EXPLORING RHEOLOGY ADDITIVES FOR ROBOCASTING 3D ALUMINA-STRUCTURED SUPPORTS

An Undergraduate Research Scholars Thesis

by

FAWZIYA AHMED AL-DARWISH

Submitted to the LAUNCH: Undergraduate Research office at
Texas A&M University
in partial fulfillment of requirements for the designation as an

UNDERGRADUATE RESEARCH SCHOLAR

Approved by
Faculty Research Advisors: Dr. Ma'Moun Al-Rawashdeh
Dr. Yasser Al Hamidi
Dr. Eyad Masad

May 2023

Major: Mechanical Engineering

RESEARCH COMPLIANCE CERTIFICATION

Research activities involving the use of human subjects, vertebrate animals, and/or biohazards must be reviewed and approved by the appropriate Texas A&M University regulatory research committee (i.e., IRB, IACUC, IBC) before the activity can commence. This requirement applies to activities conducted at Texas A&M and to activities conducted at non-Texas A&M facilities or institutions. In both cases, students are responsible for working with the relevant Texas A&M research compliance program to ensure and document that all Texas A&M compliance obligations are met before the study begins.

I, Fawziya Ahmed Al-Darwish, certify that all research compliance requirements related to this Undergraduate Research Scholars thesis have been addressed with my Faculty Research Advisors prior to the collection of any data used in this final thesis submission.

This project did not require approval from the Texas A&M University Research Compliance & Biosafety office.

TABLE OF CONTENTS

ABSTRACT

Exploring Rheology Additives for Robocasting 3D Alumina-Structured Supports

Fawziya Ahmed Al-Darwish
Department of Mechanical Engineering
Texas A&M University

Faculty Research Advisor: Dr. Ma'Moun Al-Rawashdeh
Department of Chemical Engineering
Texas A&M University

Faculty Research Advisor: Dr. Yasser Al Hamidi
Department of Mechanical Engineering
Texas A&M University

Faculty Research Advisor: Dr. Eyad Masad
Department of Mechanical Engineering
Texas A&M University

Regulations regarding industrial gas emissions, such as CO2, became stringent over the years. Additive manufacturing is a critical enabling technology that could develop innovative solutions for this application. This application has strict requirements on pressure drop, high temperature, pore structures, and catalytic chemical performance. Structured "intricate" ceramic materials are ideal for meeting these application requirements. This research takes advantage of the wealth of literature available for alumina ceramic extrusion but explores it for additive manufacturing via "Robocasting." This is a promising method to make complex and novel 3D-printed geometries that meet chemical and physical requirements for gas emission control

applications. Paste rheology is one of the most critical manufacturing parameters that affect the quality of the 3D printed geometry. Three rheology modifiers for alumina paste are investigated and evaluated on benchmarking 3D printed geometries made via robocasting. Then, they are assessed on their physical properties only. Chemical evaluation is outside the scope of this research and will be the natural follow-up research built on the generated knowledge reached from this research.

Through this research, it was made possible robocasting an alumina structure support and establishing the workflow of going from an alumina boehmite powder to a 3D-printed structure. The main achievement of this research was to establish a workflow and a methodology that can be followed to create a printable ceramic paste suitable for making 3D-printed catalysts.

ACKNOWLEDGEMENTS

Contributors

I would like to thank my faculty advisors, Dr. Ma'Moun Al-Rawashdeh, Dr. Yasser Al Hamidi, and Dr. Eyad Masad, for their guidance and support throughout this research. And thanks to the undergraduate research department at Texas A&M University for their guidance.

Thanks also to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

Finally, thanks to my parents for their encouragement and to my family for their patience and love.

Funding Sources

This undergraduate research was supported by Texas A&M University in Qatar.

1. INTRODUCTION

1.1 Motivation and General Introduction

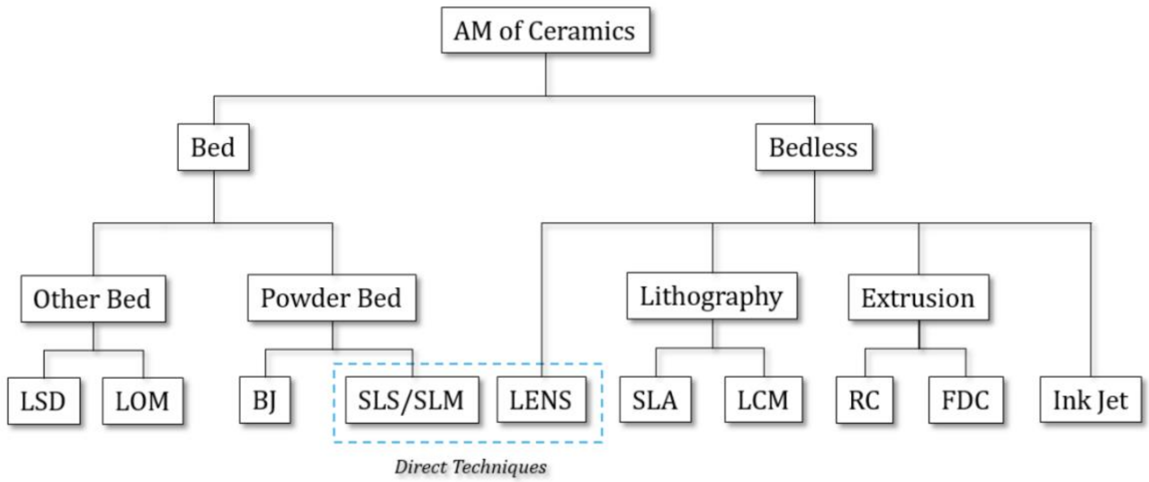
Industrial gas emissions regulations and laws have become rigorous over the past years. Additive manufacturing is a key enabling technology that could develop innovative, novel, complex solutions for this application. Additive Manufacturing (AM) process or 3D Printing and its applications are rapidly expanding in recent years. AM technology has been implemented in various industries, including the medical, engineering, aerospace, automotive, and chemical industries. AM technology has many advantages, such as design complexity, rapid prototyping, cost-effectiveness, speed, combined functionality, and waste reduction. An essential aspect of additive manufacturing is material selection. Polymers, metals, and ceramics have experienced the maximum growth in additive manufacturing till now. Ceramics have many attractive features for many applications, especially those that require high temperatures because they are thermally stable, cost-effective, and can be shaped into many structures. They can also be porous materials, making them attractive for many catalytic and chemical applications. In addition to their thermal stability and porosity, ceramics possess high hardness and wear resistance, making them suitable for various applications where high-performance materials are required. However, processing ceramics through additive manufacturing can be challenging due to their rheology, brittleness, high melting temperatures, and tendency to crack.

Designed solutions must meet strict requirements on pressure drop, high temperature, pore structures, and catalytic chemical performance. Structured “intricate” ceramic materials are an ideal candidate to meet these application requirements.

AM has become a very popular and needed technology to obtain geometrically complex structures and a high-speed design to the fabrication process [1]. AM growth in the polymer and metal fields has been exponential, with significant advancements in recent years. For instance, the development of metal powders with superior characteristics, such as high strength and thermal conductivity, has produced high-quality metal parts with excellent mechanical properties [7]. Furthermore, improvements in plastic material filaments and resins have enabled the creation of intricate and functional parts, expanding the range of applications for AM in the plastic industry [8].

However, the utilization of AM for ceramics presents unique differences and challenges [9]. Nonetheless, advancements in recent years have made it possible to create 3D-printed ceramic objects, which were previously unattainable [10].

The field of ceramic additive manufacturing has become very diverse, and there exist multiple AM technologies which enable the 3D printing of ceramics. The AM of ceramics can be categorized and separated into two main categories. The first category is processes that utilize bed (powder), and the other category is based on AM processes that don't use bed (no powder process) [2]. A schematic which displays one method to categorize ceramic 3D printing is shown in Figure 1.



LSD- Layerwise Slurry Deposition
LOM- Layered Object Manufacture
BJ- Binder jetting
SLS- Selective Laser Sintering
SLM- Selective Laser Melting
LENS- Laser Engineered Net Shaping
SLA- Stereolithography
LCM- Lithography Ceramic Manufacturing
RC- Robocasting
FDC- Fused Deposition of Ceramics

Figure 1: One method to categorize ceramic AM processes [2]

The powder-based ceramic AM processes include binder jetting, selective laser sintering (SLS), and selective laser melting (SLM). Binder jetting involves spreading a layer of ceramic powder on a build platform and selectively binding/ bonding the powder particles together with a binder or laser, as in both selective laser sintering (SLS) and selective laser melting (SLM) processes [2]. The process is repeated layer by layer until the desired 3D object is formed. The advantage of bed-based ceramic AM processes is that these processes include the ability to produce complex shapes and geometries, as well as the ability to use a variety of ceramic powder materials.

On the other hand, non-bed-based ceramic AM processes (Bed less) include stereolithography (SLA), digital light processing (DLP), and robocasting (RC). These non-bed-based processes use a liquid or paste ceramic material that is precisely cured or solidified using light or a mechanical system.

Each ceramic AM process has advantages, limitations, and challenges. For example, using binder jetting technology, it is highly impossible to create products with closed cavities, whereas it is possible using a direct energy deposition process [2]. The different capacities and limitations of each AM process make each of them suitable for different applications depending on the object design complexity, object functionality, material, etc.

Despite the challenges associated with ceramic additive manufacturing, such as the high cost of ceramic materials and the need for specialized equipment and expertise, the ability to produce complex ceramic structures with unique physical and chemical properties makes it an attractive option for a variety of applications in industries such as aerospace, biomedical, energy, chemical, and environmental.

1.2 Robocasting Ceramic AM Process

Robocasting (or micro extrusion) is one of the attractive additive manufacturing techniques to shape ceramic materials for environmental applications as catalytic materials. It allows for the creation of highly intricate and precise ceramic structures with a range of geometries and material properties. Another name for the robocasting AM process is “Direct Ink Writing” or “Direct ink Fabrication.” Robocasting utilizes a paste-like filament of ceramic material and extrudes it through a small, controlled nozzle. An extrusion paste can be prepared for a given target ceramic powder material, such as alumina. The rheology of that extrusion paste needs to be well controlled to enable a smooth robocasting process. The robocasting process is carried out by mechanically pushing the extrusion paste through a small nozzle to form a thin layer, added on top of each other to create the 3D object but as a green body, meaning still wet and has water. This green body goes through a drying step to remove water, then a calcination step to do a phase transition and give the 3D object its mechanical strength.

The process of robocasting and most AM processes works by first, designing a CAD model and then slicing it using a slicer software. Each slice will represent a layer. The properties, such as the layer height and speed, can be manually inputted and adjusted in the slicing software. Once the slicing is complete, the files are turned into a G code format which consists of a set of instructions that the printer understands. The print job is then sent/inputted to the printer through the network, SD card, or USB. The printer then translates the lines of the G code into movements and actions that allow the part to be printed layer by layer. Figure 2 displays a schematic of a typical robocasting procedure and its major components.

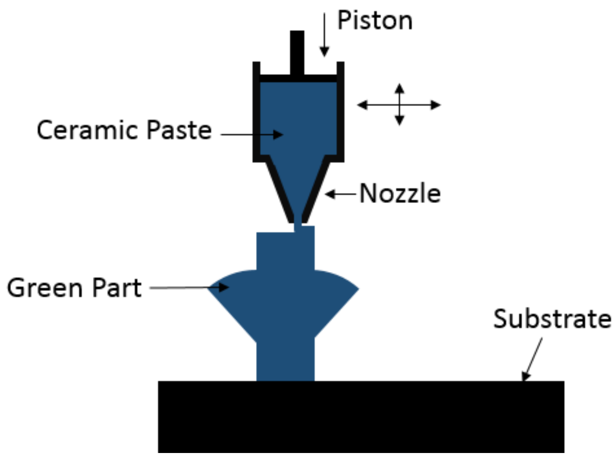


Figure 2: Robocasting Schematic [2]

Robocasting has shown promise in a variety of industries, including biomedical, aerospace, chemical, and environmental. This technology's capacity to print complicated shapes has proven extremely useful in the biomedical field, where it has been used to create dental implants and bone scaffolds [11]. Researchers have also been able to build ceramic composites with improved mechanical and thermal properties thanks to the capacity to adjust the material composition and properties inside ceramic paste [12].

Optimizing the ceramic paste to attain the appropriate qualities and functionality for the finished product is the main problem encountered while utilizing the robocasting method.

Additionally, in order to prevent problems like clogged nozzles or layer delamination, this time-consuming method necessitates exact control over both the paste formulation and printing conditions. Despite these obstacles, robocasting has shown great promise in fabricating complex ceramic structures with specific properties for various applications.

1.3 Paste Properties

The paste properties of the ceramic are crucial for a successful robocasting process. The basic requirements are [2], [3]:

- The paste must be homogeneous and free of air bubbles
- The paste should be extrudable through a small, fine nozzle

Moreover, the rheological properties of the paste must be optimized and altered by the addition of additives and agents, as well as changing the water-to-powder ratio until an extrudable and printable paste is formed. The addition of binders will help the flow and stability of the paste. In addition, the paste recipe and binder used will highly affect the printed structure's physical, mechanical, and chemical properties. For example, porosity, strength, catalytic behavior, etc.

1.3.1 Rheology Modifiers

Rheology modifiers are additives that can alter the flow properties of a material, such as viscosity. Rheology modifiers are commonly used in the robocasting process to improve the flow and printability of pastes. As the robocasting process requires the paste to be extruded through a controlled small nozzle the addition of the rheology modifiers improves the printability and stability of a paste during the printing. By altering the viscosity and flow properties of the paste, these additives can help to maintain the shape and stability of the printed structure during and after the printing process. Overall, rheology modifiers are an important tool for optimizing the robocasting process and improving the quality and performance of printed structures.

1.4 Research Objective

This research objective is to find a rheology modifier; suitable for alumina-based extrusion via the robocasting process; to explore making structured supports that meet the physical requirements of environmental emission control applications. Three rheology modifiers will be explored: Bentonite, Methyl Cellulose, and Citric Acid. Experimentations will be conducted to create pastes with each rheology modifier. Then the focus will shift to only one rheology modifier paste and further experimentations and trials will be conducted.

Bentonite is the first rheology modifier chosen. Bentonite is an absorbent aluminum phyllosilicate clay that can be mixed with alumina to create a ceramic paste for various applications. By adding bentonite to alumina, the properties of the final paste may be improved. The amount of bentonite added depends on what properties are desired by each application and can vary depending on requirements.

The second rheology modifier is Methyl Cellulose. This water-soluble polymer (derived from cellulose) is widely used as a binder in ceramics. Methyl Cellulose helps create pastes with greater plasticity and other desirable characteristics.

The final rheology modifier is Citric Acid. When added to an alumina paste, citric acid can improve its flowability and rheology as well as make it more stable.

The physical requirements will include the green body structure and stability, mechanical defects, and pressure drop for the 3D design under representative flow conditions. The below list summarizes the research objectives into three different points.

Objective 1: Review the literature to make a list of potential rheology modifiers suitable for alumina paste extrusion and get familiarized with the field

Objective 2: Establish the workflow to go from powder to printable paste

Objective 3: Create a testing methodology to help determine the printability of a paste and establish characterization methods

2. METHODS

This section will list and highlight all methods and tools used throughout the research. The first section will summarize the whole project methodology applied to complete the research. The second section will describe the method utilized to perform the literature review and obtain the references. The third section will describe the methodology associated with establishing the workflow of going from an alumina powder form to a 3D-printed structure. The fourth section will illustrate the characterization methods used to further understand and analyze the paste and 3D printed structure. The fifth and last section summarizes the material and equipment used throughout the research project.

2.1 Whole Project Methodology

The methodology that's implemented to complete and conduct the research is split into five different tasks, which are as follows:

Task 1- literature review will be conducted to identify and select three different Alumina rheology modifiers (A, B &C) and their paste preparation recipes.

Task 2- Establish the settings for the 3D printing process and finalize product geometry and dimensions using playing dough.

Task 3- Selected rheology modifiers paste recipes to be created and, finalized geometry to be robocasted (using formed pastes),

Task 4- The fabricated products will be evaluated through different physical property tests: for example, green body structure stability, shrinking volume, imaging for mechanical defects, and pressure drop.

Task 5- Procedure and testing results will then be analyzed and summarized in a report thesis for submission to the URS.

2.2 Literature Review Methodology

A structured reference search will be implemented to obtain reference material for the related topic, in addition, to exploring the ongoing research in the field of 3D printing of alumina. Highlighting the gap in the topic research and the importance of the conducted research. Google Scholar was used as the search engine to gather references and material. Specific keywords were used to collect references specific to the topic of robocasting Alumina and filter results to gather more specific material. Iteration of adding keywords is made to filter out references until a manageable number of references is outputted. By screening the titles, and papers (abstract) the number of references chosen is reduced to a good number ranging between 0-30 articles. Key information is extracted from each paper and summarized in a table format.

2.3 Workflow to go from Powder to the Printed Structure

Once potential rheology modifiers have been identified and researched, in addition to an intensive literature review being performed, the next step is to establish a general workflow to go from powder to printable paste. The workflow highlights the basic process of the experimental method. Figure 3 displays a schematic of the workflow model drawn to represent the experimental method. The first step of the workflow established is obtaining a 3D CAD model of the part utilizing SolidWorks software (generating a G-code file by utilizing slicing software "Cura"). Paste preparation comes next in the workflow. During this step, the ceramic paste is made by following the paste preparation method discussed below. The formed paste is inserted into the material cartridge, and the printer is started, which brings us to the third point, which is the printing process (robocasting process using EAZAO Zero printer). After the print job is completed, the last part is drying and calcination of the green body alumina structure.

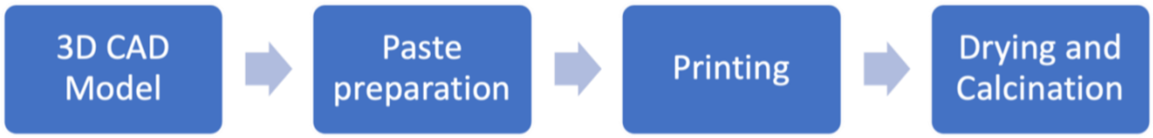


Figure 3: Establishing the workflow process

2.3.1 3D CAD Model

The first step to establishing the workflow is to design a 3D CAD model. Solidworks Software was utilized to draw the 3D CAD model. The model was reviewed, and changes were iteratively made until the design met all requirements, such as size, spacing, height, and internal geometry. The CAD file was exported as an STL format from SolidWorks, then imported to a slicer software. The part orientation, printer, material, and print setting were inputted into CURA slicing software. The part is sliced, and the print job is saved as a G-code file into an SD card, which will then be inputted into the printer.

2.3.2 Paste Preparation

The second step of the workflow is paste preparation. The paste preparation method is done using two different methods. The first method is preparing the paste with the citric acid additive (solution additive), and the second method is for creating the paste with Bentonite and Methyl Cellulose additives (powder additives).

The paste preparation method using citric acid as an additive is as follows: First, the alumina powder is grinded using a grinder machine (displayed in Table 2), then the citric acid solution is prepared. The citric acid solution is gradually added to the powder and mixed between the intervals. The paste is then kneaded by hand to make sure it's homogenous and fully combined. Figure 4 showcases a flow chart that represents method 1 (M1) to create the alumina paste with the citric acid solution as the rheology additive.

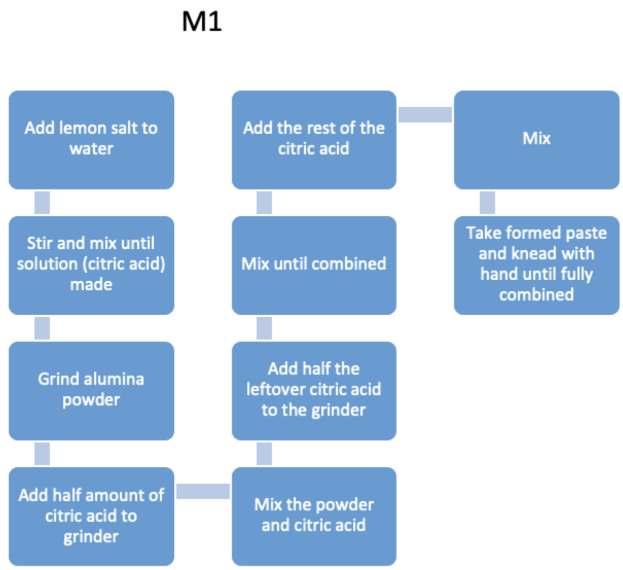


Figure 4: M1 method to prepare a ceramic paste with citric acid

For the paste preparations utilizing the powder additives (Bentonite and Methyl Cellulose), the method is as follows: First, the alumina powder is grinded using a grinder machine. The powder binder is then added to the grinder and mixed with the powder. Water is gradually added to the powder mixture and mixed between the intervals. The paste is then kneaded to make sure it's homogenous and a fully combined ceramic paste is generated. Figure 5 illustrates a flow chart of method 2 (M2) to create the alumina paste with powder Bentonite and Methyl Cellulose as the rheology additives.

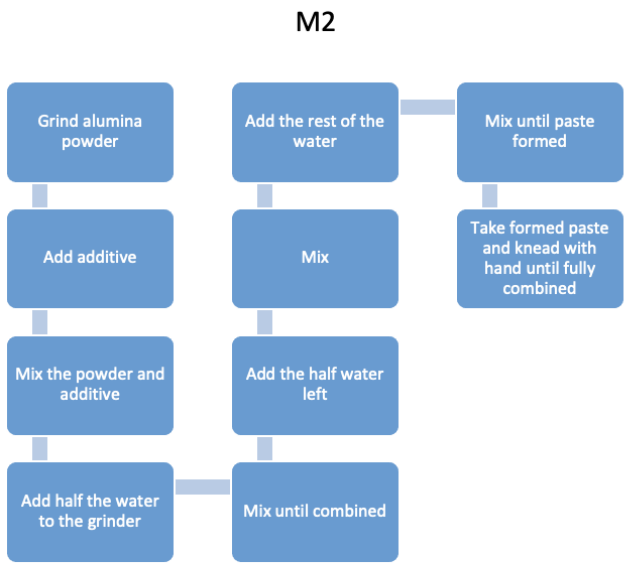


Figure 5: M2 method to prepare a ceramic paste with powder additives

2.3.3 Printing Process

The third step of the workflow is the printing process. Eazao Zero Ceramic 3D Printer (displayed in Table 2) is utilized for printing the Alumina structured supports in this research. Parts were all printed with the same printing settings, including speed, layer heights, line width, etc. except in comparison and study cases. The printing process is summarized and explained below. Eazao Zero ceramic 3D printer comes with an electric putter and a material cartridge; the paste is placed inside the material cartridge and connected to the electric putter. The electric putter, once started, pushes the ceramic paste into a tube connected to the screw-based nozzle. The nozzle then deposits circular filaments of the paste onto the platform to form the part based on the G-code instructions. Thin layers of the paste are deposited to create the required body/design layer by layer. After each layer is printed, the nozzle moves up in the z-axis direction and starts depositing the next layer on top of the previous layer.

2.3.4 Drying and Calcination

The last step of the workflow is the process of drying and calcination. After the green body 3D boehmite alumina structure is successfully printed, it needs to undergo a drying and calcination process to get rid of the water particles and excess binder in addition to achieving the physical, mechanical, and chemical properties according to its application. Two different methods were used throughout the research. The first method is allowing the robocasted alumina green body structure supports to dry at room temperature (~ 21℃) in the laboratory. The second method is utilizing the dryer oven (Table 2) and setting it to around (~ 50℃) , the structure is left in the dryer for around 1 to 2 hours.

2.4 Characterizations Methods

Part of the research methodology is associated with the evaluation of the 3D-printed playdough and Alumina structures through different physical property tests: including green body structure stability, shrinking volume, imaging for physical defects, and pressure drop. However, prior to characterizing the robocasted part. A method to test the created paste is established which helps determine whether the paste is good or bad. Each testing method will be further discussed and demonstrated below.

2.4.1 Paste Testing Method

To test whether the paste is printable or not and whether it is suitable for printing the alumina structure a single-layer testing geometry was created. The testing geometry aims to give a clear result of whether the paste is suitable to use for the printing process or not. The geometry is displayed in Figure 6.

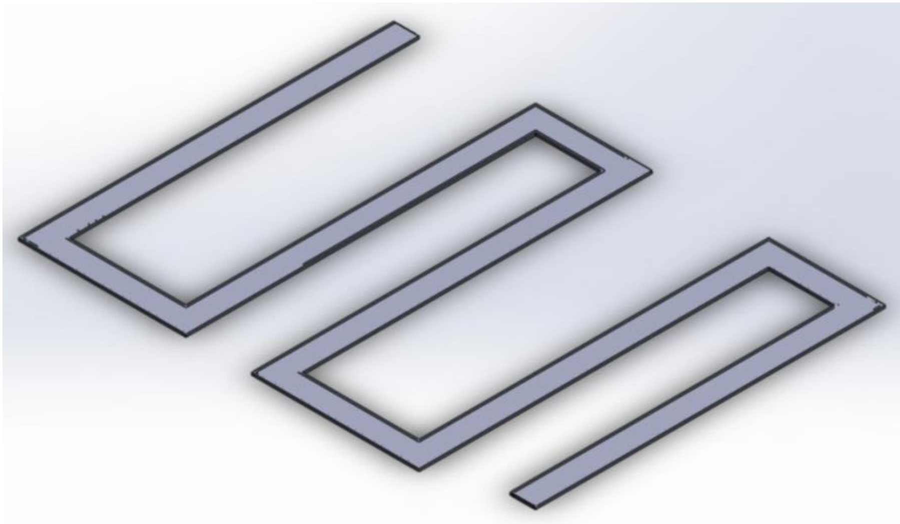


Figure 6: Testing Geometry

2.4.2 Imaging

The imaging characterization method is performed to discover the internal geometry, each layer deposition onto the previous layer, and physical defects. To perform the imaging characterization method, a setup consisting of a camera, a camera stand with adjustable height positions, and a plain surface is required. Six images are taken of each robocasted alumina structure support parts in varying positions (top / bottom/ side) and from three different height positions of the camera.

2.4.3 Shrinking Volume

The shrink volume test is another characterization method used in this research. The shrink volume test is performed to monitor how much the green body alumina structure shrinks after the drying process. To measure the shrink volume of the 3D printed alumina structure in comparison to the 3D CAD model design dimensions. This is done by taking an image of the dried object with a reference object (e.g., a nut) with known dimensions. The image is imported to Digimizer software (image processing software), and a line is drawn across the object and another line across the reference object. The number of pixels equivalent to the lines is outputted and recorded. Finally, a conversion from pixels to length is derived while knowing the dimension of the reference object. Therefore, the new shrunk dimension of the printed part is found and compared to the CAD model design. It is then possible to acquire the shrinking volume. Figure 7 displays an illustration for the picture setup with a nut as the reference object.

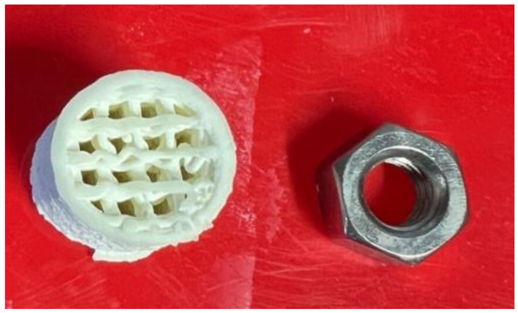


Figure 7: Example of picture setup

2.4.4 Pressure Drop

Characterizing the 3D robocasted support structures by evaluating the pressure drop is done by creating a small setup. The setup consists of a glass tube, with the structure placed in the center. Airflow is introduced at one end, and the pressure readings at both ends are recorded. Finally, the difference is computed. Different visuals can then be used to better summarize the results such as scatter/line graphs.

2.5 Materials and Equipment

In this section, the materials and equipment used throughout the research are displayed. Alumina Boehmite powder was the ceramic material that corresponds to the focus of this research. Water was also used and added to the alumina boehmite powder to create and form the ceramic paste. Methyl Cellulose, Bentonite, and Citric Acid were the chosen rheology additives for this research and were used as binding agents for the paste. Table 2 illustrates the material used throughout the research, including the alumina-type powder and the three different additives.

Table 1: Material List

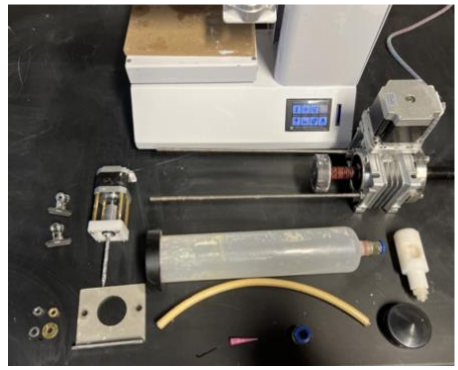
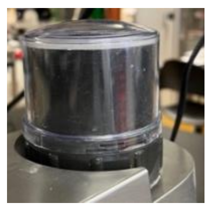
Material	
Alumina Boehmite Powder	
Methyl Cellulose	
Bentonite	
Citric Acid	

The main equipment utilized to complete and perform the experiments are as follows: firstly, the Eazao Zero Ceramic 3D Printer is the printer used in this research to robocast the Alumina structured supports. Furthermore, a grinder machine is used to grind the alumina powder into smaller particles in addition to forming the ceramic paste by mixing the alumina powder, rheology additives, and water. In addition, a dryer was used to dry the alumina structures. All equipment used throughout the research is illustrated in Table 3.

Figure 8 illustrates the 3D-printer used throughout the research.

Figure 8: Eazao Zero 3D-printer [4]

Table 2: Equipment list

Equipment	
Eazao Zero 3D Printer	Displayed in Figure 8.
Material Cartridge	
Piston	
Tube	
Nozzle	
Extruder	
Printing Platform	
Electric Putter	
Quick Connectors	
SD Card	
Grinder Machine	 
Dryer Oven	

3. RESULTS

3.1 Literature Review

As previously mentioned in section 2.2, a structured reference search was implemented to generate applicable references to the research. Google Scholar was used as the search engine. By implementing the structured reference search, the following results were obtained:

The final keywords are “Alumina rheology modifier paste robocasting.” The output was 347 references related to the topic. The keyword filtering process is shown in Figure 9. By screening the titles, the number of references chosen was 21. The 21 references are summarized, and the main information was extracted and inputted in Table 3.

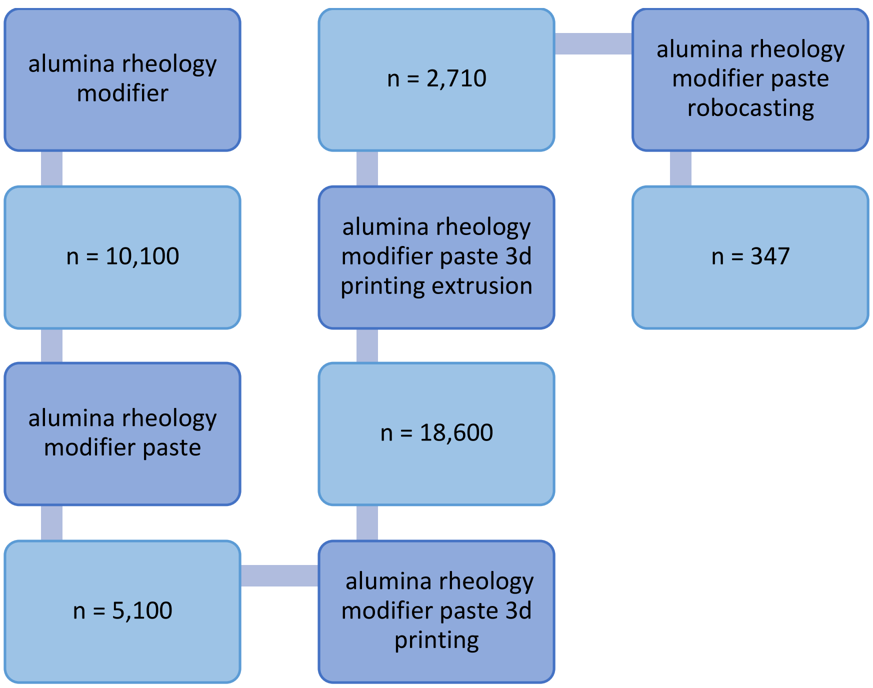


Figure 9: Keyword filtering process

Table 3: References table

#	TITLE	YEAR	UNIVERSITY	KEYWORDS	CERAMIC	ADDITIVE	PASTE/MIXING	CHARACTERIZATION	REFERENCING
1	Robocasting of highly porous ceramics scaffolds with hierarchized porosity	2021	INSA Lyon	3D printing Robocasting Porous ceramics Multiscale porosity Starch	Ceria stabilized zirconia powder	Wheat starch, potato starch and rice starch	SpeedMixer, Synergy devices limited	Weight/Density, X-ray Tomography, Scanning Electron Microscopy (SEM), Mercury intrusion porosimeter, mechanical properties	[6]
2	Research on rheological properties and extrusion behavior of aqueous alumina paste in paste-extrusion-based SFF processes	2015	Lanzhou University of Technology	Aqueous alumina paste Rheological properties Extrusion behavior Solid freeform fabrication	Zhengzhou Tianma Micopowder Co, Alumina Powder		Mixing for 24 hours, slurry paste	pH 6.5-6.7 dynamic viscoelastic properties	[13]
3	Controlling properties of ceramic formulations for porcelain robocasting	2023	University of Aveiro	Porcelain Robocasting (R3D) Additive manufacturing (AM) Rheology	Spray dried industrial porcelain powder from a Portuguese company (Porcelanas da Costa Verde S.A.	sulfuric acid (9.8 wt%) from Sigma	-	scanning electron microscopy (SEM) rheological study	[14]
4	Additive Manufacturing of Ceramics and Ceramic Composites via Robocasting	2017	Imperial College London		Alumina powder (SMA6, Baikowski, FR)		Thinky ARE-250 planetary mixer. Courtesy of Intertronics Ltd.	HR-1 rheometer	[2]
5	Additive manufacturing of advanced ceramic materials	2021	University of Nottingham, University of Birmingham	Additive manufacturing AM 3D printing Advanced ceramics Powders Colloidal processing Density Mechanical properties	Review paper				[5]
6	Robocasting of self-setting bioceramics: from paste formulation to 3D part characteristics	2021	university of Toulouse	Robocasting Self-setting ceramic Scaffolds Calcium sulphate Apatite	Calcium Sulphate	Polyvinyl alcohol (PVA), Carboxymethyl cellulose (CMC)	Varying two main parameters: the additive/reactive powders ratio and the L/S ratio.	Compression test	[15]
7	Investigation of machinability of green bodies of solid cast alumina through the addition of a poly(carboxylate ether)-based superplasticizer	2015	Graduate School of Engineering and Natural Sciences		200 nm alumina	superplasticizer		Compression test Density measurements Rheometer	[16]
8	Realization of complex-shaped and high-performance alumina ceramic cutting tools via Vat photopolymerization based 3D printing: A novel surface modification strategy through coupling agents aluminic acid ester and silane coupling agent	2023	Guangdong University of Technology, University of Southern California, Tsinghua University	3D printing Vat photopolymerization Surface modification Photopolymerization kinetics Ceramic cutting tool	Al2O3 powder TM-DAR (TAIMEI Chem-icals Co., LTD., Japan)	aluminic acid ester (ACA, Lida Chemical, China) and silane coupling agent (KH570, Aladdin, China). deionized water and ethanol	planetary ball mill for 2 h at a speed of 400 r/min	rheological analysis imaging	[17]

Table 3 continued

#	TITLE	YEAR	UNIVERSITY	KEYWORDS	CERAMIC	ADDITIVE	PASTE/MIXING	CHARACTERIZATION	REFERENCING
9	Fabrication of 3D-Printed Ceramic Structures for Portable Solar Desalination Devices	2021	National University of Singapore, Shanghai Jiaotong University	Absorption, Ceramics, Desalination, Evaporation, Silica	SiO2	high-boiling point plasticizer, PEGDA, TPO, and OB+	24 h	rheometer, Discovery HR-2	[18]
10	Variation of density in additive manufacturing of ceramic parts: A review	2021	Indian Institute of Technology (B.H.U.	Additive Manufacturing (AM) Direct Ink Writing (DIW) Porosity Ceramics	Al2O3) and zirconia (ZrO2) or non-oxides such as carbides, nitrides, and borides	PVP, 1-ethenyl-2-pyrrolidinone homo polymer			[19]
11	Aluminum concentration range for the extrudability of ceramic pastes	2022		Alumina pastes Al2O3 Robocasting Al concentration PVA/Glycerol ratio Ceramic pastes Shrinkage	Commercial alumina powder (Ceradel, mean grain size 8.3 µm and ρ = 3.97 g/cm3)	Glycerol, polyvinyl alcohol, PVA, Rhodoviol 25/140, VWR Chemicals), ISOBAM 104 (Kuraray Co., Ltd, Osaka, Japan)	green samples were dried at room temperature during 18 h in air with 50% RH, then heated in a furnace (Ceradel CT15) during 3 h at 650 ◦C with a 1 ◦C/min heating rate under static air	Density, Thermogravimetric analyses (TGA), Shrinkage, imaging, and microstructure	[20]
12	Layered extrusion forming of complex ceramic structures using starch as removable support	2019	Huazhong University of Science and Technology	Additive manufacturing Layered extrusion forming Support material Starch Ceramic parts	Ceramic paste	Starch, polyvinylpyrrolidone (PVP), and absolute ethyl alcohol	starch-based slurry that can be used as support material for the 3D printing of complex ceramic parts		[21]
13	Direct ink writing of dense alumina ceramics prepared by rapid sintering	2022	Tianjin University, Tiangong University	Al2O3 3D printing Printability of inks Rapid sintering Densification	Alumina powder (d50 = 6.65 µm, purity 95%)	NHPA, DTAC	green bodies were gained in the oven at a temperature of 80 ◦C after 6 h. dried alumina green bodies were sintered at 1500 ◦C for 3 h	Test using plastic syringe with nozzle,	[22]
14	A printability index for linking slurry rheology to the geometrical attributes of 3D-printed components	2019	University of California, Carnegie Mellon University	3D-printing Rheology Laser triangulation Quality control CAD	silicate-based mixture			X-ray diffraction (XRD), thermogravimetric analysis (TGA), Particle size distribution (PSD), D-scanning, density, printer settings, shrinkage,	[23]
15	Dispersion and rheology for direct writing lead-based piezoelectric ceramic pastes with anisotropic template particles	2020	Texas A&M		Review paper				[24]
16	Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities	2015	Texas A&M		Review paper				[25]
17	Fabrication of complex ceramic parts with sacrificial material using freeze-form extrusion fabrication	2012	Missouri S&T		alumina paste (Al2O3)	organic binder	s freeze-dried; then, the main material's binder and support material were removed through a burnout process before sintering to obtain the final part.		[26]

Table 3 continued

#	TITLE	YEAR	UNIVERSITY	KEYWORDS	CERAMIC	ADDITIVE	PASTE/MIXING	CHARACTERIZATION	REFERENCING
18	A review on the ceramic additive manufacturing technologies and availability of equipment and materials	2022	University of São Paulo, Universidad de Antioquia	3D printing; additive manufacturing; ceramics; digital light processing; stereolithography; viscosity	Review on ceramic AM technologies and their printed parts functionality				[27]
19	A review on additive manufacturing and materials for catalytic applications: Milestones, key concepts, advances and perspectives	2021	University of Jaén	Printed catalysts Printed structured catalysts Reaction ware Monoliths Additive manufacturing and catalysis	Review paper about catalyst and AM.				[28]
20	Ceramic robocasting: Recent achievements, potential, and future developments	2018			Review paper on robocasting of ceramic				[1]
21	Optimization of mechanical properties of robocast alumina parts through control of the paste rheology	2023	University of Lyon	Additive manufacturing Robocasting Rheology Strength Fracture	Alpha-alumina ceramic powder		magnetic stirrer, Speedmixer (Hauschild GmbH & Co.KG, Hamm, Germany).	Strain sweep test, rheometer, optimizing printing parameters, printability criteria	[28]

Through the literature review, it was evident that additive manufacturing of ceramics is a complex process with multiple key factors. It was also evident that in the last few years AM for ceramics has gained the interest of many researchers around the globe. Most papers were written/published in the last 5 years. After conducting the literature review, several crucial takeaways were identified.

The first takeaway mentioned in most papers is the importance of the rheology of the ceramic paste, as paste rheology is critical in determining the printability of the paste and its mechanical properties. Maillard, Mathilde, et al. demonstrates the essential requirements of the ceramic paste rheology behavior, including extrudability, aging, stiffness, yield stress, flow point, the fidelity of the shape, and flow transition index in shaping the printability of the ceramic paste in Direct Ink Writing (DIW, Robocasting) process [28]. Part of the extrudability criteria is having a homogenous paste. Many papers focus on the mixing process by using machinery and letting the ceramic powder, additives, agents, and water mix for between 2 hours to 24 hours [13][17][18][20]. This lengthy mixing process ensures the ceramic powder is thoroughly combined and homogenous to avoid water segregation and air bubbles within the paste. Moreover, many research articles use a combination of rheology additives and other agents (e.g., acid solutions) to create ceramic structures. This can be a further development of the research presented in this document.

Another key takeaway from the literature review is the characterization methods of the printed structures. Many papers focus on quantifying the rheology of the paste by using a rheometer. Using the results outputted by the rheometer they can determine a printability range. Another characterization method is through compression testing, to determine the compressive strength of the 3D-printed structures. Lastly, many papers mentioned the study of shrinkage, density, and physical defects. For physical detects testing imaging, tomography (X-ray imaging) was mostly used throughout the articles shown in Table 3.

3.2 Experiments to Achieve Printable Paste (Playing Dough Paste)

This section will illustrate the results obtained through Task 2 of the project methodology (section 2.1). The first section showcases the results of the iterations performed in order to obtain the final set of geometries. The second section showcases the results obtained regarding optimizing printer settings and further understanding the implications of layer height, speed, and line width in addition to other settings. The last section shows the results obtained from the characterization methods.

3.2.1 Fixing Design Geometry

SolidWorks software was used to generate and draw the geometrical 3D CAD models. Multiple designs were generated and edited until a design that satisfied the end visuals and goal of this research was approved. The iterative process of design optimization can be seen in Figure

7 (a). Figure 7(b) shows the stages of developing the design of the printed geometries. Figure 11 shows the final set of CAD models of the structures that will be used to print the Alumina support structures. The final set of structures is a set of six designs and each layer of the design is rotated by a specified angle. The first design is a 0° angle design, and each layer is exactly placed on top of the previous. The other designs are 9°, 18°, 30°, 45°, and 90° angled designs where each layer is rotated at a specific angle depending on the design. The designs were tested by printing them using play dough as shown in Figure 11.

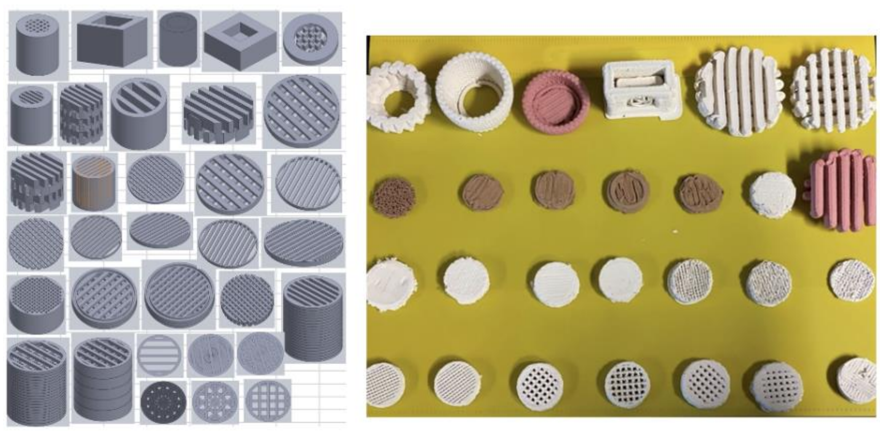


Figure 10: (a) CAD Design optimization process (b) 3D printed design optimization illustration

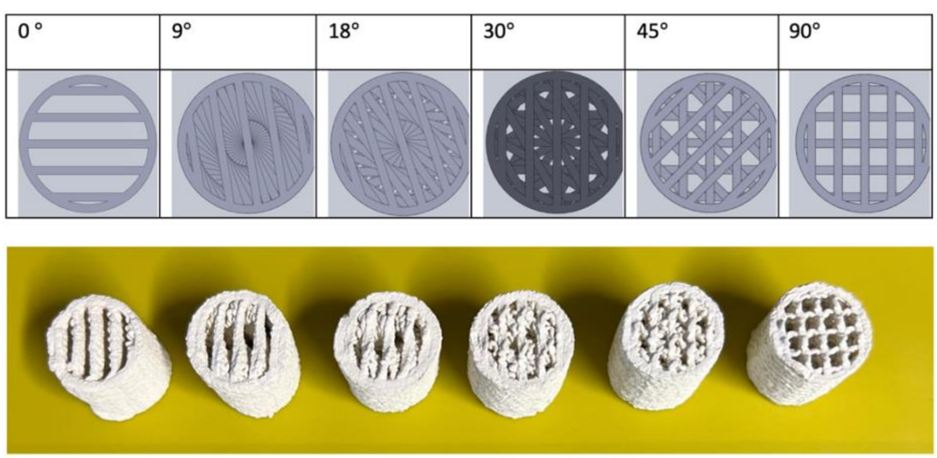


Figure 11: Final set of geometries

3.2.2 Printing Settings

During this stage, the focus was establishing the process of going from a CAD model to a printed part. In addition to exploring the printing parameters of the slicer software and their effect on the output. For example, investing the effect of increasing and decreasing the print speed, the effect of layer height, line width, and finally nozzle diameter. The design was printed multiple times with varying parameters, which resulted in a clear image of the effect of each printing setting. Therefore, optimal settings were chosen. It was deduced that a calibration between nozzle diameter and line width on both the CAD file and slicer software parameters was needed to produce a one-line geometry.

Table 4 & Table 5 show the same design printed with different printing parameters and nozzle sizes.

Table 4: Print settings optimization

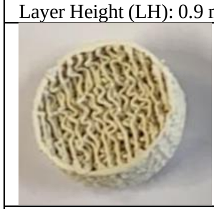
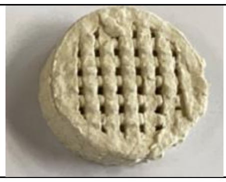
			
Nozzle: Pink Print Speed (PS): 60 mm/s Line Width (LW): 0.89 mm Layer Height (LH): 0.9 mm	Nozzle: Pink PS: 60 mm/s LW: 0.8 mm LH: 0.9 mm	Nozzle: Pink PS: 30 mm/s LW: 0.89 mm LH: 0.9 mm	Nozzle: Pink PS: 90 mm/s LW: 0.89 mm LH: 0.9 mm
			
Nozzle: Pink PS: 60 mm/s LW: 0.89 mm LH: 1.2 mm	Nozzle: Pink PS: 60 mm/s LW: 0.89 mm LH: 0.7 mm	Nozzle: Pink PS: 60 mm/s LW: 0.5 mm LH: 0.9 mm	Nozzle: Black PS: 60 mm/s LW: 0.89 mm LH: 0.9 mm

Table 5: Print settings optimization

		
Nozzle: Pink (small)	Nozzle: Black (Medium)	Nozzle: Green (Big)

Moreover, the maximum number of layers possible to print with the design was tested by printing the same design, with a different number of layers: 5,16, 20, 48, and 96. This allowed us to explore the limitations and capabilities of the printer. The taller the product, the less stable it becomes which causes it to move around while it's still printing. This causes the layers to get mixed up. Thus, the print job gets ruined. Figure 12 displays the results obtained from the different trials to monitor the object height limitation.

Figure 12: Layer height limitations results

3.2.3 Characterization Testing Trials on Playdough Samples

The following results were obtained by performing the evaluation methods on the experimental material (playdough) samples. Four different evaluation methods were performed: Mass difference testing, imaging, and pressure drop, tomography.

3.2.3.1 Mass Difference

The mass of 6 of the same geometry printed was computed and recorded. The mean and standard deviation were then computed respectively as shown in Table 6.

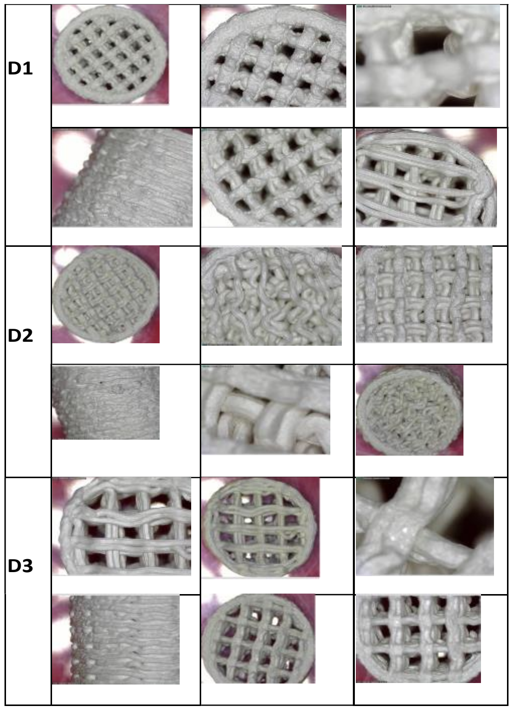
Table 6: Mass of structures test results

No	Mass of D1 [g]	Mass of D2 [g]	Mass of D3 [g]
1	2.48	2.02	1.54
2	1.67	1.62	2.06
3	2.04	1.7	1.5
4	1.96	1.71	1.78
5	1.97	1.62	1.74
6	1.73	2.16	1.65
Avr	**1.975**	**1.805**	**1.712**
St Dev	**0.2872**	**0.2284**	**0.2024**

3.2.3.2 Imaging

The results from taking images from different heights of the sample structures are displayed in Table 7. It is evident that some prints had more defects such as micro-crack, and non-straight printing lines.

Table 7: Imaging test results



3.2.3.3 Pressure Drop

By performing the pressure test on the playdough robocasted samples the results were summarized in Table 8.

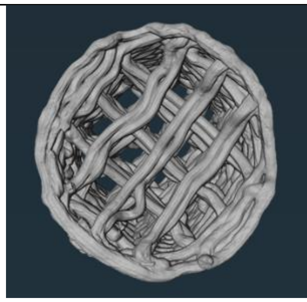
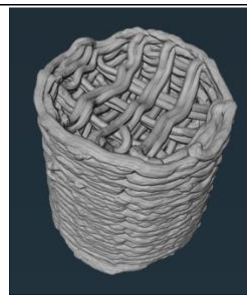
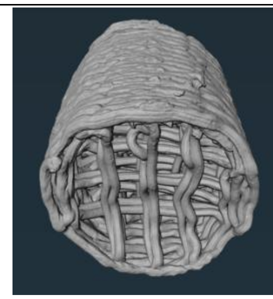
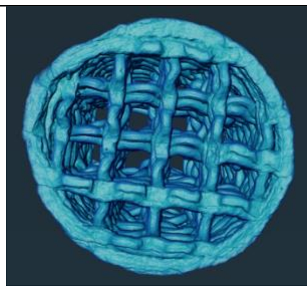
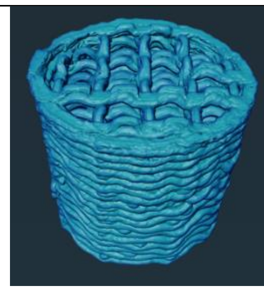
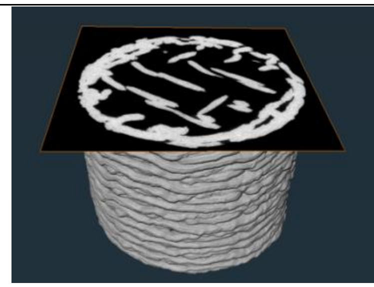
Table 8: Pressure test results

Test no	Air flow rate	Differential Pressure [mbar]
D1-3pieces	0.5	4
	1	16
	1.5	39
D2-3 pieces	0.5	4
	1	17
	1.5	46
D3- 3pieces	0.5	3
	1	15
	1.5	38
D1-6 pieces	0.5	5
	1	19
	1.5	46
D2-6 pieces	0.5	5
	1	20
	1.5	49
D3- 6 pieces	0.5	4
	1	16
	1.5	41
	Maximum	**49**

3.2.3.4 Tomography

Tomography or X-ray imaging technique was used to get 3D images of the robocasted structure to compare it to the original CAD model. Table 9 illustrates the results received from the tomography lab.

Table 9: Tomography images results

Tomography Results		
		
		

3.3 Trials to Get Alumina Printed Jobs

After establishing the settings for the printing process and product geometry and dimensions using playing dough, the research focused on being able to print the 3D CAD model finalized in the previous step. In addition, to use the knowledge and experience from experimenting with the play dough. Transitioning from the playdough to the Alumina material, the first step was establishing a method that allows the formation of an Alumina paste from alumina powder form.

In the step of going from powder alumina to a paste, many issues surfaced, including paste segregation, air bubbles, and discontinuous printing. All of which indicates that the paste isn't homogenous. Figure 13 displays images that showcase the paste discontinuous printing and water segregation that occurred during the robocasting process.

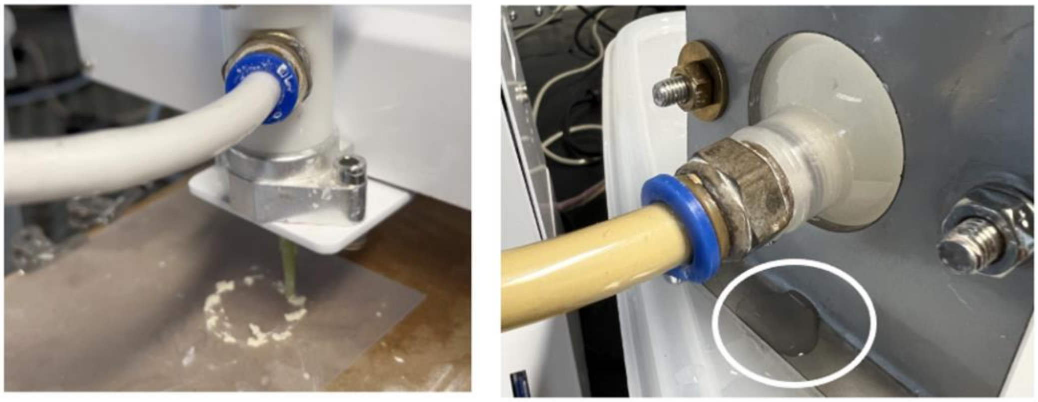


Figure 13: Issues faced during printing

To tackle this issue, different methods of paste formation were experimented with until an approach yielded a good homogenous paste. Different experimental paste recipes were created using the different experimented methods to evaluate their printability and compatibility with the Eazao zero ceramic 3D printer. Figures 4 (for the citric acid method) and 5 (for the technique utilizing powder additives) illustrate the procedures established and finalized.

After the paste formation methods were finalized, the next step is to try printing the alumina structures. Table 10 displays the first set of experiments performed as part of campaign one using Bentonite and Methyl Cellulose as additives. These paste recipes weren't successfully printed. Subsequently, using citric acid as an additive, alumina paste was formed. The experimental campaigns performed with citric acid are displayed in Table 11. The paste using citric acid as an additive was successfully printed after trying with different amounts of acid.

Table 10: Campaign one results

Recipe number	Additive type	Alumina - g	Water -g	Additive - g	Methods	Results
C1-1	Bentonite	10		1	Trial	Didn't Print
C1-2	Bentonite	10	6.2	1	Trial	Didn't Print
C1-3	Bentonite	10	20	0.5	Trial	Didn't Print
C1-4	Methyl Cellulose	20	30	0.6	Trial	Didn't Print
C1-5	Methyl Cellulose	10	40	0.5	Trial	Didn't Print
C1-6	Bentonite	10		1	Trial	Didn't Print
C1-7	Bentonite	10	6.2	1	Trial	Didn't Print

Table 11: Campaign two results

Recipe number	Additive type	Alumina - g	Water -g	Additive - g	Methods	Results
C2-1	Citric acid	20	15	10	M1	Nearly
C2-2	Citric Acid	20	18	10	M1	Successful
C2-3	Citric Acid	40	40	15	M1	Successful
C2-4	Citric Acid	40	48	15	M1	Successful
C2-5	Citric Acid	40	48	10	M1	Nearly

The repeatability of the paste (C2-4) was tested by forming the paste again under the same conditions, and the same geometry was printed six times. Figure 14 shows images of the six geometries printed using paste C2-4.

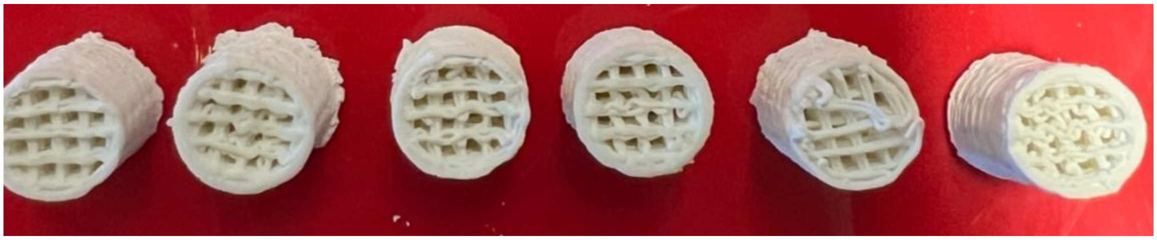


Figure 14: Repeated geometry printing results

3.4 Method for Evaluating the Alumina Paste

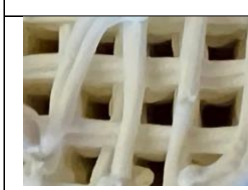
This section will show the results of the paste testing method described in section 2.4.1. The created paste testing geometry was printed with four different nozzles at two speeds (30mm/s and 60mm/s). This allowed a clear visual of the effect of printing speed on the outcome and which combination would yield the best part. Figure 15 displays the 30mm/s speed results, whereas Figure 16 shows the 60mm/s speed results. By observation, it can be concluded that speed influences the quality of the print and can lead to discontinuous printing. Evidently, it is clearly shown in Figure 16 the print job using the blue nozzle, the paste didn't get stuck to the base and curled up due to the speed. Additionally, the geometry printed for the green nozzle at 60mm/s shows discontinuous printing and paste cracking.

Figure 15:30mm/s results

Figure 16: 60mm/s results

Close-up images of the robocasted alumina structures were also taken after drying to visualize the defects, such as cracks. Table 12 displays the obtained images.

Table 12:Imaging results

Images of Citric Acid Additive Alumina Structures		
		
		
		
		

3.5 Developed Testing Methodology

This research aimed to establish the workflow on how to go from powder to 3D-printed ceramic supports using robocasting suitable for catalytic applications. Following are guideline steps that can be followed in the future when exploring new powder material for 3D printing:

1- Perform a literature review to choose three rheology additives, or based on additive availability to experiment with

2- Select printing settings, and the printing procedure. This can be done with playing dough if needed.

3- Finalize the required CAD model. Have a reference case that works well with ceramic material, and some backup CAD designs with different dimensions

4- Focus on the mixing method to get a homogenous paste

5- Create a simple CAD geometry that helps determine the printability of the paste. This is a simple geometry as straight lines as shown in section 3.4. This step will help define the printing speed, and nozzle type, and first, check the paste quality.

6- If the paste passes the testing method, try printing the CAD model

7- Establish a workflow for the new material

8- Dry under the same conditions (dryer oven)

9- Calcination to make strong supports

10- Do physical tests – imaging,

4. CONCLUSION

This research established the workflow of going from powder alumina to a 3D printed structure for alumina-based material (Boehmite) using Citric acid which was a better printable paste compared to Bentonite and Methyl Cellulose additives. Testing guidelines were developed that can be followed to aid the process of printing structure support from any ceramic powder. In this work, it was found that the mixing procedure has a significant effect on the printability of the paste which would require further research in the future. Different CAD designs and files have been established to make 3-D printed catalysts. Prototypes of some of these geometries have been successfully printed. Procedures for testing the prototypes using image analysis for physical defects and pressure drop has been successfully made.

4.1 Future Work

The following are recommendations for future research work toward achieving 3D printed catalyst with Robocasting (micro extrusion):

- Conduct more tests on the missing method and link that with rheology tests using a plate rheometer to create a printability index
- Following a design of experiment approach do a more detailed experiment with different levels of citric acid, paste water content, trying new additives.
- Perform analytical study analysis can be performed on the geometries through Solidworks analysis tools to check mechanical strength and CFD to check fluid dynamics.
- Try the developed knowledge and approach on new materials

REFERENCES

[1] E. Peng, D. Zhang, and J. Ding, “Ceramic robocasting: Recent achievements, potential, and future developments,” *Advanced Materials*, vol. 30, no. 47, p. 1802404, 2018.

[2] Feilden, Ezra, "Additive manufacturing of ceramics and ceramic composites via robocasting." 2017.

[3] M. Maillard, J. Chevalier, L. Gremillard, G. P. Baeza, E.-J. Courtial, S. Marion, and V. Garnier, “Optimization of mechanical properties of robocast alumina parts through control of the paste rheology,” Journal of the European Ceramic Society, 2022.

[4] “Eazao Zero,” Eazao, 02-Nov-2021. [Online]. Available: https://www.eazao.com/eazao-zero/.

[5] Y. Lakhdar, C. Tuck, J. Binner, A. Terry, and R. Goodridge, “Additive Manufacturing of Advanced Ceramic Materials,” Progress in Materials Science, vol. 116, p. 100736, 2021.

[6] L. Tabard, V. Garnier, E. Prud’Homme, E.-J. Courtial, S. Meille, J. Adrien, Y. Jorand, and L. Gremillard, “Robocasting of highly porous ceramics scaffolds with hierarchized porosity,” Additive Manufacturing, vol. 38, p. 101776, 2021.

[7] Y. J. Kim, C. J. Yoon, and J. H. Ko, "Additive Manufacturing of Metal Parts: Advances and Perspectives," Science and Technology of Advanced Materials, vol. 20, no. 1, pp. 665-678, 2019.

[8] J. R. Tumbleston et al., "Continuous Liquid Interface Production of 3D Objects," Science, vol. 347, no. 6228, pp. 1349-1352, 2015.

[9] B. V. K. Reddy, "Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities," Journal of the American Ceramic Society, vol. 98, no. 7, pp. 1983-2001, 2015.

[10] J. Gao, H. Sun, and Y. Xiong, "Ceramic Additive Manufacturing: From Technical Developments to Opportunities in Innovation and Business," Frontiers of Mechanical Engineering, vol. 13, no. 3, pp. 320-333, 2018.

[11] M. J. Ansari, M. R. Ghanbari, H. Karimzadeh, and M. Mirzajani, "A review on the application of ceramic 3D printing in biomedical engineering," Bio-Design and Manufacturing, vol. 2, no. 2, pp. 73-92, 2019.

[12] T. B. Sercombe, M. H. E. Ali, M. Fan, and D. H. Wang, "Recent progress in ceramic 3D printing: materials, methods, and applications," Adv. Mater. Technol., vol. 4, no. 9, p. 1900448, 2019.

[13] H. Liu, Y. Li, and D. Li, "Research on rheological properties and extrusion behavior of aqueous alumina paste in paste-extrusion-based SFF Processes," *The International Journal of Advanced Manufacturing Technology*, vol. 83, no. 9-12, pp. 2039–2047, 2015.

[14] L. S. O. Pires, J. Luís, M. H. V. Fernandes, and M. Oliveira, "Controlling properties of ceramic formulations for porcelain robocasting," *Ceramics International*, vol. 49, no. 3, pp. 4764–4774, 2023.

[15] A. Paterlini, S. Le Grill, F. Brouillet, C. Combes, D. Grossin, and G. Bertrand, "Robocasting of self-setting bioceramics: From paste formulation to 3D part characteristics," *Open Ceramics*, vol. 5, p. 100070, 2021.

[16] Avcı, Gökay, " Investigation of machinability of green bodies of solid cast alumina through the addition of a poly(carboxylate ether)-based superplasticizer." 2015.

[17] H. Wu, W. Liu, L. Lin, Y. Chen, Y. Xu, S. Wu, Z. Sun, D. An, S. Wei, and Z. Xie, "Realization of complex-shaped and high-performance alumina ceramic cutting tools via VAT photopolymerization based 3D printing: A novel surface modification strategy through coupling agents aluminic acid ester and silane coupling agent," *Journal of the European Ceramic Society*, vol. 43, no. 3, pp. 1051–1063, 2023.

[18] W. Jonhson, X. Xu, D. Zhang, W. T. Chua, Y. H. Tan, X. Liu, C. Guan, X. H. Tan, Y. Li, T. S. Herng, J. C.-H. Goh, J. Wang, H. He, and J. Ding, "Fabrication of 3D-printed ceramic structures for portable solar desalination devices," *ACS Applied Materials & Interfaces*, vol. 13, no. 19, pp. 23220–23229, 2021.

[19] S. Tiwari, P. K. Singh, and S. Kumar, "Variation of density in additive manufacturing of ceramic parts: A Review," *Materials Today: Proceedings*, vol. 47, pp. 2742–2745, 2021.

[20] N. Flores-Martinez, F. Remondiere, J. Jouin, G. Fiore, S. Oriol, and S. Rossignol, "Aluminum concentration range for the extrudability of ceramic pastes," *Open Ceramics*, vol. 9, p. 100213, 2022.

[21] L. Yang, S. Tang, G. Li, L. Qian, J. Mei, W. Jiang, and Z. Fan, “Layered extrusion forming of complex ceramic structures using starch as removable support,” Ceramics International, vol. 45, no. 17, pp. 21843–21850, 2019.

[22] N. Liu, X. Sun, Z. Chen, Z. Xu, N. Dai, G. Shi, S. Cai, X. Lv, and C. Zheng, “Direct ink writing of dense alumina ceramics prepared by Rapid Sintering,” Ceramics International, vol. 48, no. 20, pp. 30767–30778, 2022.

[23] S. Ketel, G. Falzone, B. Wang, N. Washburn, and G. Sant, “A printability index for linking slurry rheology to the geometrical attributes of 3D-printed components,” Cement and Concrete Composites, vol. 101, pp. 32–43, 2019.

[24] R. L. Walton, M. A. Fanton, R. J. Meyer, and G. L. Messing, “Dispersion and rheology for direct writing lead-based piezoelectric ceramic pastes with anisotropic template particles,” Journal of the American Ceramic Society, vol. 103, no. 11, pp. 6157–6168, 2020.

[25] A. Zocca, P. Colombo, C. M. Gomes, and J. Günster, “Additive Manufacturing of ceramics: Issues, potentialities, and opportunities,” Journal of the American Ceramic Society, vol. 98, no. 7, pp. 1983–2001, 2015.

[26] Armando Garcia Montaño, Diego, " Fabrication of complex ceramic parts with sacrificial material using freeze-form extrusion fabrication." 2012.

[27] I. L. Camargo, C. A. Fortulan, and H. A. Colorado, “A review on the ceramic additive manufacturing technologies and availability of equipment and materials,” Cerâmica, vol. 68, no. 387, pp. 329–347, 2022.

[28] O. H. Laguna, P. F. Lietor, F. J. I. Godino, and F. A. Corpas-Iglesias, “A review on additive manufacturing and materials for catalytic applications: Milestones, key concepts, advances and perspectives,” Materials & Design, vol. 208, p. 109927, 2021.

[29] M. Maillard, J. Chevalier, L. Gremillard, G. P. Baeza, E.-J. Courtial, S. Marion, and V. Garnier, “Optimization of mechanical properties of robocast alumina parts through control of the paste rheology,” Journal of the European Ceramic Society, vol. 43, no. 7, pp. 2805–2817, 2023.