bull. Utah Engng Exp. Station*, vol. 108, 1961.
- [80] B. El Kassem, Y. Heider, T. Brinz, and B. Markert, "A multivariate statistical approach to analyze the impact of material attributes and process parameters on the quality performance of an auger dosing process," *Journal of Drug Delivery Science and Technology*, vol. 60, p. 101 950, 2020.
- [81] R. Freeman, "Measuring the flow properties of consolidated, conditioned and aerated powders - a comparative study using a powder rheometer and a rotational shear cell," *Powder Technology*, Special Edition from the PSA2005 Conference, vol. 174, no. 1, pp. 25–33, 2007, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2006.10.016](https://doi.org/10.1016/j.powtec.2006.10.016).

- [82] C. Hare, U. Zafar, M. Ghadiri, T. Freeman, J. Clayton, and M. J. Murtagh, “Analysis of the dynamics of the ft4 powder rheometer,” *Powder Technology, Pharmaceutical Particle Technology*, vol. 285, pp. 123–127, 2015, ISSN: 0032-5910. DOI: [10.1016/j.powtec.2015.04.039](https://doi.org/10.1016/j.powtec.2015.04.039).
- [83] Freeman Technology, *Shear Cell Test (W7018)*, 2020.
- [84] —, *Conditioning (W7006)*, 2007.
- [85] —, *Stability and Variable Flow Rate Test (W7013)*, 2019.
- [86] —, *Density (W7007)*, 2008.
- [87] —, *The Basic Flowability Energy (W7030)*, 2013.
- [88] —, *Specific Energy (W7031)*, 2008.
- [89] —, *Stability Method (W7011)*, 2010.
- [90] —, *Variable Flow Rate Method (W7012)*, 2007.
- [91] —, *Compressibility (W7008)*, 2019.
- [92] —, *Direct Pressure Consolidation (W7009)*, 2017.
- [93] ASTM Standard B962-08, “Standard test methods for density of compacted or sintered powder metallurgy (pm) products using archimedes’ principle,” 2013. DOI: [10.1520/B0962-08](https://doi.org/10.1520/B0962-08). [Online]. Available: <https://www.astm.org/b0962-08.html>.
- [94] I. J. McColm, *Ceramic Hardness*. Boston, MA: Springer US, 1990, ISBN: 978-1-4419-3213-6. DOI: [10.1007/978-1-4757-4732-4](https://doi.org/10.1007/978-1-4757-4732-4). [Online]. Available: <http://link.springer.com/10.1007/978-1-4757-4732-4>.
- [95] J. B. Wachtman, W. R. Cannon, and M. J. Matthewson, *Mechanical Properties of Ceramics*. John Wiley & Sons, Aug. 2009, ISBN: 978-0-470-45150-2.
- [96] ASTM Standard C1326-13, “Standard test method for knoop indentation hardness of advanced ceramics,” Jan. 2018. DOI: [10.1520/C1326-13R18](https://doi.org/10.1520/C1326-13R18). [Online]. Available: <https://www.astm.org/c1326-13r18.html>.

- [97] ASTM Standard C1327-15, “Standard test method for vickers indentation hardness of advanced ceramics,” Jul. 2019. DOI: [10 . 1520 / C1327 – 15R19](https://doi.org/10.1520/C1327-15R19). [Online]. Available: <https://www.astm.org/c1327-15r19.html>.
- [98] V. E. Lysaght, *Indentation hardness testing*. Reinhold Publishing Corporation, 1949.
- [99] J. B. Quinn and G. D. Quinn, “Indentation brittleness of ceramics: A fresh approach,” *Journal of Materials Science*, vol. 32, no. 16, pp. 4331–4346, Aug. 1997, ISSN: 1573-4803. DOI: [10.1023/A:1018671823059](https://doi.org/10.1023/A:1018671823059).
- [100] ASTM Standard E384-17, “Test method for microindentation hardness of materials,” DOI: [10.1520/E0384-17](https://doi.org/10.1520/E0384-17). [Online]. Available: <http://www.astm.org/cgi-bin/resolver.cgi?E384-17>.
- [101] ASTM Standard C1161-18, “Test method for flexural strength of advanced ceramics at ambient temperature,” Feb. 2019. DOI: [10 . 1520 / C1161 – 18](https://doi.org/10.1520/C1161-18). [Online]. Available: <https://www.astm.org/c1161-18.html>.
- [102] W. Weibull, “A Statistical Distribution Function of Wide Applicability,” *Journal of applied mechanics*, 1951. [Online]. Available: [https : / / hal . archives-ouvertes.fr/hal-03112318](https://hal.archives-ouvertes.fr/hal-03112318).
- [103] ASTM Standard C1239-13, “Standard practice for reporting uniaxial strength data and estimating weibull distribution parameters for advanced ceramics,” Jul. 2018. DOI: [10 . 1520 / C1239 – 13R18](https://doi.org/10.1520/C1239-13R18). [Online]. Available: <https://www.astm.org/c1239-13r18.html>.
- [104] A. A. Griffith, “The phenomenon of rupture and flow in solids,” *Phil. Trans. Royal Soc. London, A*, vol. 221, pp. 163–198, 1920.
- [105] I. J. McColm, “Ceramic science for materials technologists,” 1983.

- [106] C. B. Carter and M. G. Norton, *Ceramic Materials*. New York, NY: Springer New York, 2013, ISBN: 978-1-4614-3522-8. DOI: [10.1007/978-1-4614-3523-5](https://doi.org/10.1007/978-1-4614-3523-5). [Online]. Available: <http://link.springer.com/10.1007/978-1-4614-3523-5>.
- [107] B. R. Golla, A. Mukhopadhyay, B. Basu, and S. K. Thimmappa, “Review on ultra-high temperature boride ceramics,” *Progress in Materials Science*, vol. 111, p. 100 651, 2020.
- [108] W. G. Fahrenholtz, E. J. Wuchina, W. E. Lee, and Y. Zhou, *Ultra-high temperature ceramics: materials for extreme environment applications*. John Wiley & Sons, 2014.
- [109] R. Ropp, “Group 16 (o, s, se, te) alkaline earth compounds,” *Encyclopedia of the Alkaline Earth Compounds*, pp. 105–197, 2013.
- [110] E. Ward, A. Okun, A. Ruder, M. Fingerhut, and K. Steenland, “A mortality study of workers at seven beryllium processing plants,” *American journal of industrial medicine*, vol. 22, no. 6, pp. 885–904, 1992.
- [111] J. F. Shackelford, Y.-H. Han, S. Kim, and S.-H. Kwon, *CRC Materials Science and Engineering Handbook*. CRC Press, 2016.
- [112] *CRC Handbook of Chemistry and Physics*, 97th ed. CRC Press, Jun. 2016, vol. 2016?2017, ISBN: 1-4987-5428-7.
- [113] M. Munro, “Evaluated material properties for a sintered α -alumina,” *Journal of the American Ceramic Society*, vol. 80, no. 8, 1919?1928, 1997, ISSN: 1551-2916. DOI: [10.1111/j.1151-2916.1997.tb03074.x](https://doi.org/10.1111/j.1151-2916.1997.tb03074.x).
- [114] P. Figiel, M. Rozmus, and B. Smuk, “Properties of alumina ceramics obtained by conventional and non-conventional methods for sintering ceramics,” *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 48, no. 1, p. 6, 2011.

- [115] Y. Han, S. Li, T. Zhu, W. Wu, D. An, and Z. Xie, “Enhanced properties of pure alumina ceramics by oscillatory pressure sintering,” *Ceramics International*, vol. 44, no. 5, pp. 5238–5241, Apr. 2018, ISSN: 02728842. DOI: [10.1016/j.ceramint.2017.12.133](https://doi.org/10.1016/j.ceramint.2017.12.133).
- [116] V. Domnich, S. Reynaud, R. A. Haber, and M. Chhowalla, “Boron carbide: Structure, properties, and stability under stress,” *Journal of the American Ceramic Society*, vol. 94, no. 11, pp. 3605–3628, 2011, ISSN: 1551-2916. DOI: [10.1111/j.1551-2916.2011.04865.x](https://doi.org/10.1111/j.1551-2916.2011.04865.x).
- [117] K. Sairam, J. Sonber, T. C. Murthy, C. Subramanian, R. Hubli, and A. Suri, “Development of B₄C-HfB₂ composites by reaction hot pressing,” *International Journal of Refractory Metals and Hard Materials*, vol. 35, pp. 32–40, 2012.
- [118] G. L. Harris, *Properties of silicon carbide*, 13. Iet, 1995.
- [119] L. L. Snead, T. Nozawa, Y. Katoh, T.-S. Byun, S. Kondo, and D. A. Petti, “Handbook of SiC properties for fuel performance modeling,” *Journal of Nuclear Materials*, Nuclear Fuels and Structural Materials 1, vol. 371, no. 1, pp. 329–377, Sep. 2007, ISSN: 0022-3115. DOI: [10.1016/j.jnucmat.2007.05.016](https://doi.org/10.1016/j.jnucmat.2007.05.016).
- [120] B. O. Yavuz and R. E. Tressler, “High temperature mechanical behavior of a chemically vapor deposited beta silicon carbide,” *Ceramics International*, vol. 18, no. 1, pp. 19–26, Jan. 1992, ISSN: 0272-8842. DOI: [10.1016/0272-8842\(92\)90057-K](https://doi.org/10.1016/0272-8842(92)90057-K).
- [121] R. G. Munro, “Material Properties of a Sintered α -SiC,” *Journal of Physical and Chemical Reference Data*, vol. 26, no. 5, pp. 1195–1203, Sep. 1997, ISSN: 0047-2689, 1529-7845. DOI: [10.1063/1.556000](https://doi.org/10.1063/1.556000).
- [122] L. Vargas-Gonzalez, R. F. Speyer, and J. Campbell, “Flexural Strength, Fracture Toughness, and Hardness of Silicon Carbide and Boron Carbide

- Armor Ceramics,” *International Journal of Applied Ceramic Technology*, vol. 7, no. 5, pp. 643–651, 2010, ISSN: 1744-7402. DOI: [10.1111/j.1744-7402.2010.02501.x](https://doi.org/10.1111/j.1744-7402.2010.02501.x).
- [123] O. Penas, R. Zenati, J. Dubois, and G. Fantozzi, “Processing, microstructure, mechanical properties of si₃n₄ obtained by slip casting and pressureless sintering,” *Ceramics International*, vol. 27, no. 5, pp. 591–596, Jan. 2001, ISSN: 0272-8842. DOI: [10.1016/S0272-8842\(01\)00006-2](https://doi.org/10.1016/S0272-8842(01)00006-2).
- [124] F. Cardarelli, *Materials Handbook: A Concise Desktop Reference*. Cham: Springer International Publishing, 2018, ISBN: 978-3-319-38923-3. DOI: [10.1007/978-3-319-38925-7](https://doi.org/10.1007/978-3-319-38925-7). [Online]. Available: <http://link.springer.com/10.1007/978-3-319-38925-7>.
- [125] H. O. Pierson, *Handbook of refractory carbides & nitrides: properties, characteristics, processing and applications*. William Andrew, 1996.
- [126] J. Sun *et al.*, “A review on binderless tungsten carbide: Development and application,” *Nano-Micro Letters*, vol. 12, no. 1, p. 13, Dec. 2019, ISSN: 2150-5551. DOI: [10.1007/s40820-019-0346-1](https://doi.org/10.1007/s40820-019-0346-1).
- [127] A. Nino, K. Takahashi, S. Sugiyama, and H. Taimatsu, “Effects of carbon addition on microstructures and mechanical properties of binderless tungsten carbide,” *Materials Transactions*, vol. 53, no. 8, pp. 1475–1480, 2012, ISSN: 1345-9678, 1347-5320. DOI: [10.2320/matertrans.M2012148](https://doi.org/10.2320/matertrans.M2012148).
- [128] P. Boch, *Ceramic materials: processes, properties and applications*. ISTE USA, 2007, ISBN: 978-1-905209-23-1.
- [129] A. J. Ruys, *Alumina Ceramics: Biomedical and Clinical Applications*. Woodhead Publishing, 2018.
- [130] A. R. Hind, S. K. Bhargava, and S. C. Grocott, “The surface chemistry of bayer process solids: A review,” *Colloids and Surfaces A: Physicochemical and*

- Engineering Aspects*, vol. 146, no. 1, pp. 359–374, Jan. 1999, ISSN: 0927-7757. DOI: [10.1016/S0927-7757\(98\)00798-5](https://doi.org/10.1016/S0927-7757(98)00798-5).
- [131] B. G. Hyde, J. G. Thompson, and R. L. Withers, “Crystal structures of principal ceramic materials,” *Materials Science and Technology*, 2006.
 - [132] R. L. Coble, “Sintering crystalline solids. i. intermediate and final state diffusion models,” *Journal of Applied Physics*, vol. 32, no. 5, pp. 787–792, May 1961, ISSN: 0021-8979. DOI: [10.1063/1.1736107](https://doi.org/10.1063/1.1736107).
 - [133] —, “Sintering crystalline solids. ii. experimental test of diffusion models in powder compacts,” *Journal of Applied Physics*, vol. 32, no. 5, pp. 793–799, May 1961, ISSN: 0021-8979. DOI: [10.1063/1.1736108](https://doi.org/10.1063/1.1736108).
 - [134] S. J. Bennison and M. P. Harmer, “Grain-growth kinetics for alumina in the absence of a liquid phase,” *Journal of the American Ceramic Society*, vol. 68, no. 1, pp. C–22, 1985.
 - [135] A. K. Suri, C. Subramanian, J. K. Sonber, and T. S. R. C. Murthy, “Synthesis and consolidation of boron carbide: A review,” *International Materials Reviews*, vol. 55, no. 1, pp. 4–40, Jan. 2010, ISSN: 0950-6608, 1743-2804. DOI: [10.1179/095066009X12506721665211](https://doi.org/10.1179/095066009X12506721665211).
 - [136] H. C. Longuet-Higgins and M. d. V. Roberts, “The electronic structure of an icosahedron of boron atoms,” *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 230, no. 1180, pp. 110–119, 1955, ISSN: 0080-4630, 2053-9169. DOI: [10.1098/rspa.1955.0115](https://doi.org/10.1098/rspa.1955.0115).
 - [137] E. Acheson, “On carborundum,” *Chem. News*, vol. 68, p. 179, 1893.
 - [138] G. R. Fisher and P. Barnes, “Towards a unified view of polytypism in silicon carbide,” *Philosophical Magazine B*, vol. 61, no. 2, pp. 217–236, 1990.
 - [139] H. Tanaka, “Sintering of silicon carbide,” in *Silicon Carbide Ceramics–1*. Springer, 1991, pp. 213–238.

- [140] S. Prochazka, “Sintering of silicon carbide,” in *Mass transport phenomena in ceramics*. Springer, 1975, pp. 421–431.
- [141] R. A. Alliegro, L. B. Coffin, and J. R. Tinklepaugh, “Pressure-sintered silicon carbide,” *Journal of the American Ceramic Society*, vol. 39, no. 11, pp. 386–389, Nov. 1956, ISSN: 0002-7820, 1551-2916. DOI: [10.1111/j.1151-2916.1956.tb15609.x](https://doi.org/10.1111/j.1151-2916.1956.tb15609.x).
- [142] H. Lange, G. Wotting, and G. Winter, “Silicon nitride—from powder synthesis to ceramic materials,” *Angewandte Chemie International Edition in English*, vol. 30, no. 12, pp. 1579–1597, 1991, ISSN: 1521-3773. DOI: [10.1002/anie.199115791](https://doi.org/10.1002/anie.199115791).
- [143] G. Petzow and M. Herrmann, “Silicon Nitride Ceramics,” *High Performance Non-Oxide Ceramics II*, pp. 47–167, 2002.
- [144] *Carbide, Nitride and Boride Materials Synthesis and Processing*. Dordrecht: Springer Netherlands, 1997, ISBN: 978-94-010-6521-4. DOI: [10.1007/978-94-009-0071-4](https://doi.org/10.1007/978-94-009-0071-4). [Online]. Available: <http://link.springer.com/10.1007/978-94-009-0071-4>.
- [145] R. V. Sara, “Phase equilibria in the system tungsten—carbon,” *Journal of the American Ceramic Society*, vol. 48, no. 5, pp. 251–257, 1965. DOI: [10.1111/j.1151-2916.1965.tb14731.x](https://doi.org/10.1111/j.1151-2916.1965.tb14731.x).
- [146] S. Bastian *et al.*, *Toxicity of tungsten carbide and cobalt-doped tungsten carbide nanoparticles in mammalian cells in vitro*, 2009.
- [147] I. W. G. on the Evaluation of Carcinogenic Risks to Humans *et al.*, “Cobalt in hard metals and cobalt sulfate, gallium arsenide, indium phosphide and vanadium pentoxide,” *IARC monographs on the evaluation of carcinogenic risks to humans*, vol. 86, p. 1, 2006.
- [148] R. German, *Sintering: from empirical observations to scientific principles*. Butterworth-Heinemann, 2014.

- [149] M. H. Bocanegra-Bernal, “Hot isostatic pressing (hip) technology and its applications to metals and ceramics,” *Journal of Materials Science*, vol. 39, no. 21, pp. 6399–6420, Nov. 2004, ISSN: 0022-2461. DOI: [10.1023/B:JMSC.0000044878.11441.90](https://doi.org/10.1023/B:JMSC.0000044878.11441.90).

Appendices

Appendix A

A.1 Sintering and Pressing

Due to the high melting points typical of ceramics, consolidation is done through the process of sintering; wherein a ceramic powder is held under a temperature typically in the range of 0.5-0.75 of its melting point.¹⁵ While it does not melt in this process, joining of particles does occur by atomic diffusion in the solid state, correspondingly referred to as solid-state sintering. At its essence, sintering is about the reduction in surface free energy. The surface of a solid (e.g., powder particle) has excess energy (energy per unit area: γ_{SV} , S for “solid” and V for “vapor”) as atoms are not fully enclosed by the solid, which would minimize free enthalpy, but instead in partial contact with the environment, or vapor. Similarly, the grain boundary, or interface, between two solids joined together also has a surplus surface free energy (γ_{GB} , GB for “grain boundary”); however, this energy is due to structural disorder of the boundary. Generally, $\gamma_{GB} < \gamma_{SV}$, so as powder particles join together energy is reduced.¹²⁸ While sintered powder has a lower energy state, external energy must be applied to overcome a potential barrier between it and the initial higher energy state of the powder.

The reduction in energy during sintering can be described to primarily occur by three methods of matter movement: consolidation, densification, and coarsening. Consolidation involves the development of necks that weld particles together. In densification, porosity is reduced when matter transferred originates from inside grain boundaries. The alternative is where the source of matter is a surface, coarsening the microstructure without decreasing porosity. In ideal sintering, densification would dominate fully after necessary consolidation occurred without grain coarsening. In reality, all three processes may occur simultaneously, and after sufficient consolidation has occurred densification and grain coarsening tend to compete with each other.

The most common of sintering methods is pressureless sintering. For this method, material must be shaped and/or pressed into a form desired for the final product, a green body, prior to heat treatment. Additives for sintering are also commonly used as they generally act to increase γ_{SV} or decrease γ_{GB} , reducing required temperature and/or duration of sintering. Amount and type of additive can also influence resultant consolidated properties, beneficially and detrimentally. The most suitable sintering aid to utilize is material dependent. Reducing necessary sintering temperature and duration may also be achieved by applying pressure during heat treatment. The addition of pressure also greatly facilitates the densification of ceramic materials, and for some enough such that the use of additives is no longer required. The most common method for this is hot pressing, in which a uniaxial pressure is provided while sintering. A more technically involved method is hot isostatic pressing, wherein a gas is used to provide a uniform hydrostatic pressure around the material during heating. Numerous non-traditional sintering methods exist: spark plasma sintering, microwave sintering, selective laser sintering, and so on. However, conventional pressureless sintering and pressure-assisted sintering find much wider use across industry. This is in part due to costs associated with non-traditional methods, greater dimensional restrictions upon the sintered product's form, and for some methods, particularly those of additive manufacturing, limitation in achieving fully densified products.

A.1.1 Pressureless Sintering

Pressureless sintering is the most technologically simple of sintering methods. However, processes required before sintering can be complex. As no pressure is applied during heat treatment, the powder must be formed into a green body of desired shape beforehand. Green body formation is commonly done by casting of a slurry or through pressing. For casting of a slurry, the ceramic powder is mixed with a solvent (usually water or organic), and dispersants and/or binders as needed, to create a colloidal suspension. In slip casting, a slurry with low binder content is

poured into a mold. The contents are then allowed to drain, liquid is pulled into the mold through capillary action, and a solid is left along the mold walls. After further drying the mold is removed with a green body remaining. Green bodies produced through slip casting are thin and have the capability to take on intricate shapes.

The other common method of green body preparation is through pressing, conducted by die compaction or cold isostatic pressing. In die compaction, a powder is restrained within a die while undergoing uniaxial compression. A single moving punch at the top may be used; however, it is more common within industry to have a moving punch at the top and bottom while the die is held fixed. The non-uniform application of pressure can induce density variations within the compact, therefore limiting possible green body forms to small and simple shapes.

On the contrary, cold isostatic pressing allows for the creation of green bodies with larger and more intricate shapes. Cold isostatic pressing is the application of a uniform hydrostatic pressure around a flexible rubber mold filled with powder. Shown in Fig. [A.1](#), there are two modes in which this is done: wet bag and dry bag pressing. In wet bag pressing the mold is filled and sealed air-tight, followed by direct submersion into a pressure vessel filled with oil and then pressed. This process is often used for large and/or complex shapes. The dry bag process does not need mold removal, as it is fixed in place within the pressure vessel. A core is inserted for the mold to form around and push against once pressure is applied. While dry bag pressing is limited to smaller and less complex shapes than wet bag, it does have the capability to be automated.

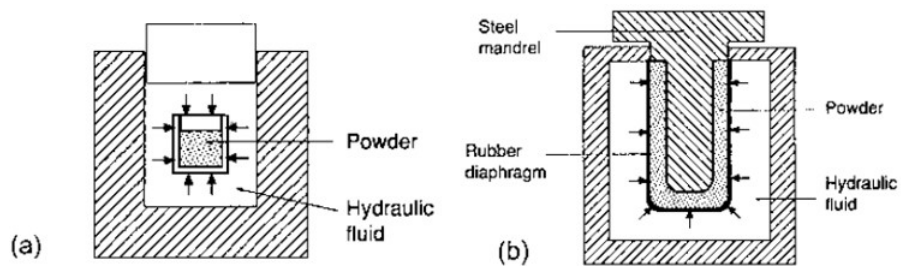


Figure A.1: The two forms of isostatic pressing: (a) wet bag and (b) dry bag. Adapted from Rahaman.¹⁵

Homogeneous filling of dies and molds is important for high-quality reproducible pressing. Fine powders do not flow well or fill uniformly, causing issues during pressing and within resultant green bodies. However, fine powders are beneficial when sintering. The solution to this is to granulate the powder before compaction through the process of spray drying. This method involves using a hot gas to rapidly dry a slurry propelled out of a spray nozzle. The general composition of the slurry used is typically similar to that for casting of a slurry, i.e., inclusion of binders, dispersants, etc. Powder granules produced through spray drying are nearly spherical in shape, greatly increasing flowability and propensity for a more homogeneous fill.

If powders are not too fine and are able to flow well into a die or mold uniformly, then spray drying is not necessary. Nonetheless, lubricants and binders still find use in such cases. Lubricants help to reduce inter-particle friction and friction against the die wall. Lower friction, particularly with the wall, helps to prevent the formation of density gradients during pressing. Binders are beneficial in that they provide additional strength to the green body.

Once a green body is prepared, and undergone any machining of its shape as needed, pressureless sintering may be done. The first required step of sintering is the burnout of volatile material within the green body. Adsorbed water and organic additives such as binders are removed from the green body through heat at a temperature well below that required for sintering. The heat-up rate is kept low and stable, often $<2^{\circ}\text{C}/\text{min}$, as otherwise organic additives may boil and evaporate, resulting in swelling and possibly cracking.¹⁵

After binder burnout, temperature is increased to the sintering temperature. Similar to binder burnout, the heat-up rate during this stage must also be controlled. Beyond furnace characteristics, the size of the sample sets a general upper bound upon the rate of temperature increase. Larger samples necessitate lower heat-up rates to reduce the formation of temperature gradients, which can cause cracking and differential densification of the sample.

The sintering temperature is chosen to be as low as possible while fulfilling densification requirements in a reasonable amount of time (usually less than 24 hours). Typically, this is done isothermally, with the sintering temperature held at a constant value. However, alternative methods may be chosen, particularly for smaller samples often used in lab experiments. In such cases the sample is heated at a constant rate until a specific temperature is reached and then immediately cooled. Other methods include the addition of one or more stages to isothermal sintering.

The final necessary stage is for the sample to cool down to room temperature. As with heat-up rates, the rate of cooling becomes more important with the size of the sample. Smaller samples may be cooled relatively fast without issue. However, larger samples require slower rates to prevent temperature gradients and cracking. Cooling rate can also affect the precipitation of secondary phases and their distribution within a doped sample. After a sample is cooled it is then ready for any post-sintering machining and processing needed.

For pressureless and pressure sintering, use of graphite furnaces is most common. However, lining like boron nitride is necessary in cases where the stoichiometry of the ceramic being sintered can be affected by carbon within the die walls and atmosphere, e.g., boron carbide. This is true even if furnace atmosphere is controlled, which it commonly is. In fact, atmosphere can play a key role as gasses can diffuse into samples and become trapped, degrading densification and final microstructure. Generally larger molecules (argon and nitrogen vs. hydrogen and helium) are used for sintering atmospheres as they are expected to be less likely to diffuse into a sample given their size. However, this is not always applicable as the diffusivity of a gas is dependent on the ceramic being sintered.¹⁵ The safest atmosphere is typically a lack of one, i.e., to sinter under vacuum.

A.1.2 Hot Pressing

As mentioned previously, pressure may be applied during sintering, usually around 10 to 70 MPa.¹²⁸ The addition of pressure increases interfacial energy among particles, thus increasing the driving force for sintering.¹⁷ This results in advantageous effects for processing and material properties: 1) decrease in densification time; 2) considerable reduction in temperatures compared to those required by pressureless sintering; 3) minimization of porosity, possibly to zero; 4) potential for grain growth inhibition.^{17,128} Hot pressing is a simpler method of pressure sintering compared to hot isostatic pressing, but nonetheless still technically complex. The typical setup is a uniaxial hot press, as shown in Fig. A.2.

Hot pressing is essentially a uniaxial die press, as is used for green body formation in pressureless sintering, heated externally. Heating is from resistance or through induction with the die, in which case the die is made from graphite.¹⁴⁸ Hot pressing does not require a green body, but it is limited to smaller and less complex shapes than what could be achieved in pressureless sintering.

A.1.3 Hot Isostatic Pressing

Hot isostatic pressing is analogous to hot pressing as cold isostatic pressing is to uniaxial die compaction. Hot isostatic pressing uses a gas, usually argon, to provide a hydrostatic pressure. The pressure used can take on higher value than what is typical in hot pressing as it is not limited by the strength of a graphite die. Furthermore, more complex shapes can be produced with hot isostatic pressing. A schematic of a hot isostatic press can be seen in Fig. A.3.

Unlike cold isostatic pressing, material under treatment may or may not be encapsulated in hot isostatic pressing. A common method is to apply hot isostatic pressing to a sample after it has undergone pressureless sintering. The sample is sintered to closed porosity (densification of about 95%) then hot isostatically pressed to remove residual porosity without significant coarsening, which can be difficult to

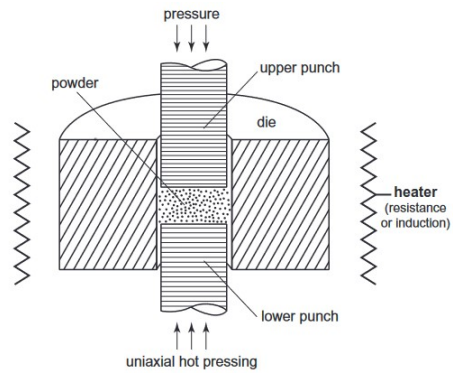


Figure A.2: Schematic of a uniaxial hot press.¹⁴⁸

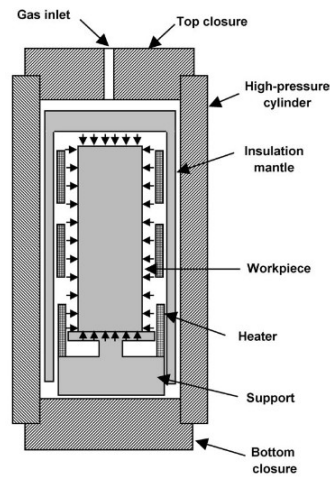


Figure A.3: Schematic of a hot isostatic press.¹⁴⁹

obtain in conventional sintering.^{15,128} If the sample does not have closed porosity, whether it be a green body with shape or simply powder, encapsulation is required, otherwise the sample cannot be densified due to the pressurizing gas filling pores and resisting the sintering stress.¹⁵

Appendix B

B.1 Particle Size Distribution and Chemical Composition Information

Table B.1: Average particle size equivalent for select FEPA-F grades.

FEPA-F Grade	Average Size (μm)
F120	107.5
F180	71.5
F240	44.5
F360	22.8
F600	9.3
F1200	3
F1500	2

Table B.2: Particle size distribution information from certificates of analysis for aluminum oxide grades. Mixed grade values were calculated from mass ratios.

Size	Vendor	d ₃ (μm)	d ₅₀ (μm)	d ₉₄ (μm)
F240	Panadyne	66.31	45.03	33.14
70/30 wt.% F240/F600	Panadyne (Mixed In-House)	50.08	34.44	25.39
F600	Panadyne	14.73	9.74	7.31
70/30 wt.% F600/F1200	Panadyne (Mixed In-House)	12.21	7.76	5.63
F1200	Panadyne	6.34	3.13	1.71
F1200	Atlantic Equipment Engineers	N/A	N/A	N/A
F1200	Metallurgical Supplies	N/A	N/A	N/A

Table B.3: Chemical composition information from certificates of analysis for aluminum oxide grades. Mixed grade values were calculated from mass ratios.

Size	Vendor	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Na ₂ O (%)	SiO ₂ (%)	Na ₂ CO ₃ & K ₂ CO ₃ (%)	TiO ₂ (%)
F240	Panadyne	99.54	0.05	0.31	0.06	-	-
70/30 wt.% F240/F600	Panadyne (Mixed In-House)	99.5	0.053	0.31	0.06	-	-
F600	Panadyne	99.52	0.06	0.31	0.06	-	-
70/30 wt.% F600/F1200	Panadyne (Mixed In-House)	99.51	0.06	0.32	0.06	-	-
F1200	Panadyne	99.50	0.07	0.35	0.06	-	-
F1200	Atlantic Equipment Engineers	99.26	0.09	0.41	0.12	-	-
F1200	Metallurgical Supplies	99.50	0.08	-	0.05	0.3	0.0995

Table B.4: Particle size distribution information from certificates of analysis for boron carbide grades. Mixed grade values were calculated from mass ratios.

Size	Vendor	d_3 [d_{10}] (μm)	d_{50} (μm)	d_{94} [d_{90}] (μm)
F240	Panadyne	61.39	45.81	32.20
70/30 wt.% F240/F600	Panadyne (Mixed In-House)	46.61	34.49	24.15
F600	Panadyne	12.20	8.14	5.39
70/30 wt.% F600/F1200	Panadyne (Mixed In-House)	9.79	6.45	4.17
F1200	Panadyne	4.17	2.51	1.33
F1500 w/ 10% Al_2O_3	GNPGraystar	[3.138]	1.676	[0.780]

Table B.5: Chemical composition information from certificates of analysis for boron carbide grades. Mixed grade values were calculated from mass ratios.

Size	Vendor	B ₄ C (%)	Total B (%)	Free B (%)	Total C (%)	Free C (%)	Fe [Fe ₂ O ₃] %	B ₂ O ₃ (%)
F240	Panadyne	96.91	77.98	N/A	20.55	N/A	0.19	N/A
70/30 wt.% F240/F600	Panadyne (Mixed In-House)	96.35	77.24	N/A	20.90	N/A	0.20	N/A
F600	Panadyne	95.04	75.50	0.22	21.71	1.95	0.21	0.20
70/30 wt.% F600/F1200	Panadyne (Mixed In-House)	94.83	75.89	0.27	21.28	2.07	0.20	0.26
F1200	Panadyne	94.33	76.80	0.40	20.27	2.34	0.17	0.39
F1500 w/ 10% Al ₂ O ₃	GNPGraystar	94.40	77.15	0.60	20.80	2.95	[0.15]	0.50

Table B.6: Particle size distribution and chemical composition information from certificates of analysis for silicon carbide grades. Mixed grade values were calculated from mass ratios.

Size	Vendor	d ₃ (μm)	d ₅₀ (μm)	d ₉₄ (μm)	SiC (%)	Free C (%)	Fe ₂ O ₃ (%)
F120	Panadyne	N/A	N/A	N/A	99.27	0.10	0.11
F180	Panadyne	N/A	N/A	N/A	98.86	0.13	0.15
F240	Panadyne	61.28	43.27	31.19	99.35	0.08	0.15
70/30 wt.% F240/F600	Panadyne (Mixed In-House)	48.06	33.30	23.38	99.23	0.10	0.07
F360	Panadyne	38.48	23.73	12.87	98.90	0.22	0.15
F600	Panadyne	17.21	8.98	5.17	99.26	0.16	0.01
70/30 wt.% F600/F1200	Panadyne (Mixed In-House)	13.72	7.29	4.11	99.24	0.20	0.01
F1200	Panadyne	5.59	3.34	1.65	99.18	0.30	0.016

Table B.7: Particle size distribution and chemical composition information from certificates of analysis for silicon nitride grades.

Grade/Size	Vendor	d ₃ (μm)	d ₅₀ (μm)	d ₉₄ (μm)	Fe (%)	Al (%)	Ca (%)
SiN-6 ($\leq 9 \mu\text{m}$)	Panadyne	N/A	6.50	N/A	0.0075	0.0139	0.0016
SiN-B ($\approx$ F1200)	Panadyne	N/A	3.70	N/A	0.0006	0.00024	0.00006
SiN-9.5 (0.6-0.8 μm)	Panadyne	N/A	N/A	N/A	N/A	N/A	N/A

Table B.8: Particle size distribution information from certificates of analysis for tungsten carbide grades.

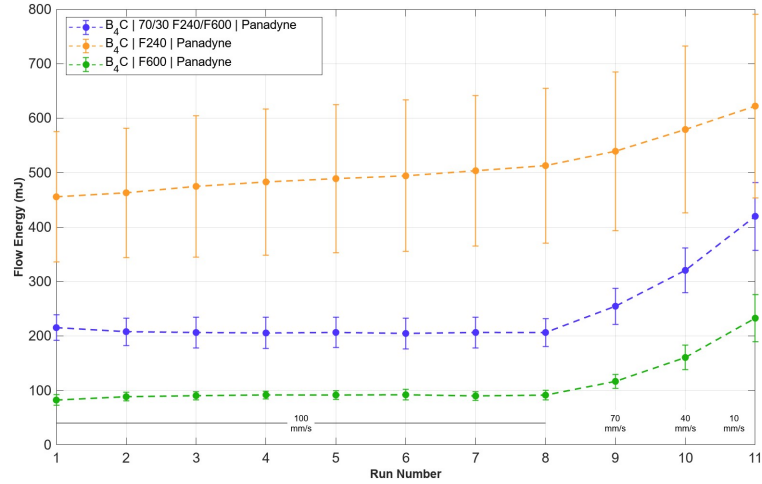
Grade/Size	Vendor	d ₁₀ (μm)	d ₅₀ (μm)	d ₉₄ (μm)
FWC 300 (25-30 μm)	Panadyne	4.01	17.09	34.3
FWC 60 (5.5-6.5 μm)	Panadyne	3.06	6.67	12.19
FWC 20 (2-4 μm)	Panadyne	1.36	2.67	5.02

Table B.9: Chemical composition information from certificates of analysis for tungsten carbide grades.

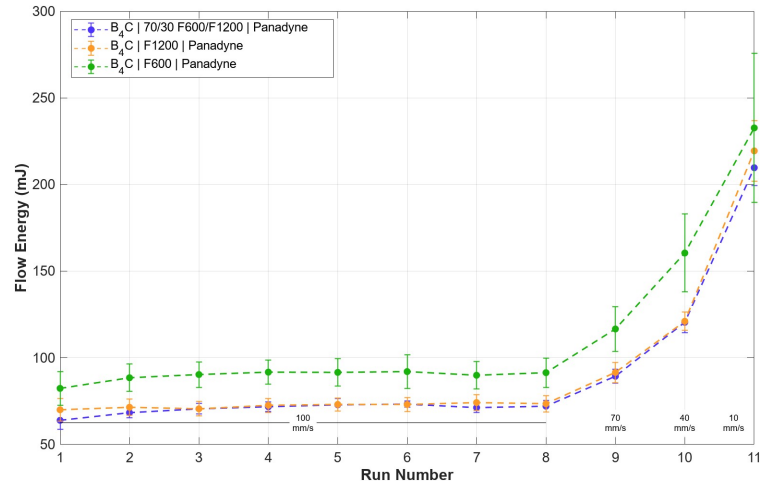
Grade/Size	Vendor	C (%)	O (%)	Fe (%)	Si (%)	Al (%)	Mn (%)	Mg (%)	Ni (%)
FWC 300 (25-30 μm)	Panadyne	0.0100	0.0057	0.0005	0.0005	0.0005	0.0005	0.0005	0.0006
FWC 60 (5.5-6.5 μm)	Panadyne	0.0160	0.0046	0.0005	0.0005	0.0005	0.0005	0.0005	0.0006
FWC 20 (2-4 μm)	Panadyne	0.0290	0.0015	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005

Appendix C

C.1 Supplementary Plots and Tables

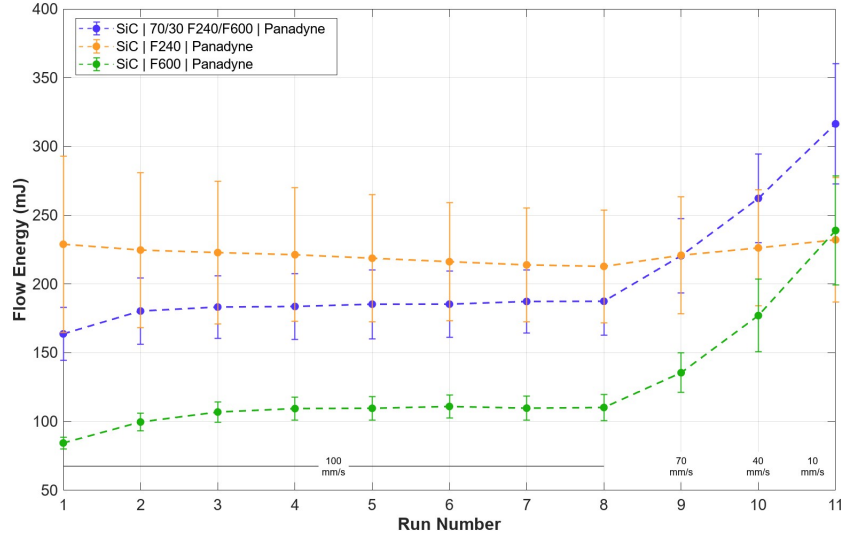


(a) Panadyne B_4C F240, 70/30% mixed F240/F600, and F600 grades

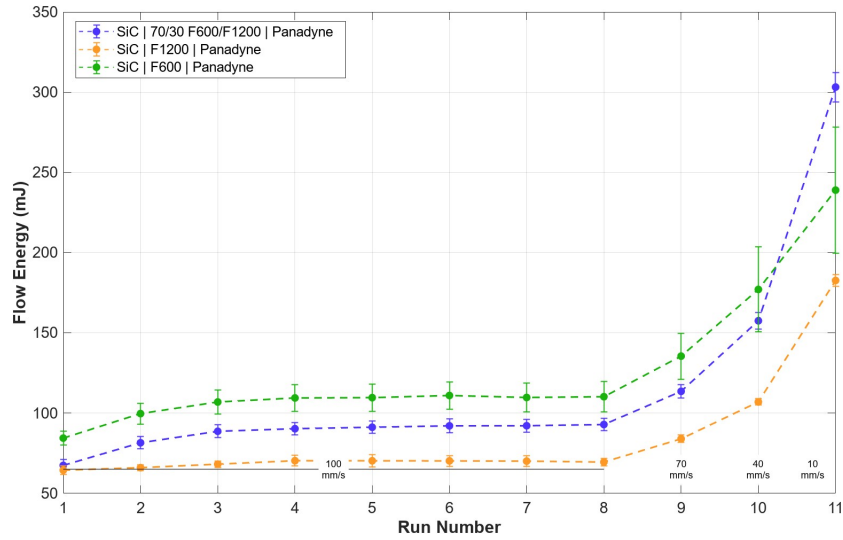


(b) Panadyne B_4C F600, 70/30% mixed F600/F1200, and F1200 grades

Figure C.1: (a) FT4 Stability and Variable Flow Rate data for Panadyne boron carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.

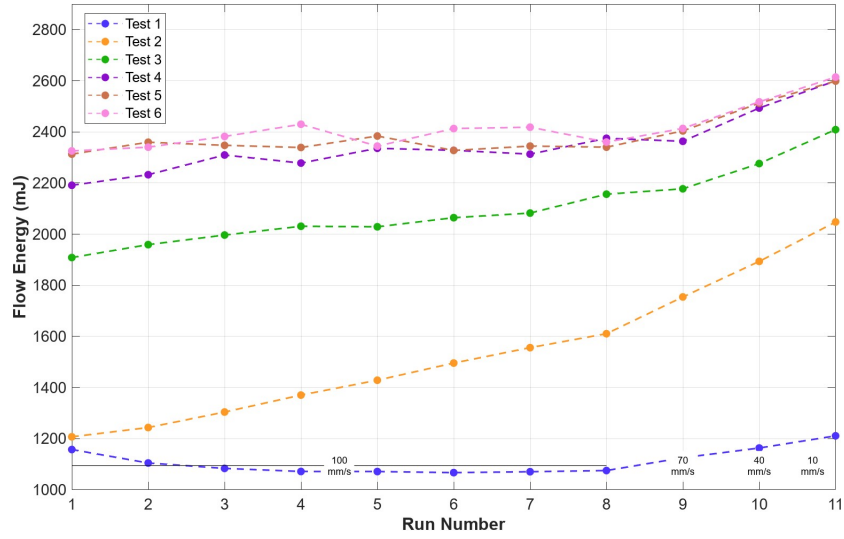


(a) Panadyne SiC F240, 70/30% mixed F240/F600, and F600 grades

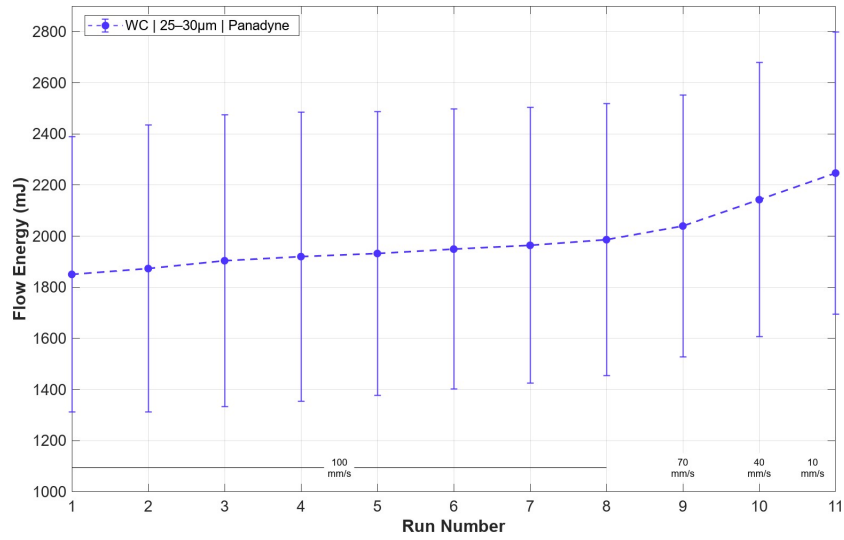


(b) Panadyne SiC F600, 70/30% mixed F600/F1200, and F1200 grades

Figure C.2: (a) FT4 Stability and Variable Flow Rate data for Panadyne silicon carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.

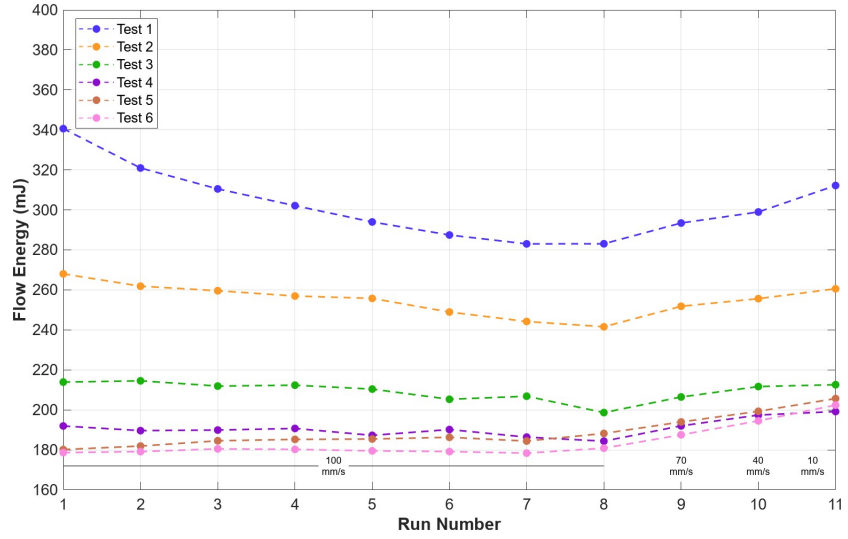


(a) Averaged SVFR data of Panadyne WC FWC 300.

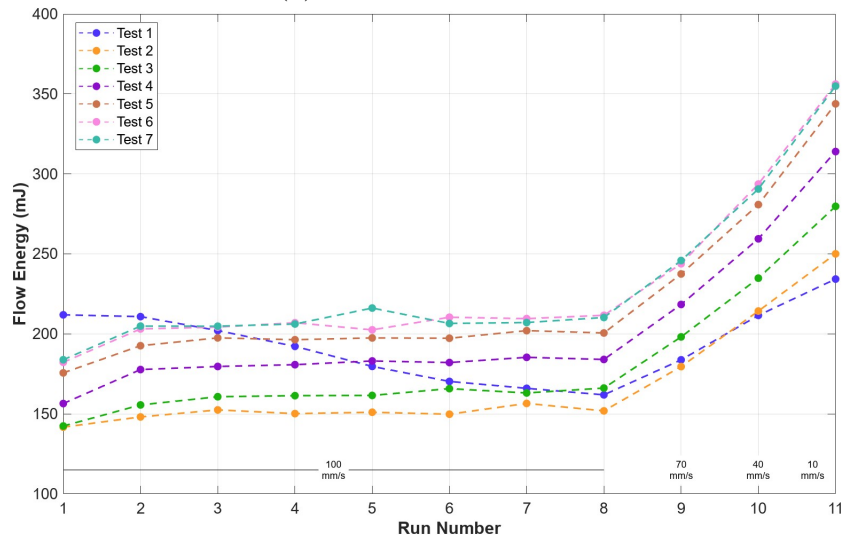


(b) SVFR data of Panadyne WC FWC 300.

Figure C.3: (a) Ungrouped and (b) grouped FT4 Stability and Variable Flow Rate (SVFR) data for six separate tests of Panadyne tungsten carbide FWC 300.

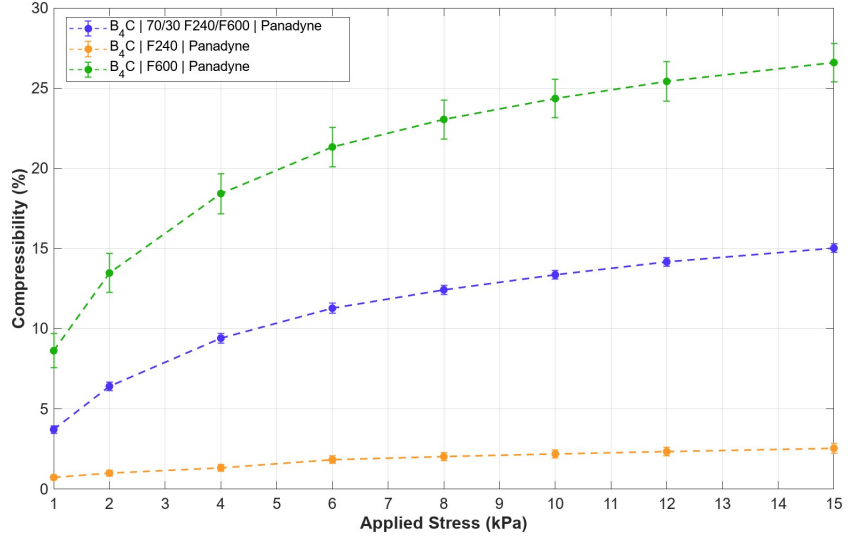


(a) Panadyne SiC F240

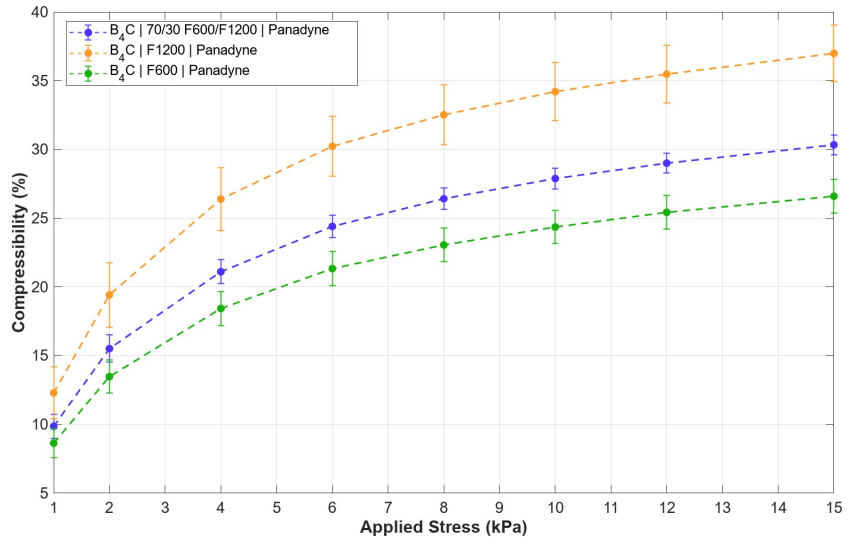


(b) Panadyne SiC 70/30% mixed F240/F600

Figure C.4: (a) Ungrouped FT4 Stability and Variable Flow Rate data for Panadyne silicon carbide F240 and (b) 70/30% mixed F240/F600.

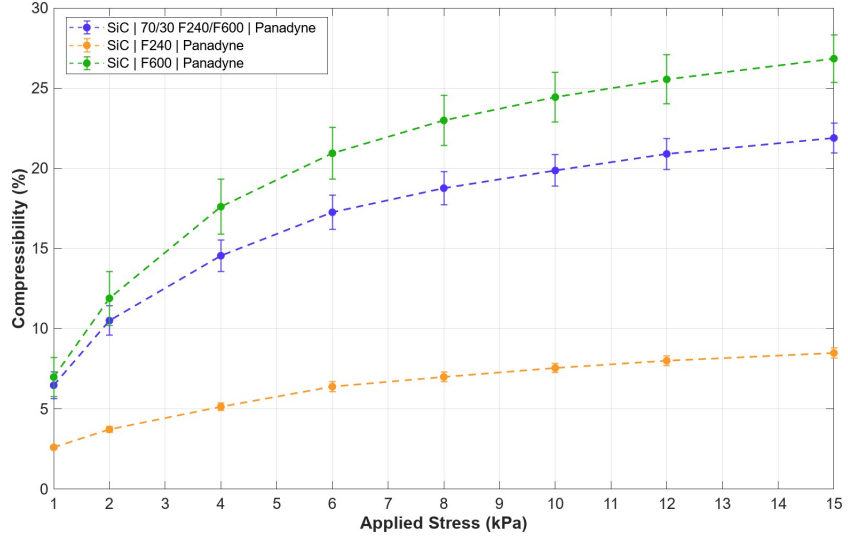


(a) Panadyne B_4C F240, 70/30% mixed F240/F600, and F600 grades

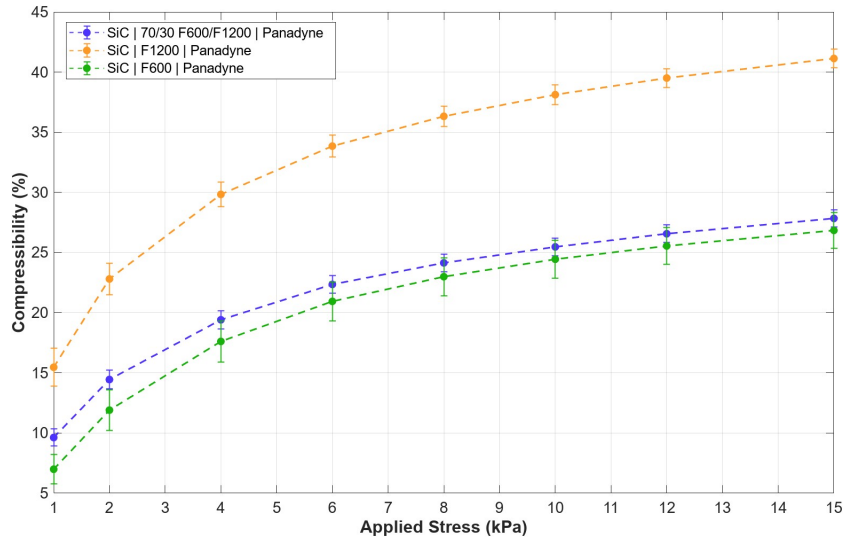


(b) Panadyne B_4C F600, 70/30% mixed F600/F1200, and F1200 grades

Figure C.5: (a) FT4 Compressibility data for Panadyne boron carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.

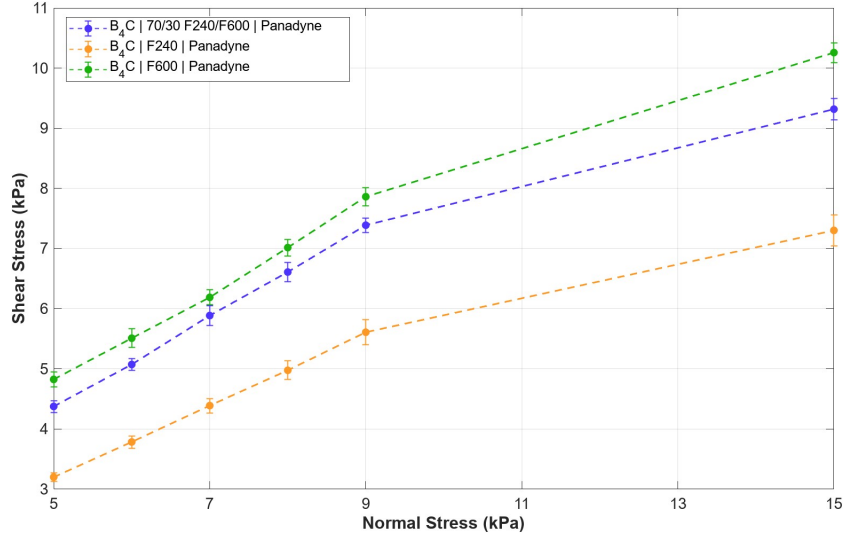


(a) Panadyne SiC F240, 70/30% mixed F240/F600, and F600 grades

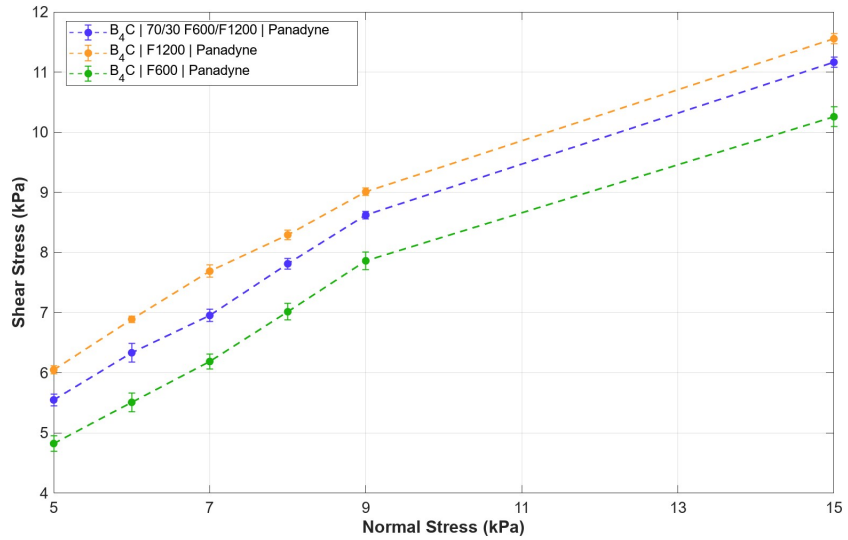


(b) Panadyne SiC F600, 70/30% mixed F600/F1200, and F1200 grades

Figure C.6: (a) FT4 Compressibility data for Panadyne silicon carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.

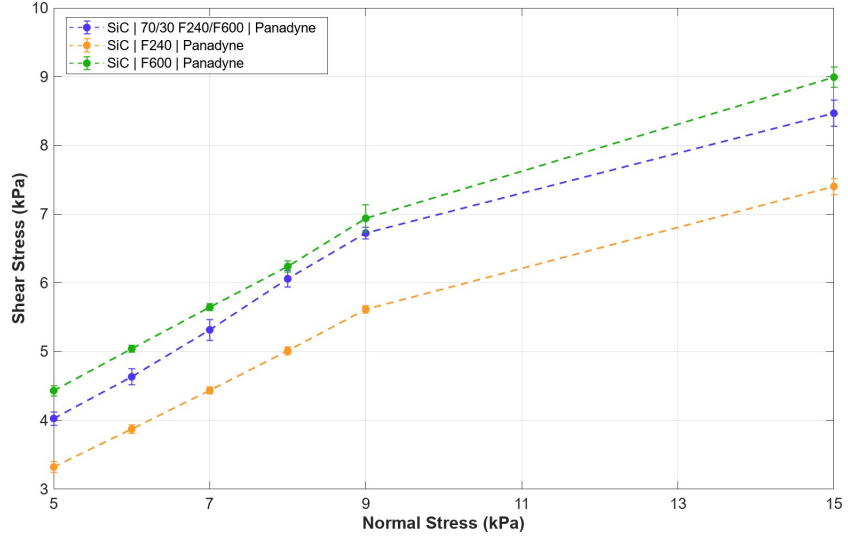


(a) Panadyne B_4C F240, 70/30% mixed F240/F600, and F600 grades

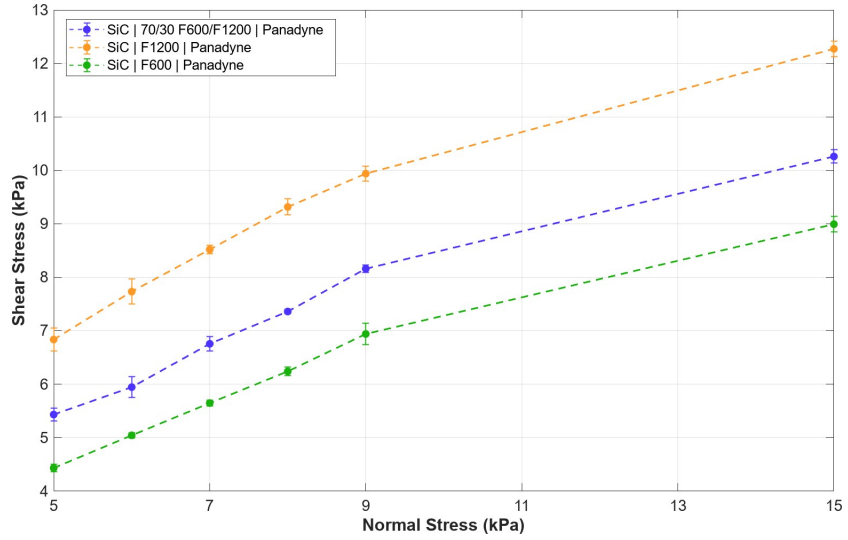


(b) Panadyne B_4C F600, 70/30% mixed F600/F1200, and F1200 grades

Figure C.7: (a) FT4 Shear Cell data for Panadyne boron carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.



(a) Panadyne SiC F240, 70/30% mixed F240/F600, and F600 grades



(b) Panadyne SiC F600, 70/30% mixed F600/F1200, and F1200 grades

Figure C.8: (a) FT4 Shear Cell data for Panadyne silicon carbide F240, 70/30% mixed F240/F600, and F600 grades and (b) F600, 70/30% mixed F600/F1200, and F1200 grades.

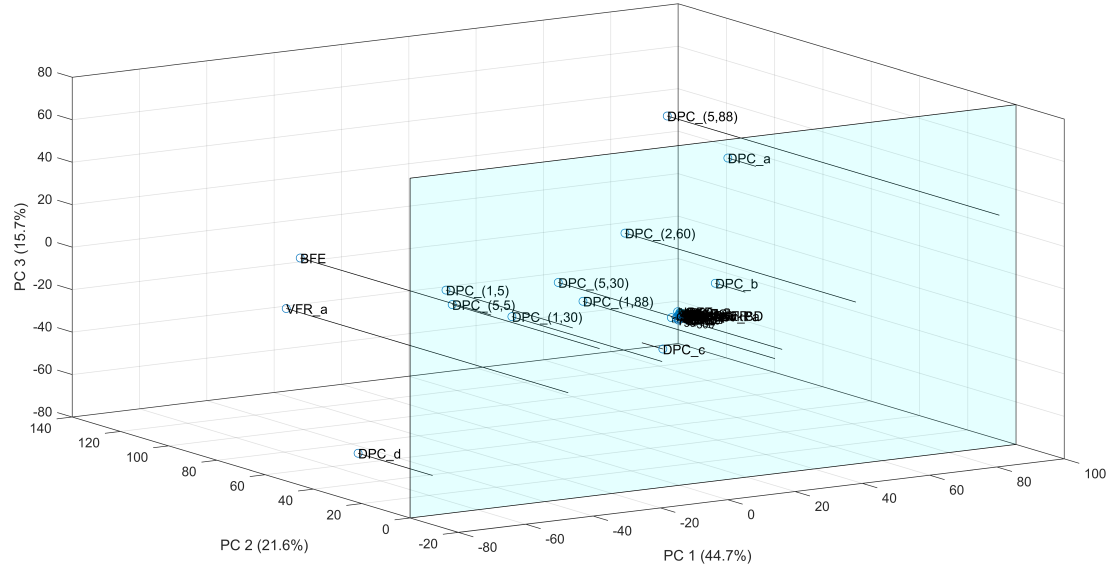


Figure C.9: Plot of loadings of first three principal components (PCs). Residuals along PC 2 are drawn for each loading from the light blue plane that intersects PC 2.

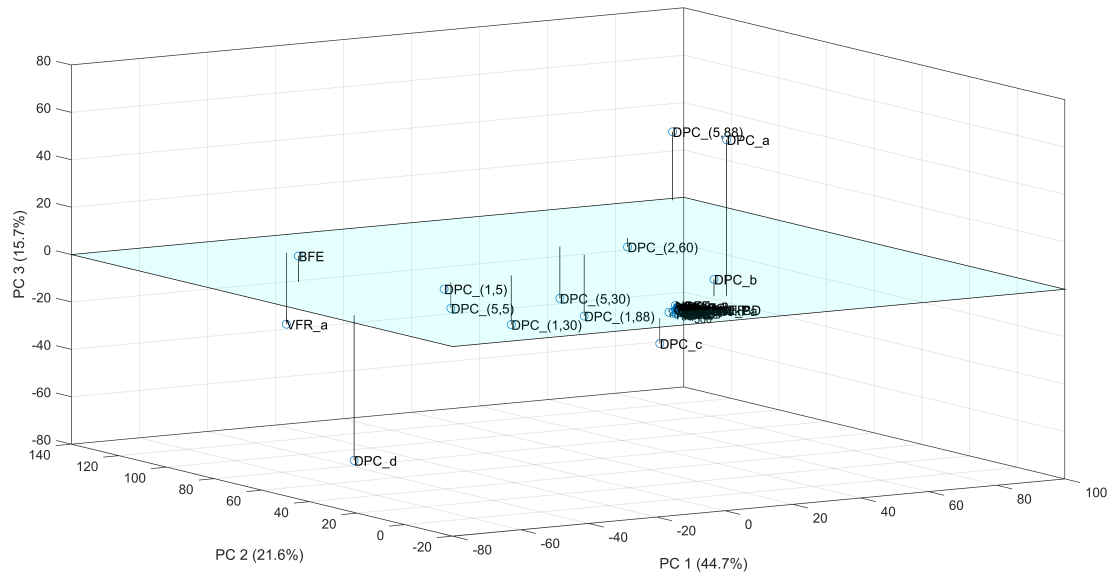


Figure C.10: Plot of loadings of first three principal components (PCs). Residuals along PC 3 are drawn for each loading from the light blue plane that intersects PC 3.

Table C.1: Shorthand names of FT4 Powder Rheometer Stability and Variable Flow Rate test outputs and descriptions thereof. An asterisk indicates the parameter is manually calculated and not directly provided by the FT4.

Parameter	Description
*d ₅₀	The 50 th percentile particle size (μm), from Certificate of Analysis provided by powder vendor.
BFE	Basic Flowability Energy - Cycle 7 measured flow energy.
*NBFE	Normalized Basic Flowability Energy - The BFE value divided by the split mass.
*Stability	The percent relative uncertainty of flow energies measured through cycles two through eight.
SI	Stability Index - Flow energy of the seventh cycle divided by the flow energy of the first cycle.
*SI _{adj}	Adjusted Stability Index - Flow energy of the eighth cycle divided by the flow energy of the second cycle.
FRI	Flow Rate Index - Cycle 11 flow energy divided by cycle 7 flow energy.
SE	Specific Energy - Average flow energy measured during upwards movement of cycles 6 and 7, divided by split mass.
CBD_SVFR	Conditioned Bulk Density - Split mass divided by split volume, measured during the SVFR test.
*VFR _a	Variable Flow Rate Fit Parameter a - From fitting equation ax^b applied to flow energy data of all cycles.
*VFR _b	Variable Flow Rate Fit Parameter b - From fitting equation ax^b applied to flow energy data of all cycles.
*VFR _R ²	R-squared value of the Variable Flow Rate Fit - From fitting equation ax^b applied to flow energy data of all cycles.

Table C.2: Shorthand names of FT4 Powder Rheometer Compressibility test outputs and descriptions thereof. An asterisk indicates the parameter is manually calculated and not directly provided by the FT4.

Parameter	Description
CBD_C	Conditioned Bulk Density - Split mass divided by split volume, measured during the Compressibility test.
CPS_15kPa	The percent change from initial volume after having been compressed by a 15 kPa normal stress.
*C_a	Compressibility Fit Parameter a - From fitting equation $a + b \log x$ applied to compressibility data.
*C_b	Compressibility Fit Parameter b - From fitting equation $a + b \log x$ applied to compressibility data.
*C_R ²	R-squared value of the Compressibility Fit - From fitting equation $a + b \log x$ applied to compressibility data.

Table C.3: Shorthand names of FT4 Powder Rheometer Shear Cell test outputs and descriptions thereof.

Parameter	Description
Cohesion	The shear stress value at which a best fit line fitted to the shear data intercepts the y-axis.
AIF	Angle of Internal Friction - The angle between the best fit line and x-axis.
AIF_EE	Effective Angle of Internal Friction - The angle between the line passing through the origin, tangential to the larger Mohr Circle and the x-axis.
AIF_SS	Steady State Angle of Internal Friction - The angle between the line passing through the origin and pre-shear point, and the x-axis.
MCS	Minor Consolidation Stress - The lesser of the two normal stress values on the x-axis from the larger Mohr Circle.
UYS	Unconfined Yield Strength - The greater of the two normal stress values on the x-axis from the smaller Mohr Circle.
MPS	Major Principal Stress - The greater of the two normal stress values on the x-axis from the larger Mohr Circle.
FF	Flow Function - The value of MPS divided by UYS.
Rel	The value of MPS minus MCS, all divided by UYS.

Table C.4: Shorthand names of FT4 Powder Rheometer Direct Pressure Consolidation test outputs and descriptions thereof. An asterisk indicates the parameter is manually calculated and not directly provided by the FT4.

Parameter	Description
DPC_split_BD	The average bulk density after splitting the vessel.
DPC_(1,5)	Average flow energy (mJ) of a sample compacted under 5 kPa using one increment.
DPC_(1,30)	Average flow energy (mJ) of a sample compacted under 30 kPa using one increment.
DPC_(1,88)	Average flow energy (mJ) of a sample compacted under 88 kPa using one increment.
DPC_(2,60)	Average flow energy (mJ) of a sample compacted under 60 kPa using two increments.
DPC_(5,5)	Average flow energy (mJ) of a sample compacted under 5 kPa using five increments.
DPC_(5,30)	Average flow energy (mJ) of a sample compacted under 30 kPa using five increments.
DPC_(5,88)	Average flow energy (mJ) of a sample compacted under 88 kPa using five increments.
*DPC_a	DPC Fit Parameter a - From the fit $a\sqrt{x} + b\sqrt{y} + cx\sqrt{y} + d$ applied to all DPC data.
*DPC_b	DPC Fit Parameter b - From the fit $a\sqrt{x} + b\sqrt{y} + cx\sqrt{y} + d$ applied to all DPC data.
*DPC_c	DPC Fit Parameter c - From the fit $a\sqrt{x} + b\sqrt{y} + cx\sqrt{y} + d$ applied to all DPC data.
*DPC_d	DPC Fit Parameter d - From the fit $a\sqrt{x} + b\sqrt{y} + cx\sqrt{y} + d$ applied to all DPC data.
*DPC_R ²	R-squared value of the DPC Fit - From the fit $a\sqrt{x} + b\sqrt{y} + cx\sqrt{y} + d$ applied to all DPC data.

Table C.5: Shorthand names of GranuTools GranuPack test outputs and descriptions thereof.

Parameter	Description
ρ_{bulk}	Initial Bulk Density.
$\rho_{tap,500}$	Tapped Density after 500 taps.
$\rho_{tap,9999}$	Tapped Density after 9999 taps.
$\rho_{\infty,500}$	Extrapolated Tapped Density - From fit applied to first 500 taps. Fit described in Results and Discussion.
$\rho_{\infty,9999}$	Extrapolated Tapped Density - From fit applied to all 9999 taps. Fit described in Results and Discussion.
HR ₅₀₀	Hausner Ratio for 500 taps - Given by: $\frac{\rho_{bulk}}{\rho_{tap,500}}$
HR ₉₉₉₉	Hausner Ratio for 9999 taps - Given by: $\frac{\rho_{bulk}}{\rho_{tap,9999}}$
C ₅₀₀	Carr Index for 500 taps - Given by: $100 \cdot \left(1 - \frac{\rho_{bulk}}{\rho_{tap,500}}\right)$
C ₉₉₉₉	Carr Index for 9999 taps - Given by: $100 \cdot \left(1 - \frac{\rho_{bulk}}{\rho_{tap,9999}}\right)$
α	Slope Index - Slope of the best fit line through the first ten data points of tapped density.

Table C.6: Shorthand names of GranuTools GranuHeap test outputs and descriptions thereof.

Parameter	Description
AOR	Angle of Repose - The average angle, relative to the collection base, of an isosceles triangle projected onto the powder heap such that it has the same surface area.
CI	Cohesive Index - Stated as the deviation between the real heap interface and the projected isosceles triangle. Presumably the difference between AORs calculated using isoh vs. height.
height	The actual height of the powder heap.
isoh	The height of the projected isosceles triangle. This value is taken from raw data values.
area_abv	“AreaAbove” in raw data - Unclear what this corresponds to. This value is taken from raw data files. Discussed in Analysis of Results .
area_blw	“AreaBelow” in raw data - Unclear what this corresponds to. This value is taken from raw data files. Discussed in Analysis of Results .

Vita

Sam Weimer attended The Ohio State University through the Land Grant Opportunity Scholarship, after having grown up in the rural town of Eaton, Ohio. Ever curious of the world around him, he worked towards a Bachelor of Science degree in Physics. Always having had a passion for learning, continuing his education towards a future career in research was the next step. To achieve this, he attended the University of Tennessee and pursued a Doctor of Philosophy degree in Nuclear Engineering, his field of interest. He will begin his career in government research following graduation.