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DEVELOPMENT OF ZEOLITE CERAMIC PASTE FOR MATERIAL EXTRUSION ADDITIVE MANUFACTURING

Sergio Lucas Santos Rocha
Gustavo Peres
Federal University of Technology of Paraná – Curitiba, Brazil
srocha@alunos.utfpr.edu.br
gustavoperes@alunos.utfpr.edu.br

Bernardo Fabrício Martins Gonçalves
bernardog@alunos.utfpr.edu.br

Luigi Roehrig Segala
segalla@alunos.utfpr.edu.br

Lucas Freitas Berti
lucasberti@utfpr.edu.br

Neri Volpato
nvolpato@utfpr.edu.br

Abstract. *Additive manufacturing (AM) has the potential to be applied in many areas. Water filtration is critical, as access to clean and safe drinking water is a global concern. In this area, a crucial component is a filter, which is a porous media made of some specific materials. The porous structure and porosity of the filters are important for their efficiency. The use of AM to print special filters can improve efficiency, cost-effectiveness, customization, innovation, material development, and sustainability. Material extrusion (MEX) is an AM technology with great potential in this area. In this case, a stable and printable ceramic paste is paramount. Zeolites, with their unique structure and porosity, have been studied extensively for their potential use in water filtration. However, the AM of zeolites is a relatively new area of research. This research aimed to develop a porous media, based on zeolites produced through MEX. This paper addresses the preliminary challenge of creating a stable and printable ceramic paste of zeolite for water treatment proposals. Two assays, X-Ray Diffraction and Multi Pycnometer of Helium, were used to determine the necessary amount of water, dispersant, and plasticizer to create the ceramic paste. The procedure was then used to produce samples of zeolite scaffolds through MEX, and the resulting zeolites were sintered. The results demonstrate the feasibility of using the zeolite paste for MEX.*

Keywords: *additive manufacturing, material extrusion, zeolite, water treatment.*

1. INTRODUCTION

Access to clean and safe drinking water is a global concern, and the development of efficient water filtration systems plays a crucial role in addressing this challenge. Additive manufacturing (AM), also known as 3D printing, has emerged as a promising technology with the potential to revolutionize various industries (Volpato, 2017). In particular, AM offers exciting opportunities for improving water filtration processes by enabling the production of specialized filters with enhanced efficiency, cost-effectiveness, customization, innovation, material development, and sustainability (Ajayi and Lamidi, 2015).

The porous structure and porosity of filters are key factors that determine their effectiveness in removing contaminants from water. Traditional manufacturing methods often struggle to achieve the desired complexity and customization required for optimal filtration performance (Dung et al., 2021). However, by harnessing the capabilities of AM, it becomes possible to fabricate filters with intricate geometries and tailored porous structures, thereby increasing the surface area available for filtration and enhancing overall filter performance.

Among the various AM technologies, material extrusion (MEX) stands out as a particularly promising approach for water filtration applications. In MEX, a stable and printable ceramic paste is essential for successfully fabricating complex structures. Extensively researched for their capacity in water filtration, zeolites stand out due to their distinctive structure and porosity. However, the application of AM to fabricate zeolite-based filters is a relatively new and unexplored area of research (Kennedy, 2021).

This study aims to address this research gap by developing a stable and printable ceramic paste composed of zeolites for water filtration applications using MEX. By utilizing zeolite-based filters, it is expected that the resulting filters will exhibit improved filtration efficiency due to their enhanced porous structure and porosity. Moreover, the ability to create filters with diverse geometries through AM opens up new possibilities for optimizing filtration performance.

To achieve this objective, the research methodology involved determining the optimal composition of the ceramic paste through X-Ray Diffraction and Multi Pycnometer of Helium assays. The resulting ceramic paste was then used to fabricate a preliminary zeolite framework via MEX.

2. LITERATURE REVIEW

AM continues to make rapid progress, with continued research and development focused on increasing speed, scalability, material options and surface quality. Besides possessing vast potential across multiple sectors, it facilitates the implementation of efficient, customizable, and sustainable production methods (Gibson, Rosen, Stucker, 2010). The seven AM technologies classified, include Fused Deposition Modeling (FDM) and Stereolithography (SLA), among others. FDM involves melting and extruding thermoplastic materials layer by layer, while SLA uses a UV laser to cure liquid resin into precise 3D objects. Other technologies include Selective Laser Sintering (SLS) for powdered materials, Digital Light Processing (DLP) for rapid resin curing, Binder Jetting for sand molds and metal parts, Material Jetting for multi-material and full-color prints, and Electron Beam Melting (EBM) for AM metal objects (García-León, Gómez-Camperos, Jaramillo, 2021).

Ceramic materials have ushered in a new era of possibilities in mechanical and material engineering through 3D printing. This cutting-edge technology enables the fabrication of intricate ceramic components with exceptional mechanical properties, including high strength, wear resistance, and thermal stability. By utilizing AM techniques, engineers can design complex geometries that optimize performance and functionality in demanding applications. The ability to create ceramic parts with tailored properties allows for the development of advanced components used in aerospace, automotive, and electronics industries, where materials must withstand extreme conditions. With continuous advancements in ceramic formulations and printing processes, the field of mechanical and material engineering is experiencing a transformative shift towards more efficient and customized solutions (Romanczuk-Ruszuk, 2023).

MEX is a broader category of AM that includes both traditional FDM for plastics and ceramic extrusion for ceramics. In the context of ceramic 3D printing, MEX specifically refers to the process of feeding ceramic materials in a filament or paste form through a heated nozzle, which is then deposited layer-by-layer to build the final object. This technique is suitable for creating large-scale ceramic components and is commonly used for architectural and industrial applications. On the other hand, direct ink writing (DIW) or robocasting is a subset of MEX that focuses on the precise deposition of ceramic-based inks or pastes. Instead of using filaments, DIW utilizes ceramic inks or pastes that are carefully controlled and extruded through a nozzle to create intricate structures with higher design flexibility and finer resolution. DIW is often preferred for applications that require detailed and complex ceramic parts, such as custom manufacturing and biomedical engineering (He, Xu, Ji, 2022).

In the realm of material engineering, AM ceramics offer unique advantages over conventional ceramics. The ability to precisely control the macrostructure during the printing process enables engineers to achieve enhanced material properties, such as improved toughness and fracture resistance. Through post-processing techniques like sintering and hot isostatic pressing, the printed ceramic parts achieve higher density and better mechanical performance. As a result, ceramic 3D printing is becoming a viable method for producing functional prototypes and end-use components, where traditional manufacturing techniques fall short. The versatility of ceramic materials, combined with the flexibility of AM, empowers material engineers to explore novel applications and create innovative solutions for various industries (Faes, 2015).

The integration of ceramic AM in mechanical engineering is propelling research and development efforts to new heights. Engineers are leveraging this technology to optimize designs, reduce component weight, and increase energy efficiency in a wide range of systems. In sectors like aerospace and automotive engineering, where lightweight and high-strength materials are paramount, ceramic 3D printing is proving instrumental in achieving these objectives. Additionally, the capability to print intricate cooling channels and complex internal structures enhances the performance of heat exchangers and other thermal management devices. With ongoing advancements and refinements in the field, ceramic AM is poised to reshape the landscape of mechanical engineering, empowering engineers to create innovative solutions that were once considered unattainable (Tiwari, 2021).

Polyethylene glycol (PEG) has emerged as a compatible and highly effective binder using MEX. Zeolites, with their porous structure and excellent adsorption properties, are well-suited for water filtration applications. However, incorporating zeolites into a stable and printable slurry has posed challenges. PEG acts as a versatile binder due to its ability to form strong intermolecular interactions with zeolite particles, enhancing the cohesion of the slurry. This compatibility ensures that the zeolite particles are uniformly dispersed throughout the slurry, resulting in a homogenous mixture that can be precisely deposited layer by layer during the AM process (Fang, 2014).

Moreover, the inclusion of a suitable dispersant in the slurry, such as Dolapix, further augments the advantages of PEG-based 3D printing for zeolite water filters. Dolapix serves as a dispersing agent, preventing the aggregation of zeolite particles and promoting a stable suspension. This ensures that the printed zeolite-based structures exhibit enhanced mechanical integrity and porosity control, both crucial factors for optimizing efficiency.

Previous research has indeed explored the potential of AM in various fields, including healthcare, aerospace, automotive, and consumer products. AM has demonstrated its ability to create complex and customized structures with high precision, enabling novel design possibilities and improved functionality. However, the specific application of AM for zeolite-based water filters using MEX remains relatively unexplored in the existing literature.

3. METHODOLOGY

In order to start the process of making the zeolite paste for material extrusion, the characterization of the zeolite powder was essential. The first laboratory test was the pycnometry. The sample of zeolite was analyzed in a helium multipicnometer made by Quantachrome, model MVP-D160-E, gas analytical helium at 20 psi at operating temperature of 22 ºC. Knowing the density of a material is crucial for AM ceramic bases as it directly impacts the structural integrity and performance of the printed object. Understanding the material's density helps in accurately calibrating the printing parameters and ensuring the proper amount of material is deposited during the printing process. This knowledge ensures that the final 3D printed ceramic object meets design specifications and exhibits the desired mechanical properties for its intended application.

The second test was the X-Ray Diffraction (XRD). The XRD analysis is a powerful technique used to study the atomic and molecular structure of crystalline materials. It involves exposing a sample to X-rays, which interact with the atoms in the crystal lattice, causing them to scatter the X-rays in different directions. The scattered X-rays are detected, and their intensity and angles are measured. From this data, the positions of atoms within the crystal and the spacing between crystal planes can be determined. XRD is widely employed in materials science, geology, chemistry, and other fields to identify and characterize crystalline materials, aiding in research and product development. For this test, the measurement condition is shown in Table 1. The XRD analysis is fundamental for 3D printing ceramic materials as it provides essential insights into the material's crystal structure and phase composition. This analysis ensures the desired ceramic phases are present, confirming the material's suitability for the intended application. It helps verify the successful sintering and formation of the desired crystal structure, ensuring the final 3D printed ceramic components possess the required mechanical and functional properties for optimal performance.

Table 1. Measurement condition for the XRD analysis.

X-Ray Tube	Target	= Cu
	Voltage	= 30.0 (kV)
	Current	= 30.0 (mA)
Slits	Divergence Slit	= 1.00000 (mm)
	Scatter Slit	= 1.00000 (mm)
	Receiving Slit	= 0.30000 (mm)
Scanning	Drive Axis	= Theta-2*Theta
	Scan Range	= 5.000 – 100.000
	Scan Mode	= Continuous Scan
	Scan Speed	= 2.0000 (deg/min)
	Sampling Pitch	= 0.0200 (deg)
	Present Time	= 0.60 (sec)

A zeolite paste suitable for extrusion-based AM was formulated by combining clinoptilolite zeolite powder #325, polyethylene glycol (PEG), Dolapix dispersant, and water. The selection of clinoptilolite zeolite powder was based on its known adsorption properties and availability. Polyethylene glycol was chosen as a binder due to its compatibility with zeolite particles and its ability to provide the required viscosity for extrusion. Dolapix dispersant was incorporated to enhance zeolite particle dispersion. The zeolite paste was prepared by carefully weighing and mixing the ingredients manually to ensure homogeneity.

The formulated zeolite paste was successfully utilized in the DIW process. The schematic is presented in Figure 1 (Tiwari, 2021). The PEG binder's compatibility with zeolite particles and the role of Dolapix in enhancing zeolite dispersion aiming smooth extrusion and homogeneity. During DIW, the paste was precisely deposited layer by layer onto the build platform, resulting in intricate 3D printed structures. Post-processing steps, like sintering, further refined the final ceramic-based zeolite structures, holding significant promise for applications in water filtration, catalysis, and engineering, addressing crucial challenges with advanced capabilities.

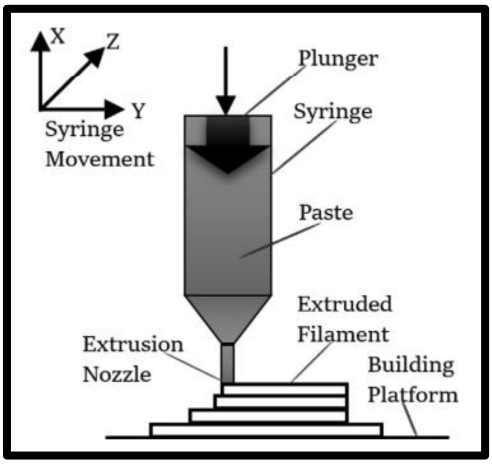

Figure 1. Schematic diagram of Direct Ink Writing (DIW) Process. (Tiwari, 2021)

In the laboratory, a series of experiments were conducted to develop various versions of a zeolite paste formulation. This involved creating multiple iterations, each with different compositions. To determine the initial compositions for these iterations, specific ratios of zeolite powder, PEG binder, Dolapix dispersant, and water were pre-established and used as a basis. These ratios were carefully selected, serving as a starting point for the formulation of the zeolite paste in each iteration.

The extrudability, printability, and stability of the paste were assessed. Extrudability tests were conducted using an in house-built extrusion system composed of the syringe, which was adapted for the printer head, Figure 2, to evaluate the flow characteristics of the paste. Printability tests involved fabricating simple test structures to assess shape retention and integrity during the printing process. The stability of the paste was evaluated by monitoring its homogeneity and consistency over time.

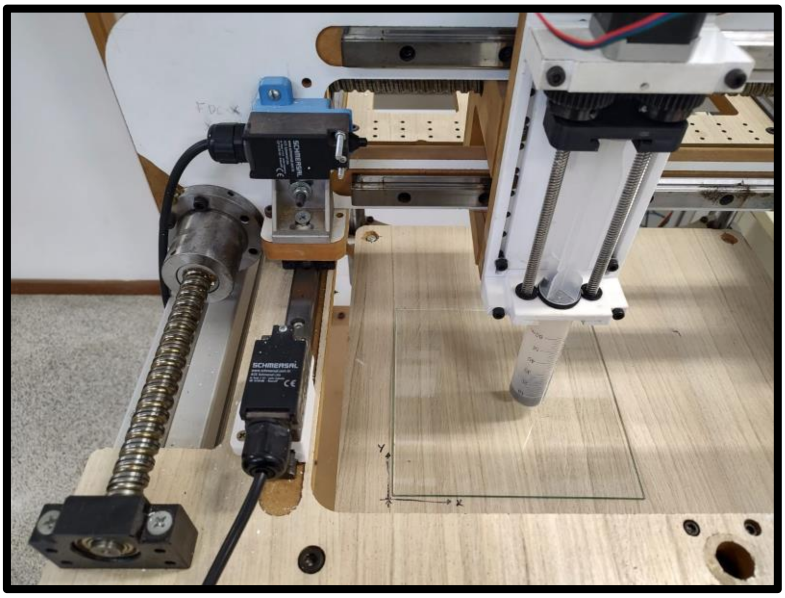

Figure 2. 3D Printer made by NUFER

Based on the results of the lab testing, an optimized zeolite paste formulation was identified as shown in Table 2. This optimized formulation was utilized for manufacturing zeolite scaffolds via MEX. The zeolite paste was loaded into a syringe equipped with a suitable nozzle (2 mm diameter), and printing parameters such as extrusion speed (15 mm/min), and layer thickness (1.75 mm) were determined based on empirical tests. Controlled extrusion was employed to deposit successive layers of the zeolite paste according to a predetermined design pattern. Figure 3 shows preliminary results of the 3D printed zeolite paste. Subsequently, the green zeolite scaffolds were carefully collected and subjected to further processing.

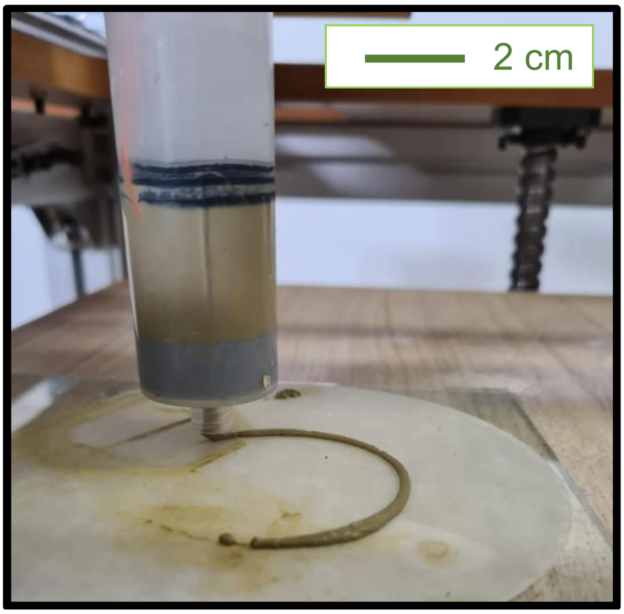

Figure 3. Extrudability of the zeolite paste using a syringe.

The printed zeolite scaffolds underwent post-processing to enhance structural integrity and eliminate residual binders or additives. The next steps are the sintering thermal treatment, which will be made with thermal agenda as follows: dry and sintering steps involving a dry process, wherein the green scaffolds were dried at room temperature about 20 ºC for 24 hours and then a sintering process, wherein dried scaffolds were heated at 950 ºC for 2 hours. Sintering conditions will be optimized to ensure zeolite structure densification while preserving the desired porosity. Following sintering, the zeolite scaffolds were allowed to cool to room temperature.

4. RESULTS

By using the software Match, it was possible to be sure about the proper zeolite mineral specie. Figure 4 shows the powder XRD results with the 2*Theta angle ranging from 5 to 60° and the pattern of the Clinoptilolite-Na (Cart JCPDF 96-900-9580). The zeolite sample phases are represented by blue lines, while the matching cataloged clinoptilolite pattern is depicted in red.

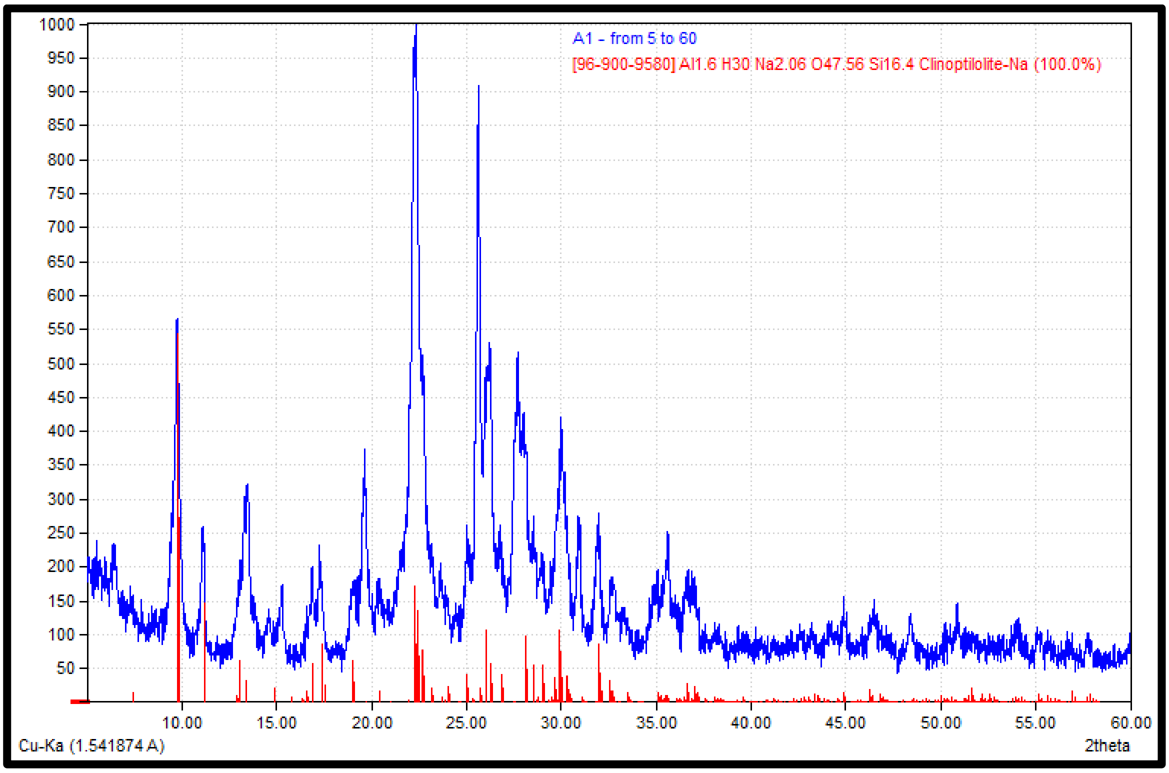

Figure 4. XRD chart matching cliniloptilite

Throughout the experimentation process, the performance was analyzed of each zeolite paste iteration to identify the most effective composition. After evaluation, the best combination quantities in mass were determined for zeolite powder, PEG binder, Dolapix dispersant, and water, which were then recorded and compiled into Table 2, showcasing the successful formulations that yielded the most desirable results.

Table 2. Combination of specific quantities of the zeolite paste.

Paste Composition	**Mass (g)**	**Percentage (%)**
Zeolite Clinoptilolite (#325)	50.00 ± 0.01	67.11
Distilled Water	18.50 ± 0.01	24.83
Polyethylene Glycol (PEG)	5.00 ± 0.01	6.71
Dolapix	1.00 ± 0.01	1.34

The smaller the nozzle diameter, the more detailed the part can be. The first attempt was with a 1 mm nozzle, but the printer lacked the power to push the material. The second attempt was with a 1.5 mm nozzle, this time the printer pushed with difficulty and the amount of material extruded per second was very small. The third attempt with a 2 mm nozzle syringe standard tip, without additional tip gave satisfactory results during printing.

The synthesis and characterization of zeolite-based paste using AM and MEX were conducted to evaluate their potential for water filtration applications. Figure 5 shows the first dry sample of extruded paste made in the laboratory.

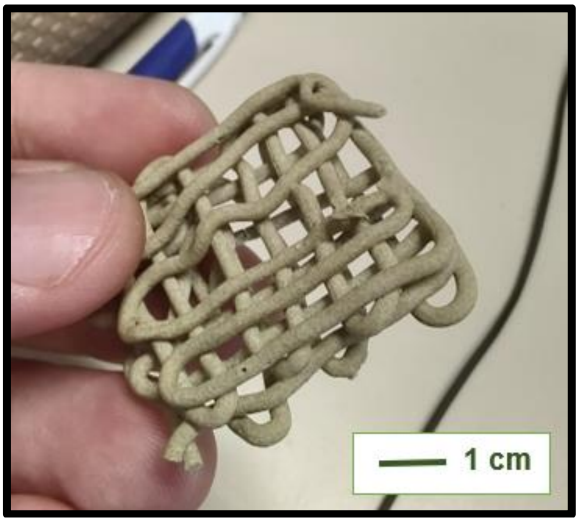

Figure 5. Dry overnight sample of manually extruded zeolite paste.

The results obtained from the analysis of the fabricated zeolite filters provide valuable insights into their structural properties and performance. The zeolite particles were observed to be evenly dispersed throughout the filters, suggesting good homogeneity. Figure 6 shows a preliminary sample made by the 3D printer. It is possible to see that the zeolite paste can be 3D printed, although further assessments are required, for the final work.

Figure 6. Wet sample from 3D printer extruded paste.

The XRD analysis confirmed the presence of the desired clinoptilolite zeolite phase in the sintered sample without any significant impurities. This indicates the successful synthesis of zeolite-based filters with the desired crystal structure. Multi Pycnometer of Helium assays were performed to evaluate the density of the dried zeolite filters. The zeolite clinoptilolite's density analysis resulted in a density of 1.152 g/cm³.

5. CONCLUSION

In conclusion, the synthesis and characterization of zeolite-based filters using AM and MEX demonstrate the potential for producing efficient water filtration systems. The XRD analysis verifies the desired crystal structure of the filters.

The low density, which suggest a high porosity, revealed by the Multi Pycnometer of Helium assays indicates the availability of ample adsorption sites for contaminants, suggesting enhanced filtration performance. These findings underscore the advantages of utilizing AM and MEX for fabricating zeolite-based filters, including the ability to tailor pore characteristics to address specific water treatment needs.

Further investigation is warranted to evaluate the filtration efficiency, adsorption capacity, and long-term durability of the fabricated zeolite filters under real-world conditions. This will provide valuable insights into their practical applicability and potential for revolutionizing water filtration technology. The successful development of zeolite-based filters using AM and MEX holds great promise for improving access to clean and safe drinking water, contributing to global efforts in addressing water scarcity and contamination.

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8. RESPONSIBILITY NOTICE

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