April 24, 2016

Mr. Geoffrey Morris
3M Oral Care
2501 Hudson Road
St. Paul, MN 55144

Dear Mr. Morris,

Enclosed you will find our analytical report on the recycling of byproducts produced during the manufacture of zirconia dental crowns, which are produced by the subtractive process of milling from zirconia blocks. The group was tasked to investigate how much byproduct is being generated and in what forms so that the zirconia could be inexpensively separated and recycled. The group was also challenged to identify feasible applications of recycled zirconia and reach out to companies that would be interested in related endeavors. The main requirement was that little to no additional cost would be inflicted on all involved parties in any proposed solution.

In a mass balance, it was determined that 93% of the zirconia blank turned into byproduct, meaning crowns only constituted 7% by mass. This was a huge finding and shows that about one million pounds of zirconia are being disposed of every year. Through testing, the group also determined that by implementing a simple and inexpensive cyclone separator, zirconia swarf (powder byproduct from the milling operation) could be pulled out of the vacuum system before combining with other materials in the baghouse system that dental labs use. The group then identified the major feasible applications from research and testing results. After doing so, the group reached out to over 25 companies and identified a promising partnership with Saint-Gobain ZirPro, a company that specializes in manufacturing zirconia ball milling media. Saint-Gobain ZirPro stated that they could potentially absorb the costs of processing and shipping, thus creating a recycling system for a one-time cost of less than $1,000 to each dental lab for the installation of a cyclone separator. The investigation into the viability of recycled zirconia in Saint-Gobain's ZirPro milling beads is ongoing.

Thank you for the opportunity to work on this project. All group members acquired new knowledge, challenged each other to be creative and hard working, and had a good time. If you have any questions, please contact us at amthomas46@gatech.edu.

Sincerely,
Henry Liu, Nicholas Kane, Tony Shu, Anna Thomas, Justin Wang, and Hayley Zhang

Project ReCap: Recycling of Dental Crown Byproducts

Submitted to: Dr. Yushin and Dr. Gable

Submitted by: Henry Liu, Nicholas Kane, Tony Shu, Anna Thomas, Justin Wang, and Hayley Zhang

MSE 4420: Capstone Design II

April 24, 2016

EXECUTIVE SUMMARY

The goal of our project was to develop a process to recycle the byproduct generated from the yttria-stabilized zirconia dental crown manufacturing process with minimal added cost. The subtractive manufacturing process used in dental labs results in only 7% of the material being turned into crowns, with the remaining 93% currently discarded. Every year, more than 1,000,000 pounds of zirconia byproducts in the form of either swarf or milled blanks are being thrown away. In keeping with a culture of sustainability and renewability, our sponsor, 3M Oral Care, is motivated to find a process to recycle or reuse this zirconia byproduct.

We studied the volume, value, and composition of byproducts generated by the zirconia dental crown manufacturing process via a number of testing and characterization methods including mass balance calculation, scanning electron microscopy (SEM), x-ray diffraction (XRD), BET (Brunauer, Emmett, and Teller) analysis, and x-ray fluorescence (XRF) spectroscopy. These results helped identify a separation process involving a cyclone separator for the collection of zirconia swarf from the dental labs' vacuum system. Upon running a massed amount of powder through a cyclone and measuring the mass of collected powder, we concluded that the efficiency of this process is over 90%.

We compiled a list of applications that could potentially use recycled zirconia based on its mechanical, thermal, electrical, and optical properties. The feasibility of each application was then evaluated based on market size, product value, purity level required, and implementation cost. These results were consolidated into a datasheet covering typical zirconia byproduct composition along with a simplified infographic depicting application feasibilities of recycled zirconia. After narrowing down our potential company list, we came to a potential collaboration with Saint-Gobain ZirPro due to their environmental consciousness initiatives.

In conclusion, we believe that installing cyclone separators in the dental labs' vacuum systems would economically increase collected zirconia swarf purity and volume. Once collected in sufficient volume, the swarf and milled blanks would be packaged and shipped to Saint-Gobain ZirPro's plant in Huntsville, AL for further processing. Saint-Gobain Zirpro indicated that they were willing to cover the shipping cost of the recycled zirconia to their facility. The capital cost of a commercial cyclone separator and installation is \$200-\$1,000, which will be covered by the dental lab. In addition, other industries which produce their own zirconia byproducts may be included in future recycling initiatives upon the efficacy of this program.

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YSZ	Yttria Stabilized Zirconia
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
BET	Brunauer–Emmett–Teller
XRF	X-ray Fluorescence

1. Introduction

1.1. Client Description

3M is a multinational conglomerate organization which specializes in materials development for both individual consumers and businesses. Known for their adhesives market, 3M is encountered by the everyday consumer in the form of Post-it notes and Scotch brand tapes, among other products. From their humble origins as the Minnesota Mining and Manufacturing Company started in 1902, 3M now boasts 88,000 employees who generate over $30 billion in revenue per year [1].

Within 3M's large product offering, the 3M Oral Care division produces a series of millable zirconia blanks for use in dental crowns which fall under their Lava family of products. Geoffrey Morris, Scientific Affairs Manager of the 3M Oral Care division, has charged us with the tasks of quantifying the amount of byproduct generated during the dental crown installation process and developing a novel solution to reduce and reuse the byproduct produced.

1.2. Project Description

Dental crowns are used to strengthen and restore degraded teeth, usually in the form of bridges or implant caps. Numerous materials can be used for the crown, such as gold, alumina, or zirconia [2]. 3M Oral Care's line of dental crowns are made of yttria-stabilized zirconia (from this point forward, known simply as zirconia), consisting of 95-97 mol % zirconia, 3-5 mol % yttria, trace amounts of rare earth elements to modify the color, and trace amounts of aluminum oxide to help stabilize the grain boundaries. Zirconia dental crowns have superior fracture toughness and a more genuine tooth-like appearance than alumina dental crowns, its main competitor.

3M Oral Care currently acts as a material supplier to dental labs which then machine the raw material into a customized crown for the consumer. The raw material for the zirconia dental crown industry in the United States is an estimated $250 million dollar market with still more room for growth [3]. During the manufacturing process, zirconia is removed by a mill to form the finalized geometry of the crown. The resulting byproduct is currently discarded, but in keeping with a culture of sustainability and renewability, 3M Oral Care is motivated to find a process to recycle or reuse this zirconia byproduct. The end goal is to identify a material mass balance throughout the manufacturing process which results in 100% of the zirconia byproduct accounted for and recycled with minimal added cost to all parties involved. Ideally, this process should also result in a new revenue stream for both parties. In summary, the problem is a process-driven issue whose solution prioritizes economic feasibility, simplicity, and stewardship of our planet.

2. Design Objective

The first objective of this project is to conduct a thorough study of the volume, value, and composition of byproduct produced throughout 3M's global production and installation of zirconia dental crowns. A comprehensive overview of the entire procedure from beginning to end will be created to provide insights into reducing total non-recycled zirconia byproduct.

The second objective is to develop a systematic solution to address both the economical and ecological impact of byproduct produced during the aforementioned process. Methods developed for recycling and reusing byproduct should ideally be economically beneficial for 3M Oral Care, the dental lab, and the consumer while keeping current infrastructure and processes as intact as possible. User needs and metrics, Table 2.1, were determined in order to enumerate the requirements of a successful system.

Table 2.1: User Needs and Metrics

Need	Metric	Unit	Ideal	Marginal	Justification
Recycling process is universal to all dental labs	Number of dental labs able to recycle byproduct	%	100%	25%	Ideally the process would work for the byproduct material from all dental lab
Byproduct material must be utilized	Amount of byproduct reused	%	100%	50%	Ideally all byproducts would be reused; however, any amount that does not end up in a landfill is a success.
Minimal added cost	Cost of process implementation	USD	<$2,000	$2,000	Ideally the process will result in a powder that can be sold for a profit. Otherwise, any associated cost of recycling should be minimized.

3. Experimental Research and Discussion

3.1. Industry Research

3.1.1. New Image Dental Lab

The team toured New Image Dental Lab located in Morrow, GA in order to see the manufacturing process of zirconia dental crowns and gauge the feasibility of recycling the zirconia byproducts. The team met with Jeff Paulen, the president of the company, and Jessica Paulen, the director of production. The first step in the manufacturing process is for the dentist to make an impression of the tooth, shown in Figure 3.1.

Figure 3.1: Impressions various dentists send to New Image

New Image then generates a model from this impression, shown in Figure 3.2. This is a CAD/CAM process that involves using modeling software to create designs. Geometric parameters from these designs are then used to control machinery to accurately create the design. By automating the manufacture of zirconia dental crowns, productivity, dimensional accuracy, and consistency can be increased.

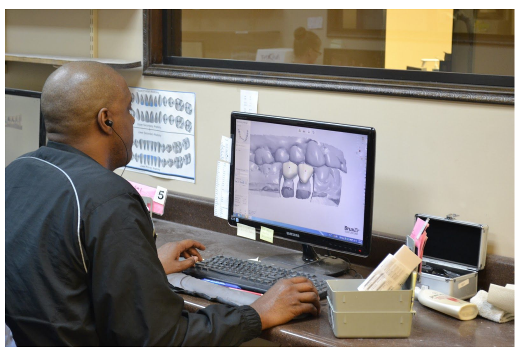

Figure 3.2: New Image employee creating a CAD model of dental crowns to be milled

The raw material used to make these crowns is a pre-sintered blank or disk of yttria-stabilized zirconia. The dental lab purchases these disks from a supplier such as 3M, though many different brands of disks can be milled using the same machinery. An example of this disk is shown in Figure 3.3.

Figure 3.3: Various pre-sintered zirconia disks

Numerous crown models are plotted on the same disk. This disk is then mounted in a five-axis milling machine and the crowns are milled out of it. Figure 3.4 shows one of the milling machines used and the internal tooling.

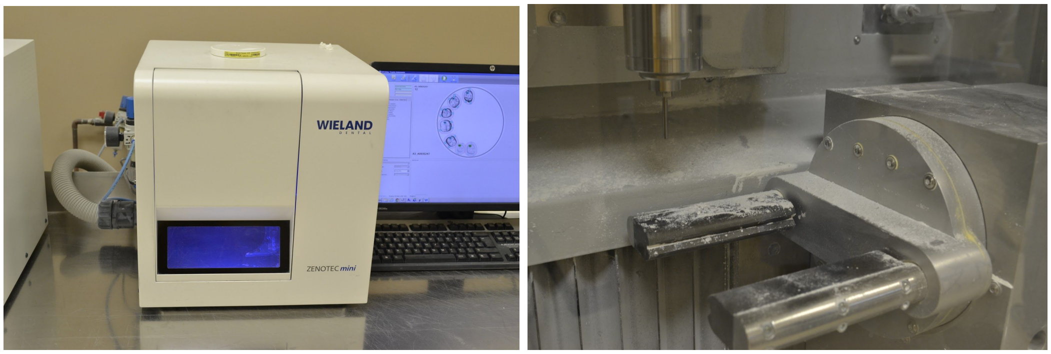

Figure 3.4: Five-axis milling machine used at New Image Dental Lab

After milling, the crowns are still connected to the blanks but are then taken out of the blank. This results in two forms of byproducts - a zirconia disk with holes where the dental crowns were milled, as shown in Figure 3.5, and zirconia swarf that is collected in a vacuum system.

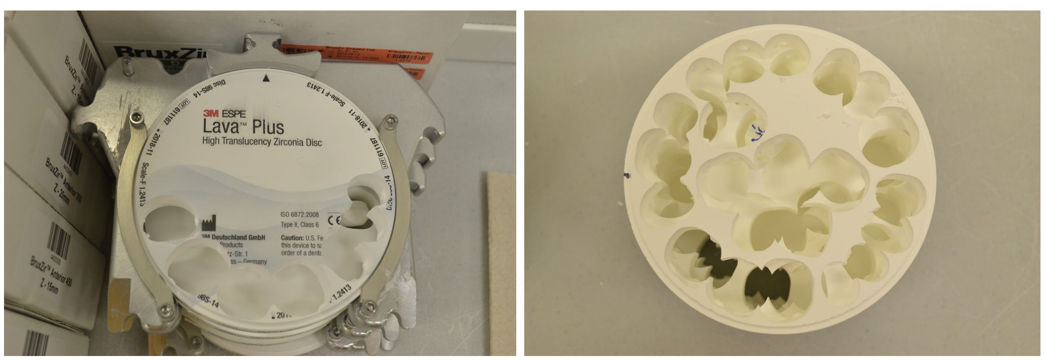

Figure 3.5: Partially milled zirconia blank (Left). Fully-milled zirconia blank (Right).

The tour of the manufacturing process at New Image provided the team with a new perspective of the zirconia recycling process. At this time, New Image gave the team a large quantity of their zirconia byproduct to characterize as well as their personal contacts with companies who deal with zirconia-based products. This gave the team great leads in the search for a company that would consider using recycled zirconia in their products. The team was also able to gauge the feasibility of implementing a minimally-intrusive recycling process. One of these considerations led to the idea that installing a cyclone separator in the air-chute would be an effective way of retrieving the zirconia swarf before it’s contaminated with other byproducts.

3.1.2. Consultation with Dr. Robert Speyer

Dr. Robert Speyer is a full professor within the Department of Materials Science and Engineering at Georgia Tech. His research involves novel production and characterization techniques involving high performance ceramic materials, especially in body armor applications. In an effort to better understand the domain and scope of the design objective given, especially in terms of economic feasibility, an interview with Dr. Speyer was conducted.

Considering the combined gypsum and zirconia byproduct consolidation streams used in New Image Dental Lab, finding a way to separate desirable zirconia from undesirable gypsum or other contaminants in the swarf portion of byproduct is paramount for a nationally scalable zirconia recycling operation. In other words, should a dental milling lab combine its zirconia swarf with any other swarf, a separation method would be necessary for further zirconia processing. In the case of gypsum ($CaSO_4 \cdot 2H_2O$), Dr. Speyer theorized that its ionic character would be susceptible to attack by acids, leaving any zirconia present unaffected. Upon researching this approach, it was found that both hydroxamic and hydrochloric acid would serve as appropriate solvents [4, 5]. However, no references to an existing process using these acids on an industrial scale to digest gypsum were found. It was concluded that a solvent-based approach to purifying mixed swarf would add an extra processing step, significant reagent cost, and significant labor costs to account for handling of hazardous substances.

Assuming zirconia powder was recoverable from combined swarf sources, the conversation shifted to potential products which could be manufactured for a low overall cost. Further assumptions were made on the purity of the recovered zirconia powder, specifically that the powder would be of reasonable purity, but still unsuitable for high purity applications such as remanufactured zirconia blanks. This assumption was based on the anticipated additional overhead costs required for ensuring a uniform zirconia composition with multi-sourced swarf. One suggestion Dr. Speyer made was using recovered zirconia powder as polishing media. This application would not be strongly dependent on recovered powder purity, and instead would depend on the particle size distribution of the recovered powder, the vast majority of which would be zirconia. Fortunately, powder size is a parameter which would be easily modulated via the standardized high-volume technique of jet-milling. In addition to a general list of ceramics companies, Dr. Speyer recommended contacting Saint-Gobain ZirPro, a company specializing in zirconia grinding media. These suggestions contributed significantly to a list of companies contacted later in the design process, as detailed in the section 4.2.4.

Finally, Dr. Speyer quoted a cost of \$20 - \$30 per pound of high grade zirconia powder with the reminder that any application of recyclable zirconia powder would also most likely have to be shipped in low quantities at close to consumer prices, adding another disadvantage to reusing zirconia powder rather than buying in bulk.

3.2. Byproduct Characterization

3.2.1. X-Ray Diffraction

The x-ray diffraction (XRD) pattern was collected on a Panalytical X'Pert Pro Alpha-1 Diffractometer at room temperature, shown in Figure 3.6. The crystalline phases were identified by XRD using a Guinier–Hagg focusing camera and Cu radiation. The crystal structure of the elements was determined by the number of peaks and their intensities. Figure 3.7 indicates the phase locations and pattern of a zirconia swarf sample sent from 3M's own dental mills. Figure 3.8 tabulates the composition data gathered from the sample. Average particle size was determined by isolating the zirconia phases from impurities such as gypsum and unidentified particles. This method implies an assumption of equivalent spherical size developed using a size-dependent property of the particle and relating it to a linear dimension. The Scherrer equation was used to determine the particle size from X-ray diffraction profiles:

$$\tau = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where τ is the volume-weighted size, θ is the Bragg angle, λ is the wavelength of the x-ray and K is a unit cell geometry dependent constant whose value is typically between 0.85 and 0.99. β is the full-width-half-max of the peak after correcting for peak broadening which is caused by the diffractometer.

One way to represent β is to use Equation 2, where β_{obs} is the measured peak width and β_m is the beak broadening due to the machine:

$$\beta = \beta_{obs}^2 - \beta_m^2 \tag{2}$$

The calculated average particle size is 55.26nm.

Figure 3.6 Panalytical X'Pert Pro Alpha-1 XRD

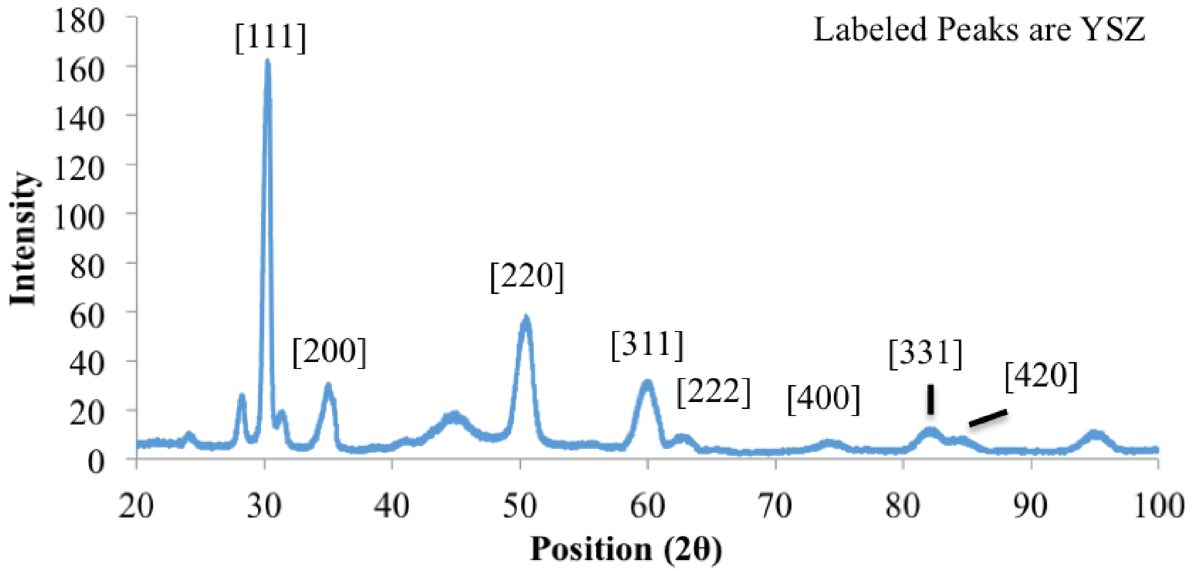

Figure 3.7: Diffraction pattern for 3M Swarf

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
04-008-7255	59	Yttrium Zirconium Oxide	0.159	0.865	Y0.065 Zr0.935 O1.968

Figure 3.8: Identified Composition for 3M Swarf

3.2.2. Microscopy

A small piece of a zirconia blank from 3M was mounted to provide a stable base for characterization. Initial microscopic images of the sample were taken with an optical microscope under 50x magnification. As shown in Figure 3.9, the slight color contrast revealed individual ceramic particles, but remains too noisy for detailed analysis. Further characterization was conducted via scanning electron microscopy (SEM) for microstructure information.

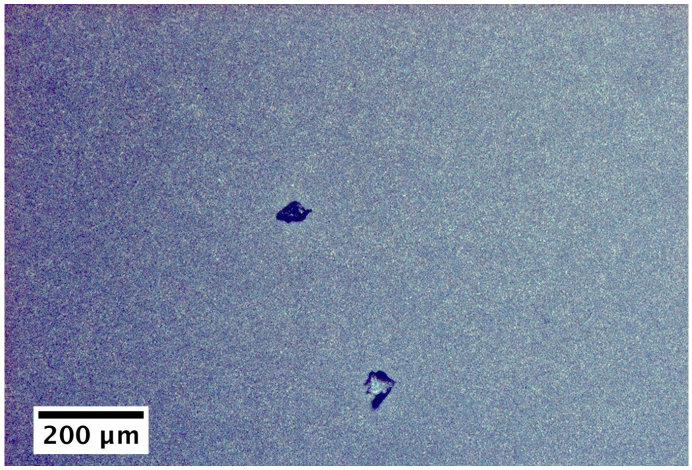

Figure 3.9: Initial zirconia optical image at 50x magnification

A 3M zirconia swarf sample was prepared on a stub by adhering powder with carbon tape and then sputtering the stub with gold. The sample was observed with an SEM up to 800x magnification.

The particle size and particle size distribution was unable to be determined from Figure 3.10. This preparation method gathered a layer of powder that was too thick for clear SEM images. Figure 3.10 shows some clear structures, but the sample experienced a high degree of charging which produced large dark areas that could not be analyzed. Therefore, a new preparation method was conducted to observe clearer images.

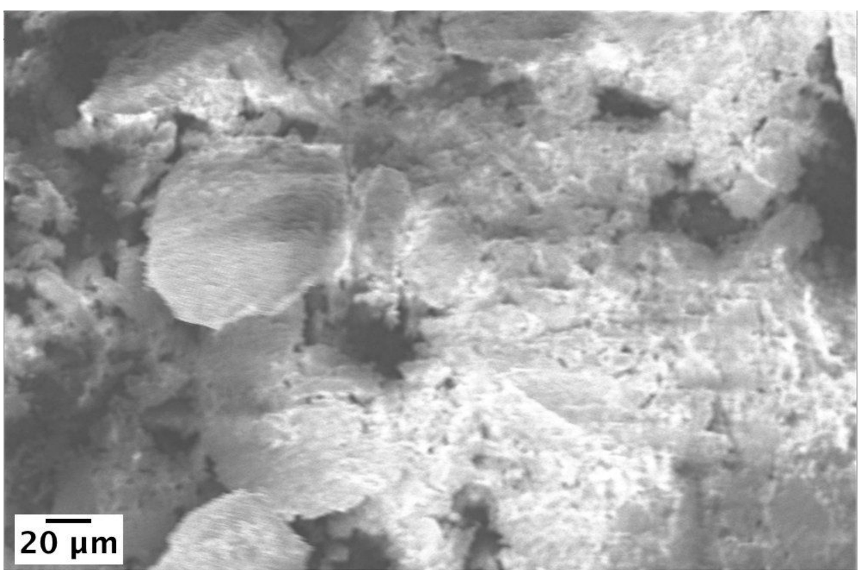

Figure 3.10: SEM image of 3M Zirconia Swarf at 800x magnification

A new method of sample preparation consisted of suspending the powder in ethanol, sonicating the mixture, placing a drop onto a stub, letting the drop dry, and then sputtering the stub with gold. The sonication was done to prevent agglomerates from forming. As seen in Figure 3.11, a sharper image was taken at a much higher magnification with this new method of sample preparation. Although some groups of particles still clumped together, the information about the particle sizes and the overall particle distribution across multiple SEM images was clearer.

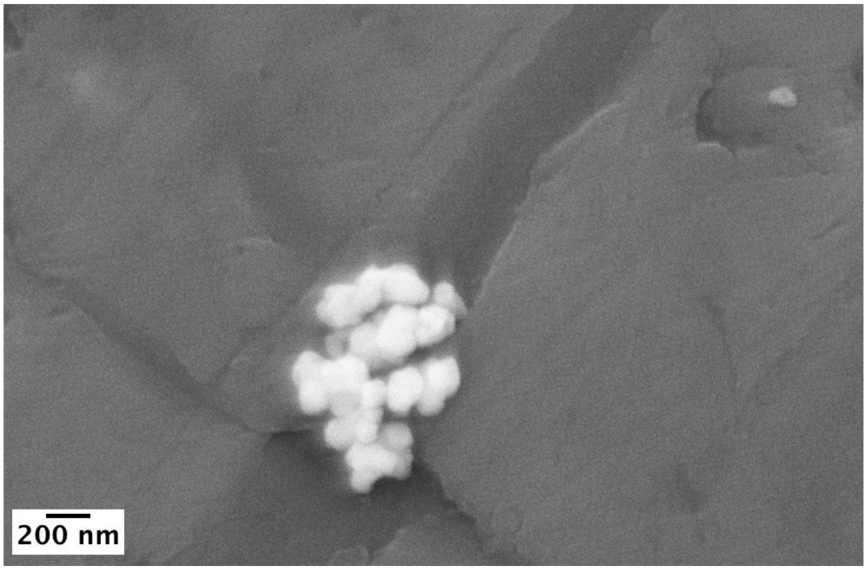

Figure 3.11: SEM image of 3M Zirconia Swarf at 77.68Kx magnification

3.2.3. Average Particle Size and Particle Size Distribution from SEM

The particle size distribution was estimated based on manual measurements of particles from four representative SEM micrographs. Over 100 manual measurements were made on these SEM micrographs by six people to generate over 500 data points. The particle size distribution was determined by making manual measurements (indicated by the blue lines) of randomly selected particles on an SEM image, as shown in Figure 3.12. These measurements were combined to give the particle size distribution, plotted in the form of a histogram, shown in Figure 3.13.

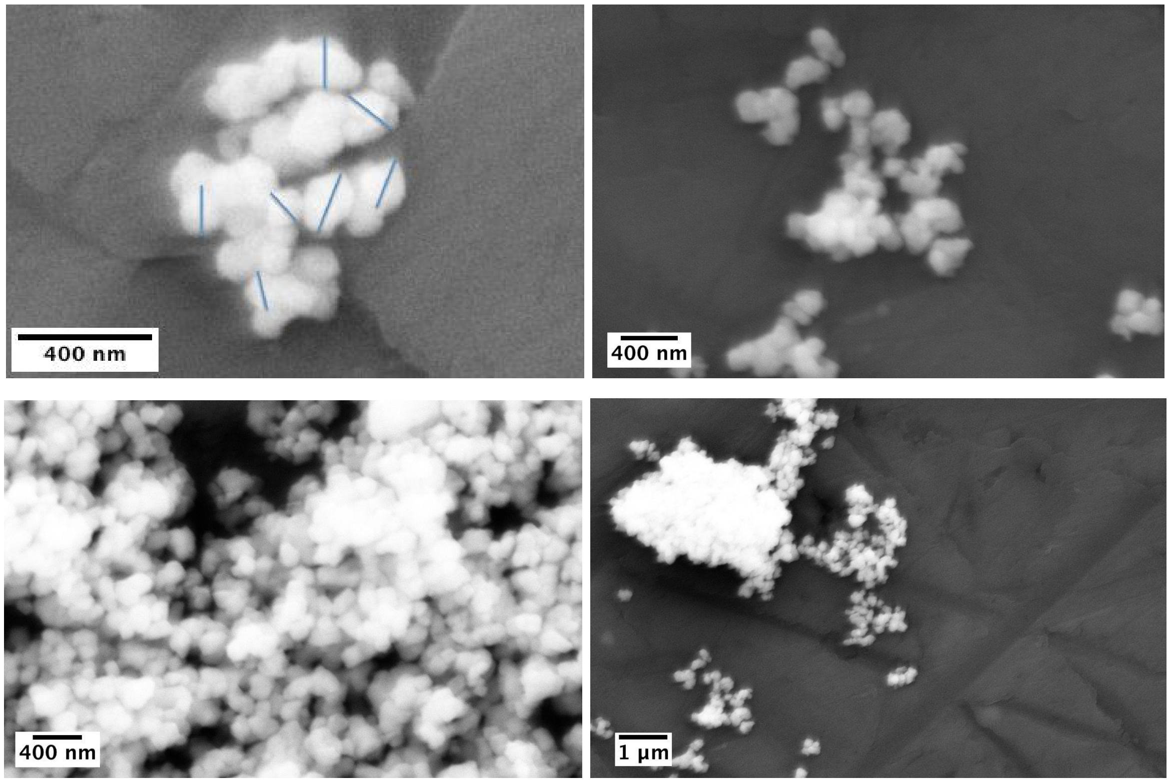

Figure 3.12: SEM images of zirconia swarf under different magnifications

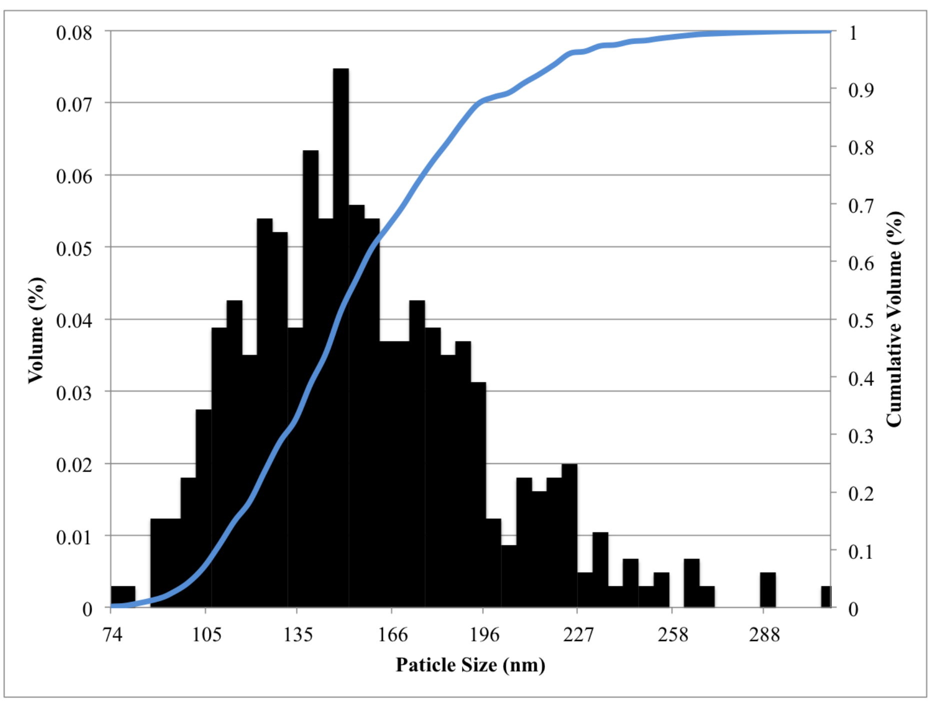

Figure 3.13: Particle size distribution of zirconia swarf

3.2.4. Brunauer-Emmett-Teller Analysis

A swarf sample from New Image was used in the BET experiment. This swarf was known to contain gypsum along with zirconia. The specific surface area of the sample was measured with a Micromeritics Tristar II surface area and porosity analyzer, shown in Figure 3.14. A powder sample was prepared by outgassing overnight in order to remove adsorbed gas and then heat treating at 900°C in order to remove impurities, such as remaining wax from the milling process. Nitrogen gas was used as the adsorbent gas and a 39 point analysis was run. The weight of the sample chamber cell was noted before and after the experiment. The final result was a specific surface area of 28 m^2/g.

Figure 3.14: Micromeritics Tristar II surface area and porosity analyzer

The BET equation is given by:

$$\frac{1}{W(\frac{P}{P_0}-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \tag{3}$$

where W is the weight of the gas adsorbed at a relative pressure, P/P_0, W_m is the weight of a complete adsorbed monolayer, and C is the BET constant. When $\frac{1}{W(\frac{P}{P_0}-1)}$ is plotted versus P/P_0, W_m is given by $\frac{1}{I+m}$, where I is the y-intercept and m is the slope of the line. The specific surface area can then be calculated by:

$$S_{BET} = \frac{W_m N s}{V a} \tag{4}$$

where N is Avogadro's number, s is the absorption cross section of the zirconia particles, V is the molar volume of the adsorbed nitrogen gas, and a is the mass of the adsorbed nitrogen gas [6].

3.2.5. Average Particle Size from BET

The average particle size was calculated from the specific surface area by making the following assumptions: the particles were all spherical, there were no agglomerates, and the sample was nonporous.

By making these assumptions, the average particle size can be calculated. The equation is given by:

$$D = \frac{6}{\rho S_{BET}} \tag{5}$$

Where ρ is the geometric density and D is the average particle diameter. From the technical specifications provided by 3M, the geometric density of the zirconia powder was determined to be 6.08 g/cm^3. From the BET experiments, the specific surface area was determined to be 28 m^2/g. From these values, the average particle size was calculated to be 35 nm [7].

3.2.6. Cyclone Separation

The principle of particulate removal devices depends on particle characteristic properties, including particle size and density. Any device that removes particles from gas streams then relies on a physical mechanism. Some particulate collection devices take advantage of the inertia differences between particles and gas. Other devices, such as settling chambers, consolidate particles in a gas stream due to gravity. Electrostatic precipitation is the process where a particle containing gas stream is introduced to an electric field, which will exert an electrostatic force on the particles and remove them from the gas stream [8].

A cyclone separator is a type of filter that removes solid particles from a gas stream by inducing a vortex in a conical container, as seen in Figure 3.15. The flow of intake air circles around the inner circumference of the container as it progresses downward until it makes a sharp turn to flow up the center of the cyclone and out the top. The inertia of the particles prevents them from making the sharp turn from cylinder walls into the central air stream with the gas, so instead they fall out of the stream and are collected at the bottom of the separator.

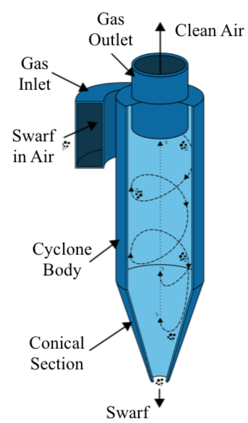

Figure 3.15: Schematic of cyclone separation

In order to save money, many labs combine their vacuum lines from all of their milling machines to feed into one dust collector. In the case of New Image Dental Lab, their gypsum and zirconia mills feed into the same collector, so the resulting powder was a mix of of gypsum and zirconia. As a proposed method of increasing the zirconia content in collected swarf, the cyclone separator will be attached to the zirconia mill vacuum line and used to remove the zirconia swarf before it reaches the main vacuum line in the dental lab. This means that the powder filtered out by the cyclone separator will be only swarf from the zirconia mills, preventing any contamination from other mills. While the cyclone separator itself has no way of separating different materials based on composition, it can remove solids from gas streams, and when used in a zirconia vacuum line containing only zirconia swarf, uncontaminated swarf can be collected.

Cyclone separators can typically remove solids ranging from one micron to one mm, and since the particle size of the zirconia swarf was well below this threshold, a test was needed to determine if the cyclone separator would be able to remove the swarf from a gas stream [9]. A VMC-300 Large Accumulator from Vaniman Manufacturing Company was used to conduct the tests. A small wet/dry shop vac was connected to the vacuum side of the accumulator and a tube was connected to the intake. Zirconia swarf was massed and then vacuumed up with the intake tube. Then, the swarf collected at the bottom of the accumulator was massed and compared to the initial mass. The difference was assumed to have passed through the accumulator into the vacuum. The data can be seen in Table 3.1. The results of the tests show that, on average, 93% of the input mass was collected in the separator.

Table 3.1: Cyclone Separator Measurements

Initial Mass (g)	Final Mass (g)	Loss (%)
106.87	97.42	8.84%
96.36	91.41	5.14%
133.78	119.63	10.58%
131.95	127.38	3.46%
111.8	109.58	1.99%
170.09	156.12	8.21%
750.85	**701.54**	**7.03%**

Before running the tests, powder was run through the accumulator to coat the walls and prevent any initial loss due to the accumulator being brand new. During the tests, more powder continued to coat the walls and build up until the accumulator experienced a force large enough knock it out. At one point, when the accumulator was set down, a large amount of powder fell out. The amount of powder was comparable to all the powder lost during the previous runs. When the collection area of the shop vac was inspected, a minute amount of powder was observed. Both of these factors indicate that the filtration rate is well above 93%.

3.2.7. Composition Analysis by Density

The material composition of swarf obtained from the milling process is a key piece of knowledge when designing the downstream recycling process. Though separation of zirconia swarf from other swarf sources during the milling process would be ideal, the possibility exists of a potential recycling process using adulterated swarf if milling labs are unable to separate their byproduct streams. In light of this, having an idea of the percent composition of the swarf is essential for determining processing steps, cost, and product yield. After being told that the swarf sample obtained from New Image Dental Lab contained plaster (largely calcium sulfate dihydrate) in addition to pure zirconia powder, a simple density-based experiment was performed to determine the proportions of both materials. Pycnometry was considered for this measurement, but it was discarded due to the assured presence of calcium sulfate hemihydrate remaining unhydrated in the plaster swarf, which would hydrate upon pycnometry with water, affecting the reading. Alcohol was also considered as testing medium, but the effects of evaporation and interactions with the material are not well-documented in literature. Considering the variable nature of adulterated swarf, it was determined that the ideal method to determine percent composition by density measurements would be via dry volume techniques.

Referencing literature for the density of gypsum powder, a value of 1.28g/mL was obtained [10]. A 15mL dry measuring spoon was used to mass a known volume of 3M's pure zirconia swarf, yielding a mass of 13.958g and nominal density of 0.93g/mL. Next, the plaster/zirconia swarf from New Image Dental Lab was massed, yielding 21.596g and a nominal density of 1.439g/mL. Given that the nominal density of the New Image Dental Lab swarf was higher than that of both zirconia and gypsum powders, it was determined that the constituent powders partially overlapped to occupy the same volume, yielding a higher density. The calculations to determine compositional percentage of both plaster and zirconia in the mixed swarf were then based on the assumption that the original 15mL volume was fully occupied by either zirconia or plaster swarf and partially occupied by the remaining component to reach 1.439g/mL. By finding the extremes of the range of possible compositions, it was determined that the minimum amount of powder shared volume is 17%, resulting in 10.9% zirconia and 91.1% gypsum by weight, while the maximum of powder shared volume could be 39.8%, resulting in 64% zirconia and 36% gypsum by weight.

Admittedly, the realm of possibilities for swarf composition is wide. However, this estimation demonstrates effectively the variability of mixed and unsorted swarf in real-world applications.

3.2.8. Chemical Composition

The chemical composition of the zirconia disk was evaluated with a PW 2424 MagiX X-ray fluorescence spectrometer, shown in Figure 3.16. The disk was crushed into powder with a mortar and pestle and then loaded into the machine.

Figure 3.16: PW 2424 MagiX X-ray Fluorescence Spectrometer

The results are shown in Table 3.2 below. The measurement could not successfully detect 100% of the compounds in the sample - this is common as elements lighter than Na (Z=11) have low x-ray yield, making it difficult for the machine to accurately measure their abundances [11]. The majority of the sample is ZrO_2, with Y_2O_3 as the next most abundant compound. This is expected for yttria-stabilized zirconia. HfO_2 as well as trace amounts of oxides such as Al_2O_3. The HfO_2 is added for color control of the crown and the Al_2O_3 is added for control of the grain boundaries during sintering [12].

Table 3.2: Chemistry results for zirconia disk

Compound	SiO_2	Al_2O_3	CaO	MgO	Na_2O	ZrO_2	HfO_2	SrO	P_2O_5	Y_2O_3	Sum
Value (%)	-0.3	0.09	-0.01	0.09	0.08	81.1	1.61	0.01	0.01	3.34	86.03

3.2.9. Mass Balance Numbers

To quantify the byproduct remaining from a typical zirconia disk after milling, a mass balance was performed on two disks as they were put through the milling process. From a starting mass of 450g each, two zirconia disks were fully milled with 18 molar crowns. Then, the mass of the unmilled disk, remaining disk, and crowns were measured and used to calculate the mass of the swarf milled out. The percentages of zirconia comprising the crowns, swarf, and remaining disk were 7%, 71%, and 22% respectively. A volume analysis of a milled disk showed that 36% of a different disk remained after milling, but due to the nature of the measurements, there was no way to calculate the percentages of the crowns and swarf. However, it can be assumed that the crowns accounted for around 7% because a similar number of crowns were milled out. These numbers show that approximately 93% of the zirconia disk becomes byproduct. Moving forward, this is assumed to be applicable to every milled zirconia disk.

One assumption made was that approximately 50 million dental crowns are made in the U.S. every year with half of them being zirconia. These figures comes from a 3rd party market research firm contracted by 3M. Another assumption was that approximately 20 crowns can be made from each disk.

$$\text{50 million dental crowns} * \frac{\text{1 zirconia crown}}{\text{2 dental crown}} = \text{25 million zirconia crowns} \tag{6}$$

$$\text{25 million crowns} * \frac{\text{1 disk}}{\text{20 crowns}} = \text{1.25 million disks} \tag{7}$$

$$\text{1.25 million disks} * \frac{\text{450 g}}{\text{1 disk}} = \text{562,500 kg zirconia} \tag{8}$$

$$\text{562,500 kg zirconia} * \frac{\text{93 g waste}}{\text{100g zirconia}} = \text{523,125 kg waste} \tag{9}$$

$$\text{523,125 kg waste} = \text{1,153,293 lbs waste} \tag{10}$$

Equations 6-10 show the calculations for the total byproduct generated in the U.S. each year. In addition the the previous assumptions listed, each disk was assumed to be a 450g 3M Lava Plus 98mm disk. Equation 10 shows that about 1.15 million pounds of zirconia byproduct is generated each year, in the form of swarf and milled out disks.

3.3. Industry

3.3.1. Properties and Applications of Zirconia Ceramics

The properties of zirconia ceramics are summarized in Table 3.3. In general, yttria-stabilized zirconia contains 3-12 mol % yttria and 88-97 mol % zirconia. The yttria content of zirconia will affect the degree to which it is stabilized [13]. Zirconia has excellent biocompatibility - in extensive *in vitro* and *in vivo* studies, no negative reactions were found and no mutagenic or cytotoxic effects on cells were observed [14]. Excellent mechanical properties of fracture toughness in addition to ideal thermal conductivity values allow zirconia to be used in a variety of demanding environments, such as thermal barrier coatings for jet engine components [13, 14]. Ceramics are often used for electrical applications because of their ability to be formed into complex shapes, good electrical insulation, and low dielectric losses [15]. Zirconia is often used for nanowires and solid oxide fuel cell (SOFC) electrolyte microlayers [16]. The solid electrolyte enables oxygen ion conduction while blocking electronic conduction. Cubic zirconia is a well known product in the jewelry world, with its great fire and resemblance to diamonds, but without the high cost [17]. Yttria can be used to help cubic crystals form, stabilizing the crystal structure [18]. From the table, it is clear that zirconia has an ideal combination of properties for many different applications.

Table 3.3: Summary of critical properties of zirconia ceramics [13, 14, 19-22]

General	● Composition: 3-12 mol % Y_2O_3 and 88-97 mol % ZrO_2 ● Biocompatibility: Both *in vitro* and *in vivo* studies have found no adverse reactions ● Density: 5.85-6.1 g/cm^3 ● Average grain size: 0.3-0.5 um
Mechanical	● Vickers Hardness: 1270 HV ● Fracture toughness: 16.8 Kgf/$mm^{2/3}$ ● Modulus: 200-210 GPa ● Compressive strength: 4900 MPa ● Flexural strength (4 point bending): 1660 MPa ● Impact strength: 137 MPa ● Bending strength: 1200 MPa
Thermal	● Thermal conductivity: 2 W/m*K ● Thermal expansion coefficient: $11x10^{-6}$ K^{-1} ● Specific heat: 500 J/kg*K
Electrical	Electrical conductivity: ● up to 1.9 S/m (for organic precursors) ● up to 0.15 S/m (for ceramic precursors) Activation energy: ● as low as 0.94 eV (for organic precursors) ● as low as 1.03 eV (for ceramic precursors)
Optical	● Prefered orientation: <111> ● Absorption coefficient: 10-60cm^{-1} ● Index of Refraction: 2.16

3.3.2. Industry Selection

After researching the properties and applications of zirconia, contacting companies, and several brainstorming sessions, a list of applications was put together, shown in the infographic discussed in section 3.3.3.1. With a list of about thirty different applications, a ranking system was implemented to determine the application's overall success as it related to this project. There were four main categories and each application was given a 1, 3 or 9 to indicate its predicted alignment with the conditions and limitations set by recycling zirconia. The categories were Market Size, Product Value, Contamination or Purity Level Required, and Cost to Implement. Market Size, where 1 is small and 9 is large, estimates how many products and what types of volumes a certain application is used. A larger market has greater appeal to companies more interested in large volumes of zirconia or initiatives related to recycling. For example, the demand of zirconia for use in fiber optic connectors was expected be much less than for use in ball milling media. Product Value, where 1 is high end and 9 is low end, is a measure of how expensive and top-tier the application is. Very high end products may be less likely to deal with recycling, because they often have high profits and this endeavor would not be worth their time. For outdoor decorating stones, zirconia would be competing against alternative and cheap silicate materials, while nuclear reactor alloy tubing would not benefit from marginal cost savings. Contamination or Purity Level Required, where 1 is little to no contamination acceptable and 9 is more tolerant of contamination, will affect how willing companies are to take a risk with recycled zirconia that may have a lower purity level due to processing or separation constraints. For example, zirconia used as an insulator in transistors is an application where an extremely high level of purity is required. Cost to Implement, where 1 is high and 9 is low, estimates the cost to introduce the recycled zirconia into a company's manufacturing process. Low costs of implementation are associated with processes where the recycled zirconia could be used mostly as-received, such as in floor tiles or ceramic glazes.

All of these categories were thoroughly discussed and evaluated for each of the applications, and the top were determined (Table 3.4, Figure 3.17). From there, companies in each industry were contacted. Unfortunately, many companies said that this would not be possible due to complications, lack of resources, or inability to deal with impurities. There were many companies that did not respond to inquiries, for reasons which can only be assumed to be one of the few listed above. However, there were some positive outcomes, discussed later.

Table 3.4: Most Feasible Applications Evaluation

Application	Market Size	Product Value	Contamination /Purity Level	Cost to Implement	Total
Tiles	9	9	9	9	36
High density ball and pebble mill grinding media	9	9	3	3	24
Mosaic art pieces	3	9	9	9	30
Aquarium gravel	3	9	9	9	30

Sand	3	9	9	9	30
Outdoor decorative stones	3	9	9	9	30
Glass Firing beads	1	9	9	9	28
Furnace cleaner	1	9	9	9	28
Abrasive	9	3	9	3	24
Thermal insulation	9	3	3	9	24
Filler material	1	3	9	9	22
Pigments and inks for pottery glazes	1	9	3	9	22

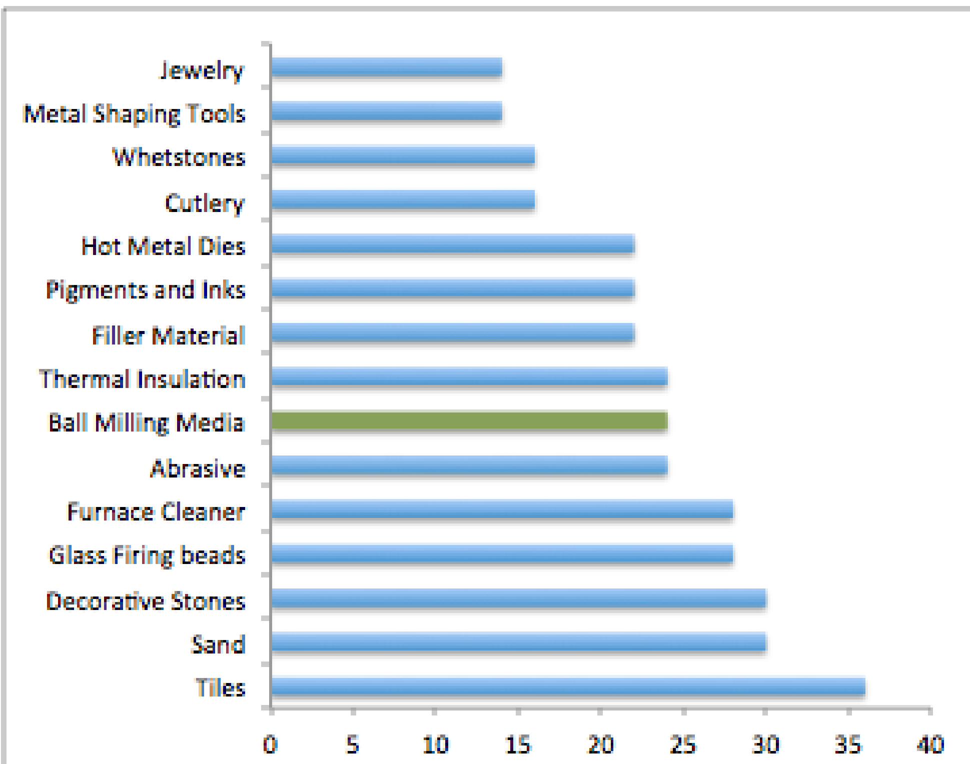

Figure 3.17: Top-scoring Potential Applications

3.3.3. Industry Outreach

3.3.3.1. Infographic

Through the course of the project, it became evident to both the client and the team, that a visual to portray our applications research and mass balance data would be useful for others to understand uses of zirconia and the volume of byproduct generated by the manufacturing process of dental crowns. A two page infographic was created (Figures 3.18, 3.19). The first page lists the various applications of zirconia, grouped by critical properties. The approximate value of each application is shown as well. The second page of the infographic shows the mass balance calculations made as well as an outline of the manufacturing process.

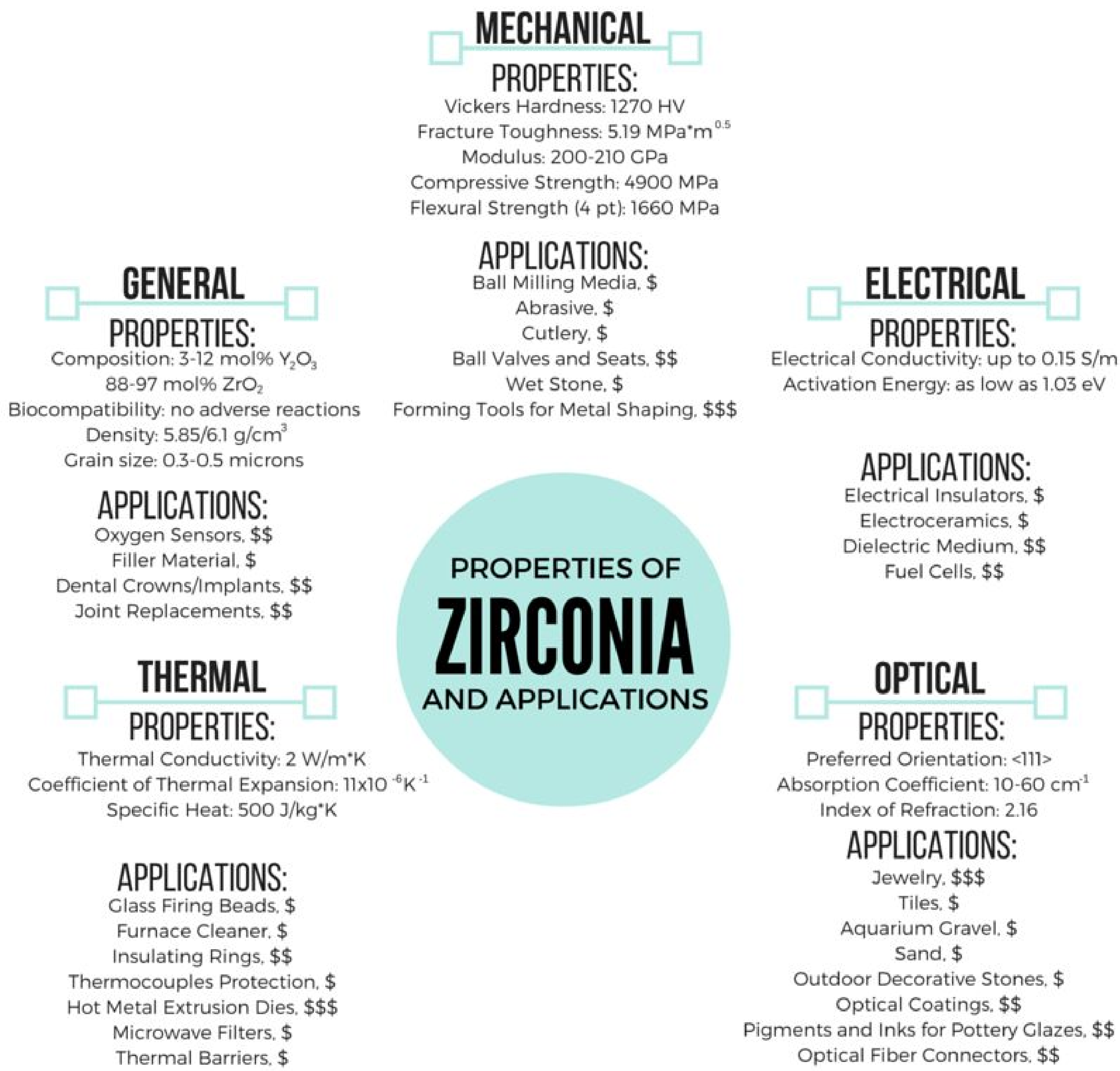

Figure 3.18: First page of infographic that shows the applications and properties of zirconia

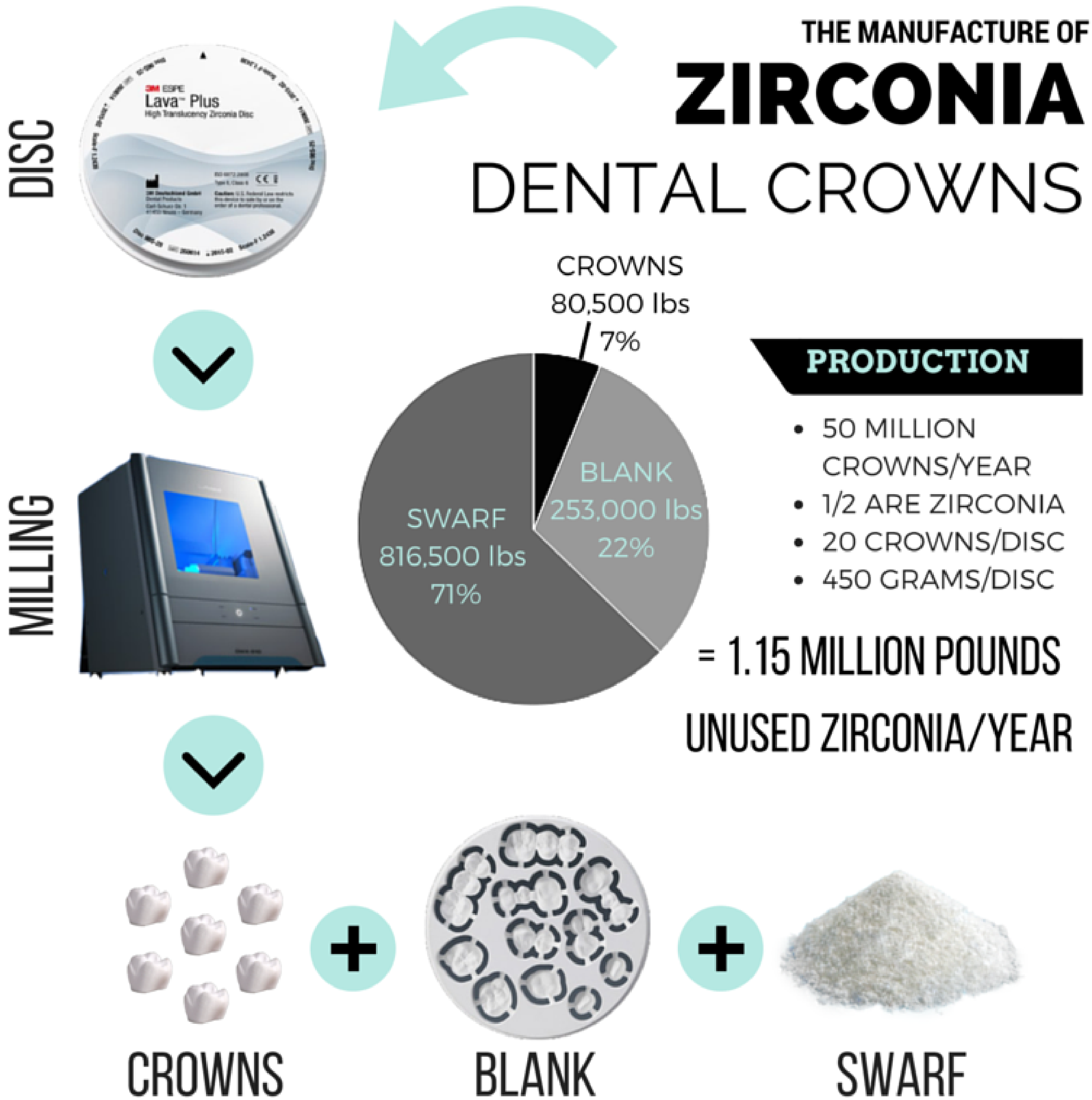

Figure 3.19: Second page of infographic that shows the manufacture of zirconia dental crowns and mass balance

3.3.3.2. Data Sheet

The data sheet in Figure 3.20 was compiled in order to have a concise handout to give to potential companies. The data sheet includes an overview of the results obtained from characterization and testing.

3M Science. Applied to Life.™

Specifications of All Dental Crown Byproduct

Data from the Georgia Institute of Technology in Collaboration with 3M Oral Care

Section 1: Identification	
Product Name	Zriconia byproduct from dental crown manufacturing
Composition	3-12 mol% Y_2O_3 and 88-97 mol% ZrO_2
Crystal Structure	Tetragonal and Fluorite
Typical Form	Powder to cm sized pieces

Section 2: General Material Properties	
Typical Density	6.08g/cm^3
Typical Average Particle Size (via XRD)	52nm
Typical Average Particle Size (via SEM Micrograph)	156nm
Typical Average Particle Size (via BET)	35nm
Typical Specific Surface Area	28 m^2/g

Section 3: Typical Chemical Composition Analysis

Compound	Percent
SiO_2	-0.3
Al_2O_3	0.09
CaO	-0.01
MgO	0.09
Na_2O	0.08
ZrO_2	81.1
HfO_2	1.61
SrO	0.01
P_2O_5	0.01
Y_2O_3	3.34
Total	86.03

Section 4: SEM Micrograph

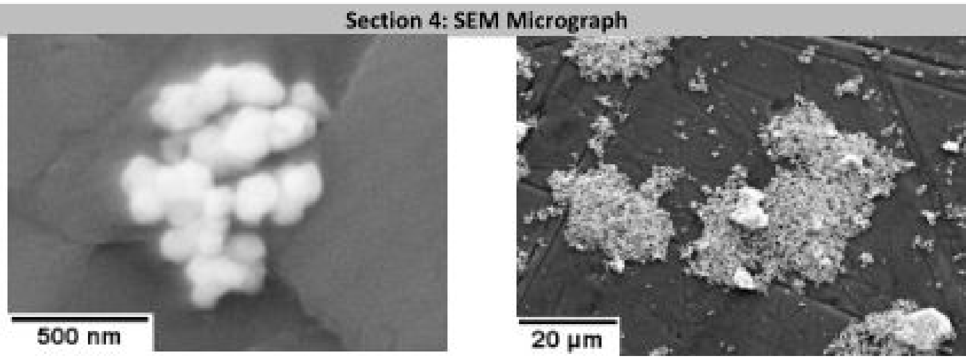

Figure 3.20: Data sheet with overview of properties of zirconia byproduct

3.3.4. Contacting Companies

After conducting the feasibility evaluation for the different applications of zirconia shown in Table A.1 (see appendix), at least two companies were identified per the highest-scoring applications and contacted. In total, 28 companies were contacted in order to gauge their interest in becoming an end source for the recycled zirconia powder and disks, see Table A.2 in the appendix. These companies specialized in a variety of different applications, such as floor tile, thermal barrier coatings, and aquarium gravel. Most companies were not interested in the recycled zirconia powder, citing concerns over its purity as well as logistical challenges involving cost and handling of transportation. However, one company in particular, Saint-Gobain ZirPro, responded positively to inquiries about setting up a zirconia recycling process.

Prior to contacting Saint-Gobain ZirPro about recycling solutions, the company had already began exploring potential processes which would allow them to reuse their byproduct from their own manufacturing streams. Fortunately, Saint-Gobain ZirPro were willing to perform a trial separation on both 3M's and New Image's dental swarf, and so 10 lbs of each were sent as samples for them to conduct their own testing in their Huntsville, AL processing plant. When discussing the logistics of consolidating swarf from many different sources across the country, the company responded positively, mentioning that their current recycling program's main priority was reusability rather than profit. Although they would be unwilling to pay a fee to the suppliers of swarf for their material, covering shipping costs was not out of the question for a national program.

4. Ethical, Environmental and Economical Considerations

In the process of characterizing sample materials and establishing company connections, comprehensive and accurate exchange of information laid the foundation for the success of this project. Both of our sample sponsors, 3M and New Image Dental Lab, were forthcoming with the expected contents of their swarf powders, mentioning possible contaminants including drill bits, zirconia blank chips, and wax mold leftovers. Doing so allowed the senior design team to focus efforts on quantifying known components of the swarf powders rather than blindly search for possible constituents, making a semester-long design cycle possible. Once the team was able to compile a datasheet, the full range of powder composition was shared with prospective companies for them to independently decide on the feasibility of taking on and repurposing zirconia swarf. The process of establishing a partnership between swarf producer and swarf recycler depends on this clear line of communication. Any falsely reported or obfuscated compositional data increases the likelihood of complications downstream, potentially affecting finely-tuned recycling processes or even the final product of the recycled zirconia and resulting in part failure.

Environmental impact is most noticeable in the omission of reusable swarf from landfills. Although mostly inert and therefore non-toxic to the environment, the prospect of reusing swarf still has the potential to remove 1.15 million pounds from landfills, space that could instead be used for waste that currently has no other destination. Because of the specific design goal of finding a low cost solution for reusing zirconia swarf, all feasible processes considered already use preexisting methods and equipment, and do not significantly further impact the environment in either known or unknown quantities. In a positive direction, the initial attempt to recycle zirconia byproducts encourages an attitude of sustainability which may facilitate better stewardship of the planet by increasing recyclability efforts in the future.

Perhaps the most challenging part of designing a sustainable recycling stream is creating an incentive system without the use of significant funding. From the dental labs' perspective, disposal of swarf is currently done at no cost other than an independently necessary trash service fee. Any alternative method of recycling swarf must then minimize cost to the lab until the perceived value of being ecologically friendly is valued the same as that cost. From the recycler's perspective, the cost to take in a new stream of zirconia swarf and process it into usable form must equal the value of any perceived ecological benefits plus the opportunity savings of using recycled versus virgin material. Finding this balance is difficult considering the thin profit margins from a recycled zirconia powder and the relatively low volume of swarf collected from dental labs, which does not facilitate an economy of scale.

5. Conclusions

Our sponsor, Geoffrey Morris of 3M Oral Care, tasked the team with two primary objectives: identifying the overall volume, composition, and value of the byproduct stream from the manufacture of zirconia dental crowns and developing a process to reduce or reuse this material stream with minimal added cost. We believe that we have successfully accomplished both objectives.

The byproduct stream was characterized in numerous ways, including SEM, XRD, and BET measurements. The mass balance was identified by extrapolating calculations made using one milled zirconia disk. The end result indicates that only 7% of the zirconia becomes a dental crown. The remaining 93%, or almost 1.1 million pounds annually, is currently unused.

To minimize cost of swarf processing and ease of zirconia powder separation, it is recommended that all dental labs incorporate a cyclone separator into their swarf collection vacuum lines if there are not already dedicated zirconia collection methods in place. For a centralized vacuum network like the one used at New Image, inserting a cyclone separator in-between all zirconia producing equipment and the consolidation junction where gypsum and other byproducts are combined should significantly increase zirconia swarf purity and consistency across all dental labs. This minimally invasive procedure is compatible with most pre-existing venting layouts and does not require extensive modification of the vacuum system. There would be a one-time installation fee involved, ranging anywhere from $500 to $2,000 depending on cyclone separator used and tubing layout along with labor source. While non-negligible, this cost should be covered by the dental lab.

When a sufficient amount of zirconia swarf has accumulated according to Saint-Gobain ZirPro's discretion, the swarf and milled disks should be shipped at ZirPro's expense to their recycling plant in Huntsville, AL. Because this swarf is already of relatively high purity, ZirPro is either able to directly inject this material into their current processing stream, or else minimally preprocess the material before consolidating it and manufacturing final products. All parties involved will have access to the datasheet and results obtained from this project's characterization initiatives for quality assurance purposes.

Given the numerous zirconia byproduct sources encompassed by all the companies the project has contacted, the success of this initial recycling stream for zirconia dental crowns has the potential to expand and cover a significantly larger volume of zirconia byproduct. This scalability may create a favorable economy of scale, establishing a solid financial foundation upon which to build a new revenue stream based on ceramic recycling.

ACKNOWLEDGEMENTS

Throughout the course of this project, we have received extraordinary help from individuals and corporations as a whole. We want to first recognize our sponsor, Geoffrey Morris, and 3M as a whole, for providing us with this project. We are fortunate and grateful that this project entails not only testing and using our materials knowledge, but also a great room of freedom and creativity to be successful and to determine solutions to this issue. Geoffrey has provided us with insights related to being an engineer at 3M, being a distinguished alumnus of Georgia Tech, and, of course, being successful in this project. Geoffrey was a pleasure to work with and constantly challenged us to be innovative and enthusiastic.

We also want to thank Dr. Yushin for meeting with us every week and not hesitating to give us his honest opinion. We would not be where we are in our project today without Dr. Yushin's provoking insights and challenges. Dr. Gable has also given us a great deal of advice, specifically regarding technical writing and design. Both Dr. Yushin and Dr. Gable have been great resources to us and we are grateful for the amount of time they put into reviewing all of our steps and giving constructive feedback.

We also would like to thank several others who helped us along the way. Jeff Paulen, from New Image Dental Lab, made time for us to tour his lab and ask as many questions as we wanted. Jeff also provided us with contacts to reach out to, helping us build a network in the industry. Kyle Galenza, from Vaniman Manufacturing Company, provided us with a cyclone separator to test. We are grateful to how fast he responded and sent it to us from California. Dr. Losego provided us use of his lab for testing, and Dr. Speyer provided his inputs early on in the project. Special thanks to Angie Beggs for printing our poster several times and to Hope Payne for helping us with reimbursements and answering our myriad of questions related to financing.

Morgan Thermal Ceramics was also very helpful in classifying some of our samples and deeply investigating the potential of using the recycled product. Finally, we want to greatly thank Saint-Gobain for being so responsive and willing to help us with the project. We are excited to see how the relationships and possibilities develop.

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APPENDIX
Supplemental Tables

Table A.1: Full Applications and Evaluations

Category	Application	Market Size (1 small to 9 large)	High End-ness (1 High end to 9 Low End)	Contamination/Purity Level (1 Pure to 9 Impure)	Cost to Implement (1 High to 9 Low	Total
Optical	Tiles	9	9	9	9	36
Optical	Mosaic art pieces	3	9	9	9	30
Optical	Aquarium gravel	3	9	9	9	30
Optical	Sand	3	9	9	9	30
Optical	Outdoor decorative stones	3	9	9	9	30
Thermal	Glass Firing beads	1	9	9	9	28
Thermal	Furnace cleaner	1	9	9	9	28
Mechanical	Ball Milling Media	9	9	3	3	24
Mechanical	Abrasive	9	3	9	3	24
Thermal	Thermal insulation	9	3	3	9	24
General	Filler material	1	3	9	9	22
Optical	Pigments and inks for pottery glazes	1	9	3	9	22
Thermal	Hot metal extrusion dies	3	9	1	9	22
Mechanical	Cutlery	9	3	1	3	16
Mechanical	Whetstone	1	3	3	9	16
Mechanical	Seaming rolls, wire dies, guides and forming tools for metal shaping	9	3	1	1	14
Optical	Jewelry	9	3	1	1	14
Electrical	Electrical Insulator (large-scale)	3	3	3	3	12
Thermal	Thermal barrier coating	9	1	1	1	12
General	Oxygen Sensors	1	1	1	3	6
Mechanical	Precision ball valves and seats	1	1	1	3	6

Optical	Optical fiber connectors	1	1	1	3	6
Thermal	Thermocouples protection	1	1	1	3	6
Electrical	Electroceramic (capacitors, etc.)	1	1	1	1	4
Electrical	Dielectric/Fuel Cell applications	1	1	1	1	4
Optical	Optical coating	1	1	1	1	4
Thermal	Nuclear reactors alloy tubing	1	1	1	1	4
Thermal	Microwave filters	1	1	1	1	4

Table A.2: Companies contacted

Company	Description	Date	Comments
Zircar	Refractory Material (Thermal insulation)	2/24/2016	Not interested
Applied Ceramics	Refractories, Catalytic Converters	2/28/2016	Not interested
Ceradyne	High performance ceramics	2/28/2016	Not interested
Coors	High performance ceramics	2/28/2016	Not interested
American Olean	Floor Tiles	2/29/2016	Put in further contact with regional distributors, then uninterested
CeramTec	High performance ceramics	2/29/2016	No response.
Estes	Aquarium Gravel	2/29/2016	Emailed Rick and John, called to follow up, not interested.
Florida Tile	Floor Tiles	2/29/2016	Heard back from sales rep-put me in contact with their glaze supplier who then was uninterested.
Marazzi	Floor Tiles	2/29/2016	No response.
Morgan Adv. Ceramics	Refractory Materials	2/29/2016	Heard back from Jeff Hagerty and Will Patton. They are optimistic that they zirconia can be used somewhere, the next steps are to send them a follow-up email with technical

			details and some powder samples. Eventually determined that not possible.
Nature's Ocean	Aquarium Gravel	2/29/2016	Said would not work.
Tetra	Aquarium gravel	2/29/2016	Not interested.
Saint-Gobain Zirpro	Zirconia Grinding Media	2/29/2016	Potentially interested-requested chemical analysis of powder samples. Continued conversation, see later.
Trebol	Glaze supplier for floor tiles	3/1/2016	No response.
Endeka Ceramics	Glaze supplier for floor tiles	3/1/2016	No response.
GlenMills	Grinding Media and Ball Media	3/1/2016	Only a middle man - told to call Jeff Girman at St. Gobain Zirpro.
Morgan Adv. Ceramics	Refractory Materials	3/1/2016	Gary Kenammer reported that they can't use it at the Augusta plant
Tosoh	Raw Material	3/1/2016	Tosoh only deals with very high quality zirconia. Any sort of impurity is not tolerable. They use a hydrolysis process where they introduce yttria chloride into a slurry, calcine the mixture, then spray dry it into fine particles. They're currently looking to massively ramp up production of zirconia products due to overwhelming demand, and they don't have time to deal with recycling. Jay's best advice was to google ceramic recycling companies and look into refractory products, since those have much larger grain sizes and can tolerate much more impurity.
Zircoa	Refractory Material and Grinding Media	3/1/2016	Not interested
Saint-Gobain Zirpro	Zirconia Grinding Media	3/1/2016	Success! Jeff mentioned a zirconia plant in Huntsville, Alabama that may be interested in recycling initiatives. He mentioned that his company is

			especially looking into sustainable use of resources.
Ferro pigments (Germany)	Glaze pigments	3/2/2016	No response.
Zircoment (UK)	Glaze pigments	3/2/2016	No response.
Zibo Belief Glaze Company	Ceramic pigment	3/2/2016	Not interested.
Norton	Fused Alumina-Zirconia-Silica Braces	3/2/2016	No response.
Silvia Barbi	Pigment/Tile	3/7/2016	Emailed back and forth to discuss her research about recycled YSZ in tiles/pigments
Vaniman	Cyclone Separators	3/14/2016	Supplied the team with a separator free of charge.
Praxair	Thermal barrier coatings	3/28/2016	Not interested.
Sulzer Metco	Thermal barrier coatings	3/28/2016	Not interested.
Starck	Thermal barrier coatings	3/28/2016	No response.