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**3D-Printed Geopolymer-Based Supports
for High-Temperature Catalytic Processes**

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**3D-Printed Geopolymer-Based Supports for
High-Temperature Catalytic Processes**

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Prof. Dr. Dachamir Hotza
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To my parents, Eliane and Silmar, to whom I owe absolutely everything.

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***“Do not go gentle into that good night.
Rage, rage against the dying of the light.”***

- Dylan Thomas
as quoted by
the fictional character
Professor. Dr. John Brand
in the movie ‘Interstellar’

ABSTRACT

Alkali-activated materials (AAMs), such as geopolymers, are formed through a reaction between an alumino-silicate precursor and alkaline activators primarily based on sodium and potassium. The outcome is an amorphous material akin to ceramics, derived from diverse sources, including industrial waste. Their versatility makes them economically and environmentally appealing, extending beyond Portland cement replacement, finding applications in various fields. This study delves into the potential of geopolymers as sustainable and cost-effective alternatives to traditional ceramic catalytic supports. Through additive manufacturing, biaxially porous geopolymers monoliths were created. The research was structured into four parts. In the first section, a literature review highlighted geopolymers' catalytic potential, spanning energy production, air purification, water treatment, and other diverse applications. The second part utilized additive manufacturing to fabricate open-porous geopolymers, varying metakaolin types (MKB, more distributed with a medium particle size, less pure, and less amorphous, and MKI) and alkaline activators. Specific rheological tests were successfully applied. The third part examined the materials' thermal behavior before and after printing, including calcination at 800°C, revealing significant changes in porosity and specific surface area, without directly impacting mechanical strength. In the fourth part, printed geopolymers were impregnated with nickel and tested in methane steam reforming. The additive manufacturing of biaxially porous geopolymers is significantly influenced by certain raw material parameters, notably particle size and amorphization. The required extrusion pressure, defined by the yield stress in rheological tests, increases with reactivity, while the available pressure time decreases. The printed monoliths exhibited thermal resistance, contracting markedly after the initial 800°C calcination, evidenced by a significant decrease in porosity (Δ -4% to Δ -5%), as well as specific surface area reduction (Δ -23 m²/g on average), with no direct influence on mechanical strength or significant expansion during subsequent heat exposure. On average, the printed pieces displayed compression strength of at least 10 MPa regardless of thermal treatment. Evidence of metal-support interaction structures emerged, suggesting the formation of compounds undetectable by X-ray diffraction due to the support's amorphous nature. In the catalytic evaluation, methane conversion remained stable for two hours, with consistent hydrogen yields. At 900°C, MKB proved more effective compared to MKI.

Post-regeneration of the catalyst at 800°C in air, nickel-impregnated geopolymers exhibited superior methane reforming results, demonstrating their viable reuse, and confirming the catalyst's preservative properties as suggested in existing literature. This study underscores not only the promising application of geopolymers in catalysis but also the significance of additive manufacturing in creating effective, cost-efficient, and environmentally sustainable catalytic materials.

Keywords: Geopolymers, additive manufacturing, 3D printing, catalysis, methane steam reforming

RESUMO

Os materiais alcalinamente ativados (AAMs), incluindo os geopolímeros, surgem de uma reação entre um precursor alumino silicato e ativadores alcalinos baseados em sódio e potássio. O resultado é um material amorfo com características semelhantes às cerâmicas, obtido a partir de fontes variadas, incluindo resíduos industriais. Sua versatilidade torna-os atraentes economicamente e ambientalmente, indo além da substituição do cimento Portland, sendo explorados em diversas aplicações. Este estudo investiga o potencial dos geopolímeros como alternativas sustentáveis e econômicas aos suportes catalíticos cerâmicos tradicionais. Utilizando a manufatura aditiva, foram produzidos monólitos geopoliméricos com porosidade biaxial. A pesquisa foi dividida em quatro partes. Na primeira parte, uma revisão bibliográfica destaca o potencial dos geopolímeros na catálise, abrangendo três principais áreas: produção de energia, despoluição do ar e tratamento de água. Na segunda parte, a manufatura aditiva foi empregada para criar monólitos geopoliméricos com porosidade aberta, variando os tipos de metacaulim (MKB, de maior distribuição e tamanho médio de partícula, menos puro e menos amorfo, e MKI) e ativadores alcalinos. Protocolos de teste reológico específicos foram aplicados com sucesso. Na terceira parte, o comportamento térmico dos materiais antes e após a impressão foi analisado, incluindo calcinação a 800 °C, revelando mudanças significativas na porosidade e área de superfície específica, mas sem afetar diretamente a resistência mecânica. Na quarta parte, os geopolímeros impressos foram impregnados com níquel e testados na reforma a vapor de metano. A manufatura aditiva de monólitos geopoliméricos com porosidade biaxial é altamente influenciada por alguns parâmetros da matéria-prima, do qual se destacam o tamanho de partícula e a amorfização. A pressão necessária para extrusão da pasta, definida pela tensão de cisalhamento nos ensaios reológicos, aumenta de acordo com o aumento da reatividade, enquanto o tempo disponível para pressão diminui. Os monólitos impressos apresentam propriedades de resistência térmica, com acentuada retração após a primeira calcinação a 800 °C, evidenciada pela diminuição expressiva da porosidade (Δ -4% a Δ -5%), assim como na área de superfície específica (Δ -23 m²/g em média), porém sem influência direta sobre a resistência mecânica e sem dilatação expressiva durante exposição subsequente ao calor. Na média, as peças impressas possuem resistência à compressão superior a 10 MPa independente do tratamento térmico. Há evidência de formação de estruturas de interação metal-suporte,

sugerindo a criação de compostos não detectados por difração de raios-X devido à natureza amorfa do suporte. Na avaliação catalítica, a conversão de metano permaneceu estável durante duas horas, com rendimentos de hidrogênio constantes. A 900 °C, os resultados foram mais eficazes com MKB em comparação com MKI. Após a regeneração do catalisador a 800 °C em ar, os monólitos geopoliméricos impregnados com níquel exibiram melhores resultados na reforma de metano, demonstrando sua reutilização viável e confirmando as propriedades preservativas do catalisador conforme sugerido na literatura. Este estudo enfatiza não apenas a promissora aplicação dos geopolímeros na catálise, mas também a importância da manufatura aditiva na criação de materiais catalíticos eficazes, econômicos e ambientalmente sustentáveis para aplicações em altas temperatura, sendo o primeiro a explorar a possibilidade até a sua publicação.

Palavras-chave: geopolímeros, manufatura aditiva, impressão 3D, catálise, reforma a vapor de metano

RESUMO EXPANDIDO

Introdução

Materiais alcalinamente ativados (AAM), dos quais fazem parte os geopolímeros, são o resultado de uma reação entre um precursor aluminossilicato e ativadores alcalinos tipicamente baseados em sódio e/ou potássio. Da reação resulta um material majoritariamente amorfo endurecido de propriedades próximas das cerâmicas. Precursores e ativadores podem ser obtidos de uma diversificada gama de fontes, tanto comercialmente disponíveis quanto derivadas de resíduos industriais, o que torna essa classe de materiais em uma opção versátil, economicamente e ambientalmente atrativa para muitas finalidades. Inicialmente adotados como substitutos principais ao cimento Portland, esses materiais são hoje explorados em aplicações muito além da construção civil. Também pelo custo, estabilidade, capacidade de reutilização e compatibilidade com metais, os AAM são uma alternativa interessante para produção de catalisadores. Pela elevada estabilidade térmica, eles podem também ser uma alternativa a materiais tradicionalmente utilizados em processos catalíticos realizado a altas temperaturas, como as cordieritas e os carbetos de silício. No entanto, a literatura explorando tal possibilidade é extremamente limitada. Nesse trabalho, geopolímeros são produzidos por manufatura aditiva como suportes estruturados para processos catalíticos em altas temperaturas e testados na reforma a vapor de metano a 800 °C e 900 °C, as temperaturas mais altas a que o processo comercial pode chegar. Até a data da publicação da tese, este é o primeiro trabalho a abordar a produção e o comportamento de geopolímeros em catálise a altas temperaturas.

Objetivos

O principal objetivo foi validar os geopolímeros como alternativas de baixo custo efetivo e ambientalmente amigáveis a suportes catalíticos cerâmicos tradicionais. Para tanto, foi necessário o desenvolvimento de processos eficientes de manufatura aditiva a partir da caracterização de matérias-primas, processos e produtos, além da avaliação de desempenho em aplicação.

Metodologia

O trabalho foi dividido em quatro partes principais. Na primeira, uma extensa revisão bibliográfica sobre AAMs em processos catalíticos é apresentada ao leitor. As

aplicações em catálise foram sumarizadas em quatro grandes áreas: produção de energia, despoluição de ar, tratamento de água e aplicações diversas. Na segunda parte, uma exploração empírica do processo de manufatura aditiva de monólitos geopoliméricos com porosidade aberta nos eixos vertical e horizontal. A partir de duas pastas com teores diferentes de dois tipos de metacaulim, MKB e MKI, com os mesmos ativadores alcalinos: hidróxido de sódio e silicato de sódio. PEG-400 foi utilizado como aditivo reológico. Nessa etapa, o processo de impressão e a caracterização das matérias-primas, do processo e dos monólitos são apresentados, assim como a justificativa para utilização de PEG-400. Um protocolo próprio de teste reológico é aplicado com sucesso às pastas testadas. Na terceira parte, o comportamento térmico dos materiais, antes e após a impressão, é explorado a partir da análise antes e após calcinação a 800 °C. Na quarta e última parte, os geopolímeros impressos são aplicados na reforma a vapor de metano. A caracterização dos suportes impregnados com níquel é avaliada e os resultados de reforma são apresentados de acordo com a taxa de conversão de metano e concomitante geração de hidrogênio ao longo de 2 horas a 800 °C ou a 900 °C sob condições experimentais arbitrariamente definidas.

Resultados e Discussão

Da revisão bibliográfica, são encontrados alguns resultados que apoiam a escolha de AAMs como materiais suportes de catalisador, uma vez que o caráter básico previne a sinterização dos metais suportados e a formação de carbono em forma física sobre a superfície (coquerização). Devido às características morfológicas dos materiais, eles podem ser interessantes também pelas propriedades de adsorção, habilitando-os para processos cíclicos em aplicações sustentáveis. A versatilidade de matérias-primas e métodos de produção habilitam os geopolímeros como opções viáveis em processos catalíticos. A manufatura aditiva de monólitos geopoliméricos com porosidade biaxial é altamente influenciada por alguns parâmetros da matéria-prima, do qual se destacam o tamanho de partícula e a amorfização. A pressão necessária para extrusão da pasta, definida pela tensão de cisalhamento nos ensaios reológicos, aumenta de acordo com o aumento da reatividade, enquanto o tempo disponível para pressão diminui. Os monólitos impressos apresentam propriedades de resistência térmica, com acentuada retração após a primeira calcinação a 800 °C, evidenciada pela diminuição expressiva da porosidade (Δ -4% a Δ -5%), assim como

na área de superfície específica (Δ -23 m²/g em média), porém sem influência direta sobre a resistência mecânica e sem dilatação expressiva durante exposição subsequente ao calor. Na média, as peças impressas possuem resistência à compressão superior a 10 MPa independente do tratamento térmico. Comportamento contrário foi observado em amostras maciças, cuja resistência à compressão é largamente influenciada pela temperatura, com decréscimo acentuado após a calcinação. Após a impregnação de níquel e calcinação, os monólitos apresentam propriedades tanto de suportes quanto de catalisadores em si, com picos de redução de hidrogênio relacionados tanto à presença de óxido de níquel quanto a estruturas de forte interação metal-suporte, tais como NiAl₂SiO₈ e outras formações semelhantes não detectadas por difração de raios-X. A não detecção por DRX pode estar relacionado à natureza amorfa do suporte. A conversão de metano manteve-se estável durante duas horas para ambas as formulações testadas, assim como o rendimento de hidrogênio, sem diferenças evidentes entre formulações. A 900 °C, a reação produziu maiores rendimento de hidrogênio e conversão de metano, sendo mais efetiva com MKB (~60% e ~45%, respectivamente) do que com MKI (~30% e ~50%, respectivamente). A 800 °C, as incertezas experimentais impossibilitam conclusões do tipo. Por fim, após a regeneração de um catalisador a 800 °C em ar, foram obtidos resultados de reforma de metano superiores aos iniciais, mostrando a viabilidade de reutilização dos monólitos geopoliméricos impregnados com níquel e confirmando as propriedades de preservação do catalisador durante o processo inicialmente sugeridas na literatura e na caracterização dos produtos.

Considerações Finais

A partir da literatura e da metodologia proposta, as caracterizações e as propriedades dos materiais obtidos permitem que se conclua que os geopolímeros podem ser utilizados em processos catalíticos a altas temperaturas. A metodologia proposta, inovadora em muitos aspectos, principalmente no que se refere a propriedades reológicas, viabiliza com sucesso a produção e avaliação de performance de materiais geopoliméricos impressos em 3D em processos catalíticos em altas temperaturas. Os geopolímeros derivados de metacaulim estudados possuem grande afinidade de interação com o catalisador metálico (níquel), levando a formação de estruturas altamente estáveis com capacidade de redução de hidrogênio até 1000 °C e alta capacidade de regeneração de catalisador após o uso

por 2 horas em condições altamente oxidativas e favoráveis à formação de coque - reforma à vapor de metano em 800 °C e 900 °C. Trabalhos futuros poderão tratar de inclusão de fillers para maior estabilidade térmica durante a calcinação dos suportes ou adotar catalisadores bi-metálicos, assim como otimizar parâmetros de catálise, uma vez que a viabilidade dos geopolímeros como suportes de catalisador para processos em altas temperaturas resta aqui comprovada.

Palavras-chave: geopolímeros, manufatura aditiva, impressão 3D, catálise, suportes, reforma a vapor de metano, altas temperaturas.

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1 INTRODUCTION

1.1 *Context and motivation*

Alkali-activated materials (AAM) are the result of a reaction between an aluminosilicate precursor and alkaline activators, typically based on sodium and potassium. This reaction yields a hardened amorphous material with ceramic-like properties. While many authors refer to low-calcium AAM as 'geopolymers,' the nomenclature for such materials remains a subject of ongoing debate within the academic community [1], [2].

A wide range of aluminosilicate and alkali activators of different availability, reactivity, cost, and value may be employed as raw materials of AAM, including byproducts and industrial wastes, meaning that this class of materials is versatile, locally adaptable, and a great alternative for environmentally friendly solutions [2]–[5].

Mainly considered as a main substitute for Portland Cement, being adopted as binders since the 1950s [6], AAM have gained considerable attention for applications beyond civil construction, adsorbents, carrier media in bioreactors, medicines, anti-microbial agents, energy storage, pH buffers, solidification/stabilization of contaminants, refractory ceramics and binders, impermeable materials, and radioactive waste containers, among others [7]–[10].

The most common raw materials used to make geopolymer are metakaolin and fly ashes as a source of aluminosilicate, and NaOH, KOH, sodium silicate, and potassium silicate as a source of alkali activators [7]. The resulting product is amorphous and exhibits favorable characteristics as catalyst supports, including ion exchange capabilities, a mesoporous structure, high mechanical strength, and durability [8]. The geopolymeric catalyst supports can be functionalized and/or modified to enhance specific reaction kinetics [5].

The increased interest in geopolymers as alternative supports for catalytic processes can be attributed to their cost-effectiveness, high stability, and reusability [11]. The compatibility of geopolymers with metals makes them a valuable option for serving as catalyst supports [12]. Similarly to conventional supports, such as cordierite or silicon carbide, the thermal stability of geopolymers is another notable advantage [11].

Furthermore, the possibility of using various industrial wastes, such as fly ash, stone cutting waste, furnace blast slag, steel slag, magnesium slag, and silicon-

manganese slag, as alternative feedstocks presents an opportunity to enhance the sustainability and cost-effectiveness of geopolymers production [13]. To make efficient use of these materials in catalytic applications, it is essential to tackle the challenges related to controlling morphology, surface area, pore structure, accommodating active species, and optimizing synthesis conditions [14].

This Thesis addresses the use of geopolymeric materials in catalytic processes. First, an extensive review of the state-of-the-art geopolymer-enhanced catalytic reactions is presented. Secondly, geopolymer-supported structured catalysts obtained by additive manufacturing are assessed for high-temperature methane steam reforming. Up to the publication of the Thesis, this is the first academic work to explore this approach.

1.2 Objectives

1.2.1 General objective

The main objective of this work is to evaluate the potential of 3D-printed geopolymer monoliths as a cost and environmentally-effective alternative to conventional ceramic catalyst supports in high temperature catalytic processes.

1.2.2 Specific objectives

The following specific objectives are sought:

- Characterizing the raw materials.
- Developing an efficient additive manufacturing process to obtain geopolymeric monoliths suitable for high-temperature catalysis.
- Assessing the rheology of 3D-printable pastes composed of two commercially available calcined clays.
- Evaluating the monoliths' physical and chemical properties.
- Evaluating the performance of nickel-impregnated monoliths for high-temperature Methane Steam Reforming.

2 GEOPOLYMERS IN CATALYSIS APPLICATIONS: A REVIEW¹

In this chapter, it is offered an extensive review of the latest research on the use of geopolymers in catalytic applications. The chapter is organized around the following key areas:

- Challenges and prospects in geopolymers as support for catalysts
- The impact of material structure and properties on catalysis
- Raw materials utilized in geopolymer synthesis
- Primary processing approaches
- Prominent application areas, including energy generation, pollution control, and air emission management.

2.1 *Databases and search methodology*

This state-of-the-art review thoroughly evaluates and discusses the articles related to alkali-activated materials and geopolymer catalysts. Extensive research was conducted using Scopus, Springer, Wiley, Google Scholar, Taylor and Francis Online, ACS Publications, and the Royal Society of Chemistry databases. The papers were filtered using the keywords “alkali-activated AND catalysis” and “alkali-activated AND catalyst”, “geopolymer AND catalysis”, “geopolymer AND catalyst”. Other articles about “geopolymers” were also evaluated since they comprise the field of alkali-activated materials in academic literature. Finally, “geopolymers” and “catalytic processes” were included to help build the bases for understanding typical alkali-activation and geopolymerization-route processed catalysts.

2.2 *Catalytic processes: challenges and perspectives*

Catalytic processes are considered the driving force of the chemical industry, with more than 80% of chemical products being produced through catalytic reactions, which can be either homogeneous or heterogeneous. Heterogeneous catalysis is the most commonly used type of catalysis, in which the catalyst is solid, and the product is either liquid or gaseous. The process temperatures typically range from 100 to 600 °C, and some require even higher temperatures. The shapes of the catalysts are diverse, ranging from powders to monoliths with varying sizes and geometries. Fixed-

¹Accepted for publication with minor changes in November 2023 as “Alkali-activated materials for catalytic applications: A state-of-the-art review”, in Materials Science & Engineering B (Qualis: A1; Impact factor: 3.6; CiteScore: 4.7)

bed reactors, with dimensions typically in the range of tens of cubic meters, are commonly used to house these catalysts. [15].

The water-gas shift reaction (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) has gained increasing attention due to its importance in hydrogen production and purification applications [16]. One of the biggest problems in catalytic reforms is long-term instability and carbon deposition due to C-C bond scission. In addition to the noble metals, Ni has been the best cost-benefit for use in hydrocarbon reformers, having high catalytic activity for breaking C-C and O-H bonds and hydrogenation (H_2). The disadvantage is coke formation. The support also strongly influences the efficiency of catalysis and coke formation. It can facilitate the reforming reaction, promoting the migration of OH^- towards the metallic catalyst in the presence of water vapor at high temperatures. Furthermore, better dispersion of the metal in the support can increase the efficiency of the process [17].

Cordierite is a classic automotive catalytic substrate for catalytic converters since it has high thermal stability and mechanical resistance. However, its low specific surface area, i.e., $\sim 0.7 \text{ m}^2/\text{g}$, compared to conventional support catalysts (100 to 1000 m^2/g) is a drawback for its use directly as a catalyst support. In these cases, the surface area can be increased before or simultaneously with the loading of a high surface area material, e.g., $\gamma\text{-Al}_2\text{O}_3$, allowing a better catalyst dispersion. Techniques such as wash or dip coating with high surface area ceramic pastes can also be used [15].

The loading of the active component onto the support can occur in different ways. The most common are washing or coating of paste, impregnation, adsorption, ion exchange, and deposition or precipitation. In addition to these processes, heat treatments are usually required to remove solvents and chemically reduce metals [15].

Impregnation is the most common way of distributing metal ions on the support surface. It consists of immersing the support in an aqueous solution of a suitable soluble salt. Nitrates or simple salts of organic acids are the most common, as heat treatment easily removes them. The impregnation conditions (concentration, solid/liquid ratio, temperature, and pH value) can vary over a wide range and depend on the type of metal and the desired amount [15]. This process is inefficient, and new solutions are being sought to increase catalytic efficiency and support properties.

Other challenges are described in the following topics according to the specific characteristics of each application.

2.3 *Geopolymer characteristics for catalysis applications*

The study of geopolymer materials had its first contributions in 1967 with the work of Victor Glukhovsky, who activated blast furnace slag and named his product “soil cement”. Over the years, other authors have contributed to the studies of these chemically bonded ceramics. In 1979, Joseph Davidovits coined the term “geopolymer” corresponding to calcined clays and alkaline activators based on sodium and potassium [1]. The cementitious properties were the first to be studied, creating alternative nomenclatures related to the topic, such as “geocement”, “polymeric inorganic concrete”, “inorganic aluminosilicate polymer” [18], and “alkali-activated cement” [19]. In this wide range of geopolymeric materials, we can also mention those that are activated by acid (phosphate-based) in Al-O-P-O type binder systems [20], or those containing Fe in their structure (Fe-O-Si-O-Al-O-Si-O) [1], [21], [22], with other nomenclatures such as “chemically bonded ceramics”, “chemically bonded phosphates” [23] or “inorganic phosphate cement” [24]. Over time, the study of applications for alkaline-activated materials has expanded to a wider range of fields, such as environmental remediation and catalytic processes, increasing the interest in such materials in diverse areas of research.

2.4 *Geopolymers: alkali promoted catalytic materials?*

Alkali-activated materials might go through geopolymerization, a process that involves the formation of polymeric Si–O–Al bonds [25], [26] with a structure linked to the nature of the alkaline activator and the SiO₂/Al₂O₃ [26].

Variations of these bonds are poly(sialate) (-Si-O-Al-O-), Poly(sialate-siloxy) (-Si-O-Al-O-Si-O-) and poly(sialate-disiloxy) (-Si-O-Al-O-Si-O-Si-O-) [25]. Sialate is an abbreviation for silica-oxo-aluminate and consists of tetrahedrons of silica (SiO₄) and aluminum (AlO₄) bonded alternately by oxygen in the presence of positive ions (Na⁺, K⁺, Li⁺, Ca⁺², Ba⁺², NH₄⁺, H₃O⁺). These positive ions are intended to balance the negative charge of Al⁺³ in the fourth coordination.

The empirical formula for polysialate is shown in Equation 1, where *M* is the cation (potassium, sodium, or calcium), *n* is the degree of polycondensation, *z* is the index (1, 2, or 3) of the amount of SiO₂ present in the reaction and *w* is the amount of water [25].

$$M_n \{ -(SiO_2)_z - AlO_2 \}_n \times wH_2O \quad (Equation 1)$$

The molar relationships between the constituents in the chemical reactions of geopolymers can affect the material's properties in its fresh and hardened state. The literature indicates that low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios result in greater specific surface area and thus increase the adsorption capacity [27], [28]. On the other hand, increasing the ratio favors the development of mechanical properties [27].

Most catalysts are transition metals (nickel, iron, platinum, palladium, rhodium, etc.), and it is possible to include them in the geopolymer formulation to obtain a suitable material for catalysis without the need for additional processes. The metal is present as a composite phase or raw material in such cases, as detailed in Section 4.2.

In other cases, introducing these elements by ion exchange makes the product suitable for a particular application. Zhang et al. [29] studied a new cementitious catalyst based on Ni and Ca prepared by polymerization and ion exchange reactions using steel slag. During ion exchange, first, there was an exchange with NH_4^+ and later an exchange with Ni^{2+} . The results showed that the ion exchange technique almost completely replaced Na^+ with Ni^{2+} . The product obtained was tested in photocatalytic degradation of methylene blue dye, showing an efficiency of 94.39% under UV irradiation. The high degradation is due to the synergistic effect of nickel ions with iron and calcium iron oxides [29]. Through the same route, in a different report, their team was also able to replace Na^+ with Fe_2O_3 and efficiency of 97.3% on the degradation of Congo Red after 100 min [21].

One of the peculiarities of geopolymer materials is their alkaline composition due to their activation with materials such as sodium and potassium hydroxide and sodium silicate during their processing. In this sense, some works in the literature regarding the influence of alkalis in catalysis bring interesting clues about the behavior of these materials as catalytic support for different purposes.

Dongil et al. [16] studied binary (Ni/graphene) and ternary (Ni- CeO_2 /graphene) systems using urea and sodium hydroxide as precipitating agents for the active phases on the graphene support. The catalyst formed had its catalytic performance tested in WGS. The results showed that residual Na in samples prepared with sodium hydroxide facilitated the reduction of ceria. Likewise, the catalytic activity was improved with the addition of Na. This improvement is explained by the reaction mechanisms favored by Ni-O-Na bonds [16].

Pt/ZrO₂-based catalysts doped with different Na contents (0.5; 1.0; 1.8; 2.5; and 5.0 wt%) were obtained, characterized, and compared with the efficiency of the reference catalyst without sodium by Martinelli et al. [30]. Surface area and pore volume progressively decreased with increasing sodium load, while no significant effect was observed on pore distribution. These results suggest that some uniform blockage of the pores has occurred. The presence of Na promotes the basicity of the system so that a greater amount of CO₂ (acid) decomposes on the surface of the catalyst. In this sense, the results confirmed that the promotion of alkalis, mainly 1.8% Na, facilitates the decarboxylation and decarbonylation step [30].

Rahmanzadeh and Taghizadeh [31] evaluated sorption-enhanced ethanol steam reforming using Ce-Ni/MCM-41 as a catalyst in the presence of Na or zirconia and CaO as sorbent. The results indicated that the different dopants used in the CaO sorbent and the increasing Na charge improved the specific surface area, reducing the particle size and consequently progressing the CO₂ sorption capacity. Finally, the hydrogen production with Na-Zr-CaO was ~94%, a value of 24% more than the conventional ethanol steam reforming reaction [31].

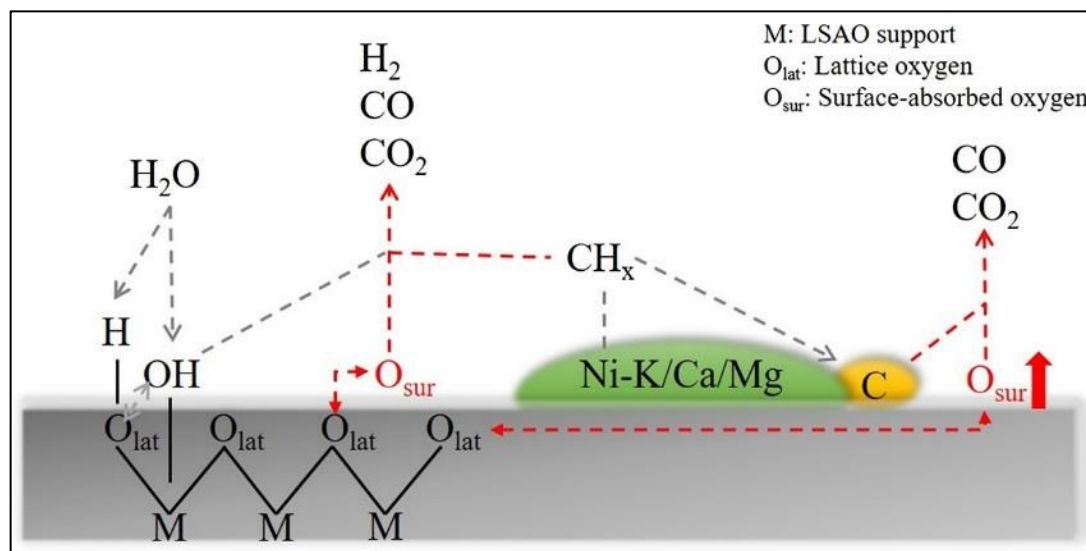
Studies demonstrate that including light alkali, especially Na, in the metal/ZrO₂ set improves steam reforming reactions at low temperatures. Martinelli, Watson, and Jacob [32] evaluated unpromoted and Na-promoted Pt/m-ZrO₂ catalysts for catalytic and selectivity activities under steady-state conditions in a fixed-bed reactor. The results showed that Na doping decreases catalytic activity but significantly increases CO₂ selectivity, improving H₂ selectivity [32].

Domok et al. [33] evaluated the reforming reaction of ethanol and water using Pt/Al₂O₃ catalysts doped with 1% K. The results showed that K in the catalyst destabilizes the acetate groups and improves reforming reactions [33].

The application of biomass steam gasification holds significant promise for the generation of high-purity hydrogen, with perovskites demonstrating favorable suitability as catalyst supports to eliminate the formation of biomass tar during reforming. The presence of various alkaline and alkaline earth metals in the biomass feedstock can be liberated during the reaction and influence the catalytic efficacy. Zhang et al. [34] used K, Ca, and Mg in Ni/La_{0.7}Sr_{0.3}AlO_{3-x} catalyst to steam reforming toluene. The presence of K, Ca, and Mg led to a reduction of more than 60% of coke formation, even improving the sintering of the composite and decreasing the reaction temperature. They illustrated the mechanism in Figure 1. The authors concluded that

the presence of these metals promotes the ability to absorb oxygen on the surface, increasing the oxidation of intermediate reaction products or deposited carbon [34].

Figure 1 - Alkali and alkaline earth metals enhance the interaction between Ni particles and the perovskite support, suppressing the Ni sintering [34].



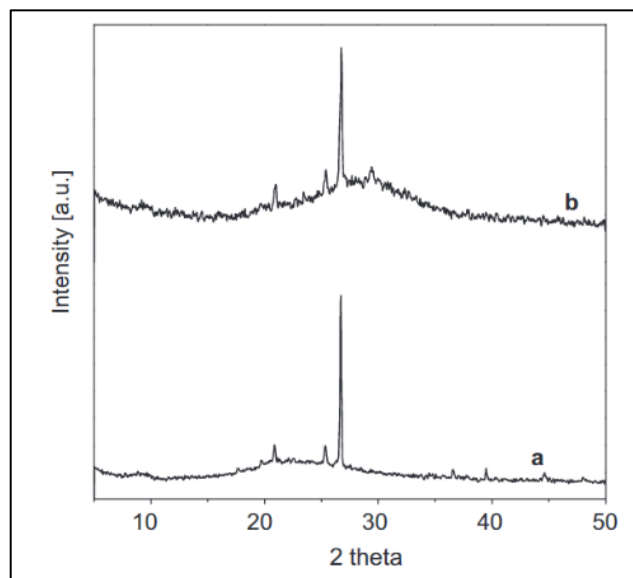
The studies suggest that alkalis are not a problem for catalytic applications. It can also be seen that the presence of these alkalis in the support benefits the process, such as reducing coke formation during the reforming reactions. On the other hand, the alkali doping content must be taken carefully since catalytic activity can be decreased under high alkali concentrations [32].

Zeolites are useful catalysts in various reactions, such as acidic, basic, and redox catalysis. Their efficiency is due to their suitable properties, such as high specific surface area, uniform porosity, accessible and interconnected pore volume, high adsorption capacity, ion exchange capacity, and shape selectivity [35]. Bortnovsky et al. [36] investigated the possibility of metal ion exchange in geopolymers and the results showed that Na geopolymers exhibit ion-exchange properties similar to zeolitic materials. The Na⁺ ions balance the Al atoms of the geopolymer matrix, which NH₄⁺ or Co²⁺ ions can replace. Like zeolites, all Al atoms are accessible through rings containing at least eight Al and Si atoms [36].

The amorphous structure of geopolymers is observed in XRD analysis before and after alkaline activation of a partially amorphous aluminosilicate such as metakaolin – Figure 2. They are assumed as the amorphous analogs of zeolites Due to their compositional similarity [37], making it a promising material for catalytic uses.

Furthermore, literature works using zeolites as support for hydrocarbon reform can further confirm the susceptibility of geopolymers for this application.

Figure 2 - XRD pattern of (a) metakaolin and (b) metakaolin-derived geopolymer. [17]



Bizkarra et al. [38] studied the steam reforming of bio-oil/bio-glycerol using L zeolites as catalytic support with and without alkali metals (Cs or Na) exchanged at temperatures of 700 and 800 °C. This study used two different sizes and morphologies of zeolites (nanocrystal and disc). The ion exchange with Cs and Na neither improved the catalytic effect nor reduced the carbon formation in the catalysts. The exchange of Cs caused an important drop in the yield of H_2 at 700 °C, while the exchange for Na caused the sintering of the zeolite structure. The catalytic activities of the Na-containing catalysts were the lowest at all temperatures. The most suitable zeolites were those with a disk shape, being more active and resistant to deactivation [38].

Some researchers have evaluated ethanol reform using multi-metals as a catalyst to reduce reaction temperatures and increase efficiency. Zheng et al. [39] studied Ni, Cu, and Fe-based catalysts for ethanol reform and obtained good performance, high catalytic activity, high H_2 selectivity, and low unwanted products. The results showed that the Cu sites facilitate the dehydrogenation of ethanol in the initial stage and, together with Ni, catalyzed the dissociation of C-C bonds in acetaldehyde, forming CO and CH_4 . A synergistic effect between the Ni, Cu, and Fe phases in the catalyst proved to be highly resistant to coke formation compared to catalysts using only Ni [39].

Khandan et al. [40] evaluated the reforming of liquefied petroleum gas (a mixture of hydrocarbons, predominantly propane, and n-butane) with nickel catalysts supported on four types of zeolites (H-Y, Na-Y, HZSM5, and Ferrierite). The results showed that the type of support and the specific surface area strongly influence activity and selectivity. Na-Y type zeolites exhibited higher specific surface area ($696.4 \text{ m}^2/\text{g}$), low coke formation, higher LGP conversion, and H_2 yield equal to 48.6%. Coke formation on the catalyst surface caused the filling of pores and active catalytic regions, reducing the specific surface area and catalyst performance [40]. In this sense, the zeolitic geopolymers containing Faujasite obtained in previous works [41], [42] suggest that these materials may have great potential for catalysis.

2.5 Raw materials: aluminosilicate sources and alkaline activators

In a traditional geopolymer, the materials commonly used in the synthesis are metakaolin and fly ash, as a source of aluminum and silicon, and activators such as sodium hydroxide (NaOH) and sodium silicate (in a molar ratio $\text{Na}_2\text{O}/\text{SiO}_2 \sim 3.2$) as an alkaline source and of silicon.

In addition to the commercial sources of raw materials mentioned above, several researchers have studied alternative source materials in recent years. They are usually industrial wastes that can partially or fully replace aluminosilicates or activators, such as biomass ash [41], [42], manganese residue [43], slag [44], glass [44], and stone-cutting waste [3], [45].

Toniolo and Boccaccini [46] reported the importance of mixing different materials for successful geopolymerization. In their work, the authors describe several industrial wastes that are not used individually, as they do not have adequate molar ratios for the process. Among the waste mentioned are palm oil biomass ash (POFA), rice husk ash, red mud, glass residue, and waste with heavy metals. The authors have also stated that each waste may have another potential for geopolymerization, not just the appropriate molar ratios. As an example, red mud can be mentioned, contributing due to its high alkalinity and reducing the use of commercial activators in the mixture [46]. Importantly, these industrial wastes are frequently present in oxide form rather than entirely as metastable compounds, with some being inert and stable. Many factors impact the reactivity of these substances, particularly when examining industrial waste, such as fly ash.

Soutsos et al. [47] investigated thirteen types of fly ash from different origins in geopolymer formulations. Other materials, such as blast furnace slag, were added to the formulations to assess their interaction with the ash. The results demonstrated that the ash samples required high curing temperatures with high concentrations of activators. The main factors affecting ash reactivity were particle size, loss on ignition, and amorphous content. The partial replacement of ash by blast furnace slag was beneficial for geopolymerization, avoiding the need for high curing temperatures and improving compressive strength [47].

Blast furnace slag (BFS) consists mainly of calcium-magnesium aluminosilicate glass. It has been reported as the main raw material for several geopolymeric formulations [48], including for novel Ultra-High-Performance Concrete (UHPC). The waste material has been used in geopolymers and alkali-activated materials with the addition of iron (Fe_2O_3), cadmium (CdS , CdO /graphene), cerium (CeO_2), and tungsten (CaWO_4) as catalysts in photocatalysis [49], nickel for CO_2 methanation [50], and without catalyst addition for hydrogen production since it has Fe_2O_3 and TiO_2 in its composition [51].

Slags of magnesium [52], [53] and manganese [43], [54], [55] were reported as raw materials for geopolymers in photocatalytic applications. Some of these works have an ion exchange process of Na^+ to the catalyst or first to NH_4^+ and then to the catalyst, as did others with metakaolin and fly ash as raw materials [56]–[59].

Regarding the production of geopolymers from metakaolin and fly ash, several catalysts have been employed as raw materials, composite phase, or supported catalysts, as summarized in Table 1.

Table 1 - Catalysts and respective precursors employed in association with geopolymers.

Catalyst	Precursor	Reference
C	Graphene, carbon black, biochar	Zhang et al., 2021 [22]
Ca	CaO , $\text{Ca}(\text{NO}_3)_2$	Supamathanon et al., 2021 [60]
Cr	$\text{Cr}(\text{III})$	Chen et al., 2020 [61]
Cu	CuI , CuCl_2	Falah et al., 2016 [62]
Fe	Fe_2O_3 , Fe_3O_4	Zhang et al., 2021 [22]
LSGF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.3}\text{Fe}_{0.7}\text{O}_3$	Bedon et al., 2020 [11]
Pt	$\text{Pt}[(\text{NH}_3)_4\text{Cl}_2]$	Sazama et al., 2011 [37]
Ag	AgNO_3	Luukkonen et al., 2020 [63]
Ti	TiO_2	Maiti et al., 2020 [64]
Zn	ZnO	Zhang et al., 2021 [22]

2.6 *Potential for recycling of metal-containing waste for catalysts in geopolymer synthesis*

The annual worldwide consumption of catalysts is around 800 thousand tons, 415 thousand tons by refineries, 335 thousand tons by chemical industries, and the remaining are used in other activities. In this sense, many residual catalysts are generated when these lose their catalytic activity [65]. One can think of research opportunities using catalytic waste, which contains metals or active phases in their composition to be part of alkali-activated materials, whether for reuse in catalysis or not. Most studies have utilized metals or their precursors for obtaining geopolymer-supported catalysts [1], [5], [66]. However, it is feasible to explore waste materials as potential raw materials if they contain metallic elements such as Fe, Ti, and others in their composition, which could offer benefits and present a sustainable advantage.

Manganese residue, mainly composed of Fe_2O_3 and SiO_2 was used by Cai et al. [43] along with sodium hydroxide, sodium silicate, hydrogen peroxide, sodium dodecyl sulfate, manganese sulfate monohydrate, and ammonium persulfate in a complicated synthesis route that results in Fe-based geopolymer spheres suitable for antibiotics degradation [43].

Many studies have been conducted on geopolymers and spent fluid catalytic cracking (SFCC), a waste composed of aluminosilicate reactive material generated by petroleum refinery industries. This waste is classified as hazardous and contains heavy metals such as V, Ni, and Sb [67]. Its recyclability is often limited after several regeneration processes, which cause deactivation and structural damage to the zeolite materials that typically form part of the structure [68].

Zhang et al. [69] used SFCC to replace metakaolin in geopolymer formulations. A response surface experiment investigated four factors: SFCC catalyst content, the proportion of alkaline activators, the proportion of water, and SFCC particle size. The results showed that replacing metakaolin with small amounts of SFCC improves the compressive strength of geopolymers, while large amounts of SFCC decrease the strength of the obtained product. The best formulation was with the replacement of 20%, having a compressive strength of 41.22 MPa. The reduction in the particle size of the catalyst promotes greater reactivity, reducing cracks and micropores and a consequent increase in compressive strength [69].

Other authors have been investigating the influence of this type of waste concerning other factors, such as the influence of $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio [65], solid-to-liquid ratios [70], and the addition of nanosilica [71], [72], silica fume [73] and recycled aluminum [74] in the formulations. These works generally focus on correctly disposing of hazardous waste, encapsulating the problematic elements, and using the products as construction materials.

Yu et al. studied geopolymers derived only from SFCC and silica fume. [73]. Their team used the waste materials as the main solid silicon-aluminum source, besides sodium hydroxide and sodium silicate as activators. They proposed a geopolymerization reaction mechanism and cementitious potential for it by using FTIR, MAS NMR, and SEM analysis. The highest compressive strength of ~24 MPa was obtained using 50% solid raw materials and a water glass/sodium hydroxide ratio of 1.2.

Wang et al. [68] used SFCC to produce catalytic support via the sol-gel method and then used the product to esterify rosin and glycerol. In this case, the support was not a geopolymer but used the same idea to value SFCC. An alternative was explored by Wan et al. [75] with phosphate-based geopolymers. Acidic activation with phosphoric acid was used to activate the geopolymerization of SFCC. Compressive strengths of 30 MPa were achieved, and the geopolymer network was significantly different from the ones with metakaolin [75].

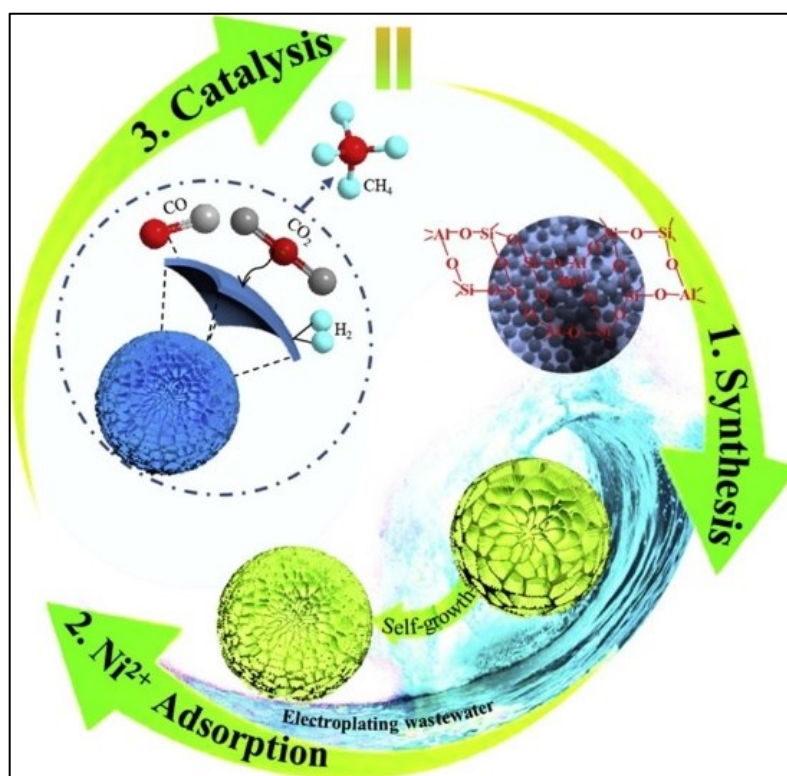
When heavy metals such as V and Ni are introduced into geopolymer formulations, there is a possibility that the metals participate in the three-dimensional network structure of geopolymers or are physically encapsulated. Another possibility of the heavy metal replaces the alkaline metal in the balance of the negative charge of Al^{+3} in the fourth coordination [67]. In such cases, the metal could be encapsulated into the structure and consequently not be available for the reaction. Still, the wear of the product during use could expose a new active phase and increase its durability or release this new active phase, thus generating more hazardous waste [67], [76].

To address the problem of leachability of the heavy metals from the geopolymers, the immobilization of vanadium and nickel in SFCC-metakaolin-based geopolymers was investigated by Zhang et al. [76]. They determined that the V content in the SFCC-metakaolin geopolymer should be lower than 1816 mg/kg to achieve leachate lower than 2 mg/L and be considered a non-hazardous metal [76]. The same matter was analyzed by Zhang et al. [67] from a different perspective. They compared

the ratios between SiO_2 , Na_2O , and SFCC in the geopolymer composition to establish ideal values for leaching toxicity. With $\text{SiO}_2/\text{Na}_2\text{O} \leq 1$ and $(\text{SiO}_2/\text{Na}_2\text{O})/\text{SFCC} \geq 0.18$, no leaching toxicity was detected.

Su et al. [77] have used a cyclic approach to heavy metal immobilization in geopolymers. Slag-based geopolymeric spheres were synthesized and placed into nickel electroplating wastewater for Ni^{2+} adsorption. They observed a self-growing behavior of the catalyst in the geopolymer surface due to the negative charge in the support surface, modifying its morphology, BET surface area, average pore size, and pore volume. Afterward, the same Ni-adsorbed spheres were used for CO_2 methanation with conversion higher than 98% at 100°C , well below the regular temperature for the process (300°C) [77], thus both recycling metal and protecting the environment in a fully circular process involving all processing and application simultaneously as depicted in Figure 3.

Figure 3 - Cyclic approach to nickel recycling from electroplating wastewater to catalysis. [77]



A summary of aluminosilicate sources, alkaline activators, and commercially available and waste-derived catalysts is shown in Table 2.

Table 2 - Summary of raw materials for the synthesis of catalyst alkaline-activated materials.

Sources	Aluminosilicate	Alkaline	Catalysts
Waste-derived	Biomass ash	Biomass ash	Electroplating wastewater
	Fly-ash	Glass	Manganese residue
	Heavy metal containing waste	Heavy metal containing waste	SFCC
	Red mud	Red mud	Slags
	Rice husk ash	Rice husk ash	
	Silica fume	Slags	
	Slags	Stone-cutting residue	
	Stone-cutting residue		
Commercially available	Calcined clay	Potassium Hidrooxide	Fe
	Biomass ash	Sodium Hidrooxide	Cd
		Sodium silicate	Ni
			Ca
			C (graphene/carbon black/biochar)
			Cr
			Cu
			LSGF
			Zn
			Ce
			W
			Ti
			Pt
			NH ⁴⁺ (ion exchange)
			Ag

2.7 Processing of geopolymers

The traditional reaction model indicates that it initially occurs with the alkaline attack of the activators on the structure of the aluminosilicates, dissolving them in aluminates and silicates. Although dissolution occurs simultaneously, there is primarily a greater release of aluminates due to the weaker bonds of this element [26].

Dissolution continues until the concentration of aluminates and silicates is sufficiently high (saturation) to destabilize the solution and start the precipitation of these species, composing a gel rich in aluminates. The initial silicates in this gel come mainly from added sodium silicate, a material that already has the silicates dissolved in the alkaline solution.

Other silicates present in solid materials (such as metakaolin) are later dissolved and precipitated, and a reorganization of the gel is obtained, increasing the proportion of silicon. The last step of the mechanism is the polymerization and the consequent hardening of the structure. The geopolymerization time depends mainly on the curing temperature and the presence of contaminants in the mixture, which can occur instantly or over days [26].

Despite originating an amorphous structure, if kept in a hot and closed environment, geopolymerization may eventually develop partially crystalline structures, containing zeolites of the sodalite, faujasite, gismondine, and P zeolite types [26], [78].

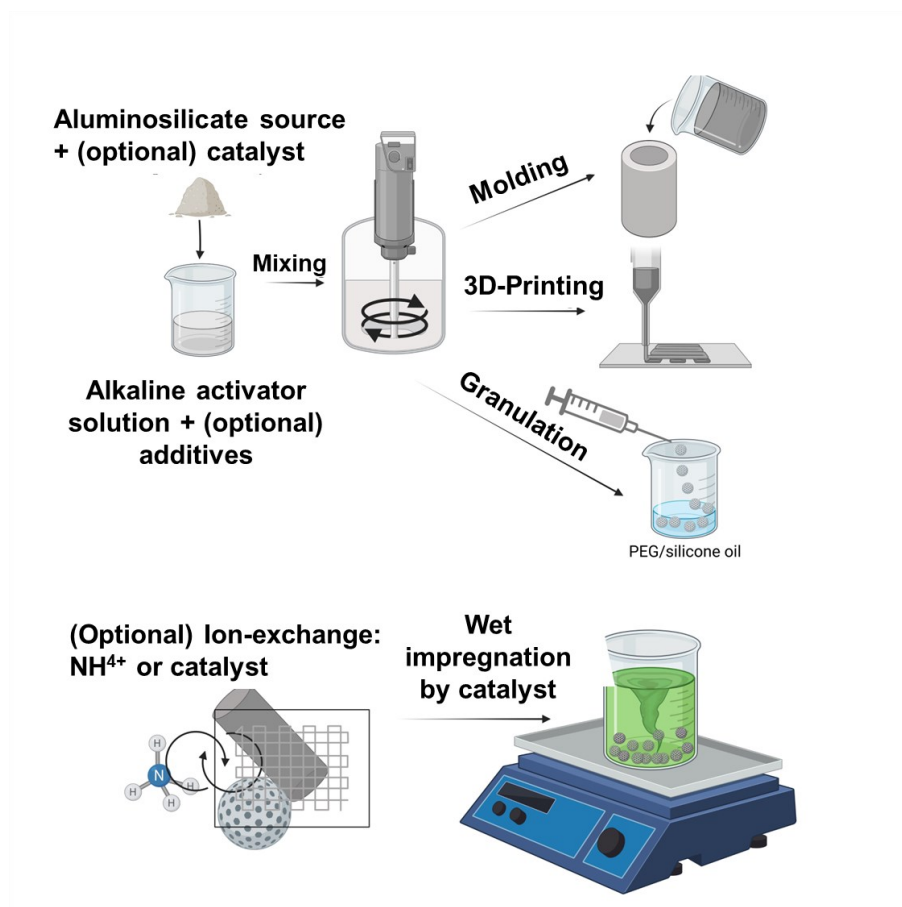
This thermal processing, however, must be done with caution, as a reduction in mechanical strength can occur, as reported in work by Suksiripattanapong *et al.* [79], where the use of temperatures higher than 85 °C caused a reduction in humidity, with the consequent formation of microcracks and reduced mechanical strength [79].

In this sense, the production of geopolymers requires care and correct compositional studies, with the need to develop easy-to-use methodologies for synthesizing geopolymers [80].

Some geopolymers, called “one-part geopolymers”, are synthesized using powdered alkaline activators to facilitate applications as a building material. Thus, the mixture only requires adding water, like conventional cement [81].

Processing is critical for developing the porous structure in alkali-activated materials and therefore plays a major role in the catalytic properties [5], [10], [63], [82]. The challenges and improvements lie in controlling morphology, surface area, pore structure, accommodation of active species, and synthesis conditions [14], [83].

Figure 4 - General overview of the processing of alkali-activated materials for catalytic applications.
Created with BioRender.com.



While several methods exist for producing these materials, most studies employ three primary approaches. These approaches begin with mixing starting materials, including at least one aluminosilicate source and alkaline activators. Figure 4 summarizes the processing of alkali-activated materials for catalytic applications. During this stage, catalysts can be incorporated into the formulations while the materials are still in their fresh state, and additives may be used to enhance porosity or other desirable properties. The paste can then be processed using one of three primary methods: (1) molding, where the container may or may not be sealed, and the resulting monoliths can be crushed to create a powder for use as a catalyst; (2) 3D-printing of open-cell monoliths; or (3) granulation, which typically involves injecting droplets of the paste into a dense medium such as PEG at temperatures close to 100 °C. Finally, catalysts can be added through impregnation or ion exchange after the pastes have cured. Thermal activation has been shown to alter the properties of samples and improve their catalytic activity [5], [8].

2.8 Alkali-activated catalysts

Although amorphous alkali-activated materials such as geopolymers are very similar to zeolitic materials, they have not been widely studied as catalytic materials. Alkali-activated materials have become an interesting alternative for preparing catalysts, mainly because wastes can be used in formulations.

They were initially designed for use as building materials and, for many years, researchers focused their studies on obtaining these materials from waste for use as building materials. However, due to their fragility and low strength, new alternatives for these materials, such as environmental solutions, began to be studied.

Geopolymers have been studied recently as new catalysts or support for them, mainly in gas and liquid phase reactions. In water, they have been applied in photocatalysis and advanced oxidation processes [8]. Table 3 summarizes the different applications of catalytic geopolymers.

Table 3 - Various applications of alkali-activated materials in catalytic reactions.

Application	Examples	Ref
Energy production	Biodiesel production	[84]–[87]
	CO ₂ methanation	[88], [89]
	H ₂ generation	[90]
Pollutants abatement	Air emissions treatment	[11], [56], [91], [92]
	Wastewater treatment	[21], [43], [49], [52], [54], [64], [101-106]
Miscellaneous applications	Beckmann rearrangement reaction	[58]
	Esterification of rosin and glycerol	[59]
	Friedel-Crafts benzylolation acylation of anisole and mesitylene	[93]
	Isopropanol dehydrogenation	[94]

2.8.1 Energy production

Energy is the basis of industrial activity and can be considered the engine of the global economy [31]. The intense exploitation of fossil fuels for energy use caused increased CO₂ concentrations in the atmosphere and, consequently, global warming due to the greenhouse effect. Furthermore, these energy reserves are finite, and research for renewable fuels becomes essential to satisfy future energy demands [31], [35], [95]. In that context, sustainable processes to produce renewable and clean energy are of great interest, with methanol and hydrogen being the most promising

fuels that could replace traditional energy sources soon [17], [34], mainly due to their high energy value and clean products generated (water) [30], [35].

For the sustainability of the process, it is essential to produce the fuel from a sustainable raw material at a viable cost [17], [34]. As seen before, geopolymers are amorphous analogs of zeolites with three-dimensional networks of SiO_4 and AlO_4 with a negative charge of the network balanced by extra structural cations that allow ion exchange [1]. These materials have advantages such as synthesis at ambient or low temperatures, mesoporosity, and low cost. These properties allow the incorporation of transition metals in the network to act as active centers in different catalytic reactions [37]. Sazama *et al.* [37] studied new heterogeneous catalysts from geopolymeric materials incorporating metallic ions of Fe, Co, Cu, and Pt. The results showed a potential selective catalytic reduction of nitrogen oxides by ammonia and the total oxidation of volatile hydrocarbons [37].

Hydrogen and carbon dioxide can be used to produce methane as substitute natural gas (SNG) in a process known as CO_2 methanation. It attracts interest since it can reduce greenhouse emissions while solving the problem of intermittency in renewable energy sources by converting temporary surpluses to hydrogen and methane in a power-to-gas strategy [50], [96].

Wan *et al.* [50] have synthesized alkali-activated materials from slag and granulated blast furnace slag with KOH, forming microspheres, and used them as support for nickel (15 wt%) in the methanation reaction. The authors showed that synthetic slag-based catalysts were more efficient for CO_2 conversion (80.2% vs. 72.8%) and had slightly higher CH_4 selectivity (99.2% vs. 98.3%), while both samples were stable for 100 h at 400 °C.

Su *et al.* [77] produced geopolymer microspheres from blast furnace slag and NaOH, later using the generated product for two applications, adopting a full-cycle solution. First, the spheres obtained were used for nickel adsorption in electroplating effluents and later in CO_2 methanation reactions. The results showed maximum adsorption of ~414 mg/g of Ni^{+2} during the treatment of the studied effluents, while in the methanation tests, the results showed CO_2 conversion greater than 99.5% at 300 °C and over 98% at 100 °C [77].

Hydrogen can be produced from water electrolysis using energy from a renewable source and then further applied to methanation. It can also be produced by catalytic steam reforming of hydrocarbons, which is well known and used over the last

decades [30]. This technology is one of the most important processes for hydrogen production and has attracted attention for its high efficiency and economy [40].

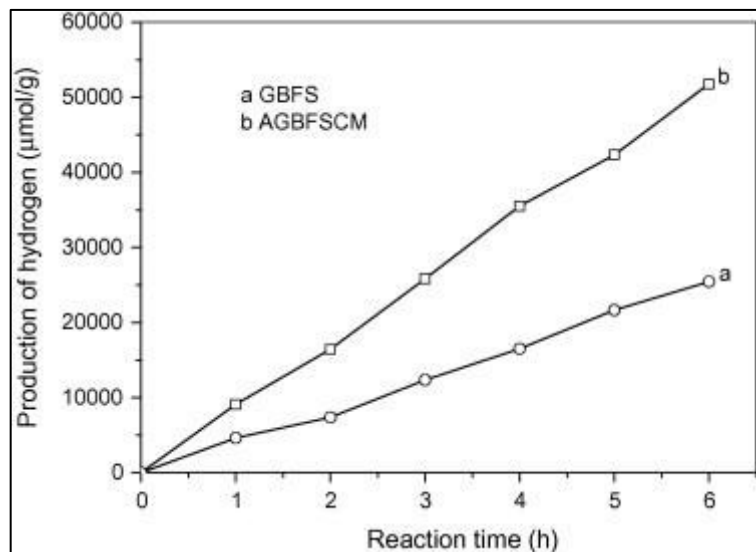
Steam reforming has been a solution to eliminate the disadvantages of storing H₂ in tanks, causing this gas to be generated from conventional fuels, such as methanol, ethanol, glycerol, bio-oil, and ethylene glycol, among others. Thus, the process becomes simpler, as these fuels are easier and safer to store, handle and transport [31], [32].

The technology of steam reforming of liquid hydrocarbons and methane is already well established employing active transition metals supported over metal oxides, e.g., Al₂O₃. However, the use of geopolymers as substrate or support for these reactions is still incipient.

Candamano et al. [17] evaluated the active nickel phase supported in geopolymeric samples for use in steam reforming (SR), partial oxidation (POX), and auto thermal steam reforming (ATR) of ethanol to syngas at temperatures of 700 °C. According to the authors, the benefits of using these materials are that geopolymers are prepared at room temperature, mesoporous, cheap, and with good thermochemical stability. These characteristics open opportunities for synthesizing new catalysts from geopolymers for heterogeneous reactions. The largest hydrogen generation was under SR conditions (~70 mol%), and only POX produced coke after 10 h. The results showed that geopolymer is a promising, low-cost, and environmentally friendly support material for ethanol-reforming reactions [17].

Photocatalytic decomposition of water for H₂ generation was achieved with alkali-activated granulated blast furnace slag without the addition of catalysts. The GBFS slag contains small amounts of TiO₂ and Fe₂O₃ [51] and generates 2.4x more hydrogen (Figure 5) after alkali-activation due to the synergistic effects of the mesoporous skeleton and its natural composition.

Figure 5 - Photocatalytic production of hydrogen under UV-light of as-received GBFS slag and alkali-activated GBFS cementitious material (AGBFSCM). [51]



An alkali-activated slag-based nanocomposite with CuO at 5 wt% was mixed with sodium silicate [53]. After irradiation of the simulated solar source for 6 h in an aqueous solution of Na_2SO_3 and Na_2S , the catalyst that relied only on its raw materials presented a performance of about half ($51.7 \mu\text{mol/g}$) of that observed in the slag-CuO nanocomposite work ($102.9 \mu\text{mol/g}$). The authors have proposed that in both cases, the matrix acts as a trap for photogenerated electrons while Na_2SiO_3 acts as a hole trap, thus providing the conditions for high activity of H_2 evolution [51], [53].

Biodiesel is produced from transesterification reactions of short-chain alcohols and triglycerides from vegetable oils or animal fats. The main homogeneous catalysts used in this process are KOH and NaOH [86]. Saputra et al [86] prepared geopolymers with rice husk ash, metakaolin, NaOH, and sodium silicate for use as a catalyst in the transesterification of *Calophyllum inophyllum* seed oil in the production of biodiesel. The most significant influence on the reaction yield was related to the catalyst content present in the samples rather than other reaction parameters. The highest yield reached ~88% biodiesel with parameters of ~99% alkyl ester and an acid number of 0.42 mg-KOH/g biodiesel [86].

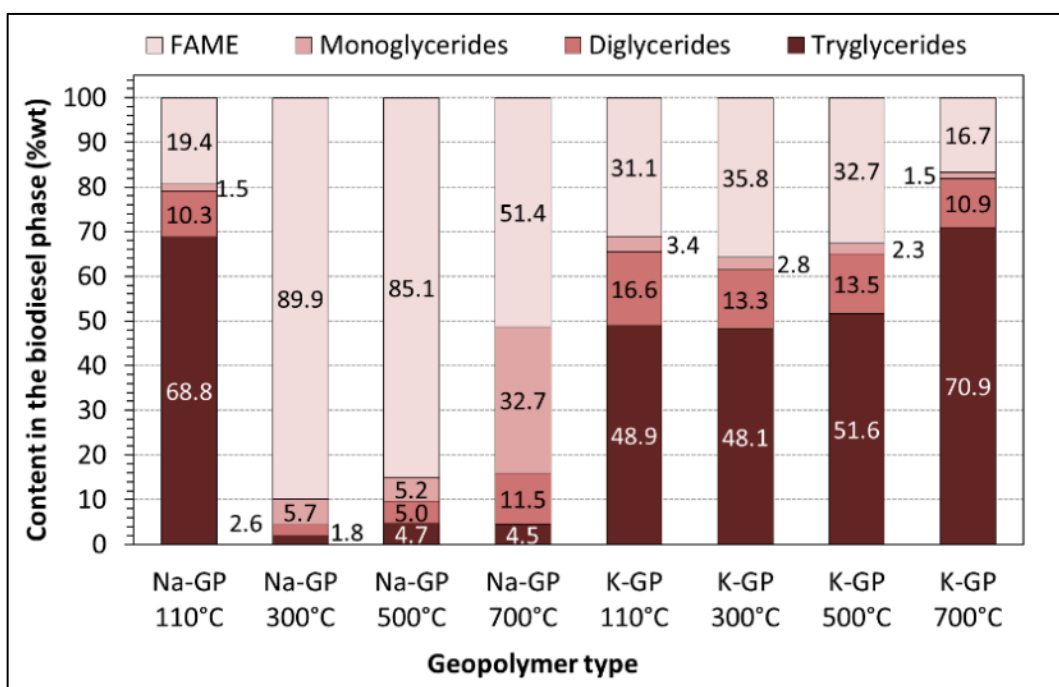
Among the various methods of obtaining biodiesel, heterogeneous catalysis has become an excellent alternative, mainly due to the easy separation and reuse of the catalyst. Kaliophilite is a type of zeolite used in several catalytic applications, with the problem of being produced at temperatures up to 1000°C [95]. He et al. [95] first proposed to obtain geopolymers from fly ash with subsequent transformation by a

hydrothermal process of the geopolymer into kaliophilite. The geopolymers were cured at 80 °C for 24 h, and the hydrothermal transformation was carried out in an autoclave (200 mL) containing a geopolymer monolith and 50 mL of KOH solution at a temperature of 180 °C for 24 h. After the hydrothermal process, the monolith with a compressive strength of 8 MPa was washed and dried at 105 °C for 12 h with subsequent grinding to obtain particles between 0.15 - 0.31 mm. The products obtained were used as heterogeneous base catalysts in biodiesel production. The programmed CO₂ desorption tests demonstrated medium and high strengths of the basic sites, mainly attributed to the hydroxyl groups, K-O and -O₂ ions. The catalysts obtained had higher yields in biodiesel production (99.2%) using a molar ratio of methanol/canola oil =15.1, reaction temperature = 85 °C, and 6 h reaction time. Furthermore, the catalysts obtained could be reused for four cycles without suffering significant deactivation [95].

Sharma et al. [97] studied a new class of solid base catalysts to produce biodiesel from hierarchically porous geopolymers modified with different amounts of Ca. For catalysts containing more than 8% by weight of Ca, conversions were obtained of almost 100% in one hour under reflux conditions with methanol solvent, maintaining catalytic activity after multiple regeneration cycles. The results demonstrate that geopolymers can be developed as cost-effective catalysts for use in the production of biodiesel [97].

Botti et al. [98] evaluated the catalytic activity of sodium and potassium-based geopolymers without the addition of any metal catalyst after different heat treatments (110 to 700 °C) in the transesterification of soybean oil. Potassium-based formulations exhibited higher specific surface area and lower mean pore size (28 to 62 m²/g; 9 nm) compared to sodium (6 to 32 m²/g; 17 nm). After heat treatment, there was a decrease in surface area in samples with sodium due to more significant shrinkage, but no link was observed between the specific surface area and the composition of the biodiesel phase. Na-based geopolymers performed better in soybean oil transesterification with values of 85.1 and 89.9% for samples treated at 500 and 300 °C respectively, as seen in Figure 6. The results were mainly attributed to higher average pore size in Na-geopolymers, thus a more effective mass transfer rate of reactants to the catalytic sites [98].

Figure 6 – Geopolymer powders synthesized using sodium and subjected to thermal treatment between 300 °C and 700 °C exhibit higher levels of Fatty Acid Methyl Ester (FAME) content compared to their potassium-based counterparts. [98]

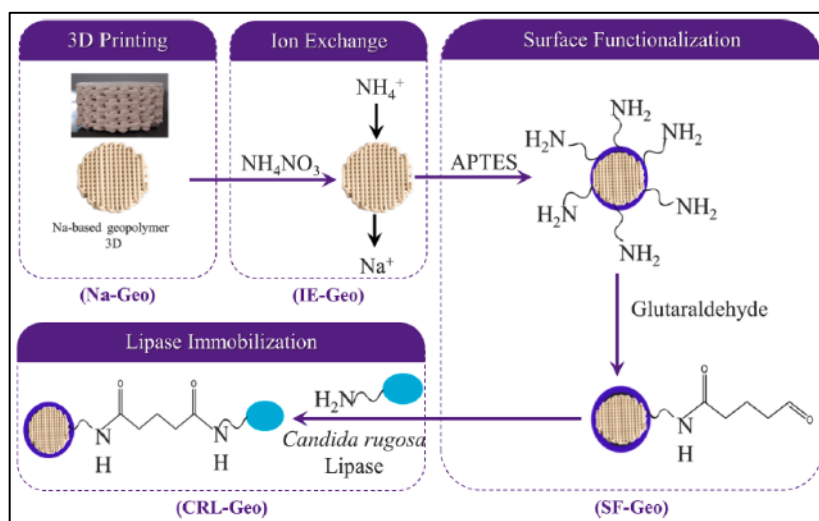


Innocentini et al. [99] applied 3D printing to fabricate Na-based geopolymer porous components with non-random pore channels, high surface area, and low-pressure drop. Compared to random porous structures, these materials allow more homogeneous properties, constant permeability and tortuosity of flow paths, and better mechanical properties. A geopolymer was previously obtained using metakaolin, sodium silicate, sodium hydroxide, and water. The molar ratios were: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.3$ and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 18.5$. After synthesis, the geopolymer was milled (45-125 μm) and then mixed at 1700 RPM for 10 min with polyethylene glycol, metakaolin, and an alkaline solution to provide a pseudoplastic behavior. The paste was kept at 4 °C for 30 min before printing. The porous monolith was tested for heterogeneous transesterification of soybean oil with methanol. An amount of 3% by weight of catalyst with a porosity of 56.4% and specific surface area of 14.3 g/m^2 yielded 43.5% by weight of biodiesel in a 4 h transesterification of soybean oil using a 150 mol% excess of methanol at 70 °C under reflux conditions [99].

Dos Santos et al. [100] produced geopolymers by Direct Ink Writing to serve as catalytic support for *Candida rugosa* lipase and to be used in the hydrolysis of cooking oil waste, a preliminary step in the biodiesel process. The experimental steps were 3D printing of geopolymers, ion exchange with NH_4^+ , surface functionalization, and lipase

immobilization (Figure 7). The samples obtained had a total porosity of 57.2% with a permeability coefficient $k_1 = (9.05 \pm 0.41) \times 10^{-9} \text{ m}^2$ and $k_2 = (3.64 \pm 0.26) \times 10^{-4} \text{ m}$. The results of hydrolytic activity showed efficiency in the immobilization of the enzyme, reaching $847.7 \pm 9.7 \text{ U/g}$ and free fatty acid content of 75 wt% [100].

Figure 7 - Experimental steps of lipase immobilization on geopolymers. [89]



The research of heterogeneous acid catalysts in biodiesel production includes various materials, such as M/MCM-41 (M = Mg, Co, and Zn), MgAl-layered double hydroxides (LDH), and metal oxides. Furthermore, basic metallic supports such as CaO-La₂O₃, CaO, and MgO/SiO₂ are also found in the literature. The production of catalysts based on MgO, MgSiO₄, kaolinite, and alkali metals can increase the catalytic activity in esterification reactions. In this sense, Sayed et al. [101] obtained new geopolymers synthesized with natural silica and synthetic MgAl-layered double hydroxides (MgAl-LDH) nanostructure and MCM-41 loaded with heterogeneous potassium-based catalysts for use in waste sunflower oil transesterification. The best experimental conditions were with 4 h of reaction, 4 wt% of catalyst, methanol/oil ratio equal to 15:1, and temperature of 120 °C, reaching a maximum yield of 94.6%. The results showed that the catalysts obtained presented properties compatible with international standards, with significant stability after 4 cycles of transesterification [101].

A summary of works regarding abatement of air pollutants is given on Table 4, with the type of catalyst process in which the material was tested, the raw materials employed in the geopolymer synthesis, the active phase (catalyst) and how the active phase was introduced into the material (catalyst processing).

Table 4 - Summary of works for energy production with geopolymer-enhanced catalytic reactions. The “catalyst processing” column refers to the method employed to mix geopolymers and the catalyst. GP= Geopolymer. SH = Sodium Hydroxide. SS = Sodium Silicate. KH = Potassium Hydroxide. KS = Potassium Silicate.

Reaction	Activators and other raw materials	Catalyst	Catalyst Processing	Ref.
Adsorption, CO ₂ methanation	SH	Ni	GP-supported	[77]
CO ₂ Methanation	KH	Ni	GP-supported	[50]
H ₂ generation from ethanol reform	SH, SS	Ni	GP-supported	[17]
Hydrolysis of waste cooking oil	SH, PEG-1000	<i>Candida rugosa</i> lipase (enzyme)	NH ₄ ion exchange, surface functionalized with APTES, and then GP-supported	[100]
Methane oxidation	SH, SS	La _{0.6} Sr _{0.4} Ga _{0.3} Fe _{0.7} O	GP-supported	[11]
Photocatalysis for H ₂ generation	SS	Ti, Fe	From raw material (aluminosilicate source)	[51]
Photocatalysis for H ₂ generation	SS	Ni, Cu	NH ₄ ion exchange and then GP-supported	[53]
Transesterification	SH, KH, SS	Mg, K	From raw material	[101]
Transesterification	SH, SS, KH, KS	Basic sites	From raw material	[98]
Transesterification	KH, KS	Kaliophilite basic sites	From geopolymer hydrothermal treatment	[95]
Transesterification	Rice husk ash, SH	Basic sites	From the synthesis process	[86]
Transesterification	SH, SS	Basic sites	From the synthesis process	[99]
Transesterification	Al, KH	Ca	GP-supported	[60]
Transesterification	KH, Canola oil	Ca	GP-supported	[97]

2.8.2 Pollutants abatement

Water pollution causes societal problems, and its treatment is extremely important for environmental protection. The textile industry uses a variety of chemical compounds that contaminate water, such as dyes, heavy metals, and surfactants, which are most often dangerous and difficult to treat [54], [102]. Among the various alternatives for treating these effluents, photocatalysis can be mentioned, which consists of the degradation of the organic pollutant in the presence of UV and a photocatalyst material (TiO_2 , ZnO , Fe_2O_3) [102].

The photocatalyst material, usually a metal or a semiconductor, may be attached to the geopolymer surface *via* ion-exchange. In such cases, an exchange of Na^+ to NH_4^+ precedes a second ion exchange from NH_4^+ to the catalyst metal [21], [52], [54], [63], [103]. The metal or semiconductor is usually mixed as a raw material, either as a composite phase or supported at the surface.

Luukkonen et al. [104] compared geopolymers manufactured by 3D printing, direct foaming, or granulation for water treatment applications and evaluated how different impregnation methods affect disinfecting and catalytic properties. The study involved introducing Ag or Cu to filters through various methods such as dissolution in fresh paste, addition of metal-containing bentonite to the fresh paste, dipping the filters in colloidal solution, or ion-exchange for NH_4^+ followed by ion-exchange with 0.1 M of the selected metal salt. Granulation was also employed by mixing the salts with an alkaline solution and metakaolin prior to the process. Notably, 3D-printed samples exhibited desirable features, such as lower leaching levels and highest compressive strength. Direct-foamed geopolymer modified with Ag nanoparticles also demonstrated low leaching but low compressive strength. In contrast, the addition of Cu salt to granules resulted in the lowest leaching level. However, ion-exchange exhibited considerable ion instability and was not deemed suitable for use as viable materials. Notably, the team did not test the samples for water treatment and identified further practical testing as a future research goal [104].

Contamination of water by antibiotics, even in low concentrations, can cause resistance to *bacteria*, such as *Escherichia coli*, and become a public health problem for society. In this sense, research for removing residual tetracycline (TC) in the environment is a great challenge and extremely important. Huang et al. [105] developed ceramic membranes from biochar and geopolymers (BC/GM) for oxidative

degradation of TC in water. The geopolymer matrix had the functionality of porous support with a bimodal hierarchical porous structure between 3.54 and 16.53 nm. The results showed that almost 100% of the compound was removed using 0.15 g BC/GM, 1 mL of hydrogen peroxide, pH 5.0, and 60 °C for 5 h. The formed geopolymers still had good stability after five cycles [105].

Cai et al. [43] achieved TC removal of ~98% within 30 min with the photocatalytic activity of MnO₂ supported via ion-exchange on metakaolin-based geopolymer microspheres modified by manganese residue and calcined at 500 °C in N₂ atmosphere. Compared to bare MnO₂, the catalyst geopolymer was 4.5 faster. The removal efficiency of several dyes and other organic contaminants was close to 100%. They attributed the results to the C-decorated surface structure and its synergistic effect with the metal oxide catalyst, suggesting that geopolymers might be a feasible support to boost the environmental applications of MnO₂ [43].

A graphene and bottom ash-based geopolymer was Mn²⁺ doped and CuO loaded in a four-step process of alkaline activation, ion exchange, co-impregnation, and calcination by Zhang et al. [106]. The NH₄⁺ ion-exchanged sample was wet-impregnated by Cu(NO₃)₂·H₂O and Mn(NO₃) and calcined at 400 °C. The samples were both used for photocatalytic degradation of dye and hydrogen generation. Degradation rates of direct sky blue 5B were ~100% for 15 wt% of CuO samples, and the highest H₂ yield was achieved with 20 wt% of CuO. The authors suggest that there is still much to understand about the new materials, such as the influence of graphene amount, type of semiconductors, and geopolymer composition [106].

Graphene and steel-slag were alkali-activated, and the material was used as a support for the ion-exchange of NH₄⁺ followed by wet-impregnation with Cd(NO₃)₂·4H₂O by Zhang et al. [107]. CdO loadings of 1 wt%, 8 wt%, and 16 wt% were tested. Photocatalytic activity reached values close to 100% after 100 min for degradation of DBF dye. The results were attributed to synergistic effects between graphene and CdO [107].

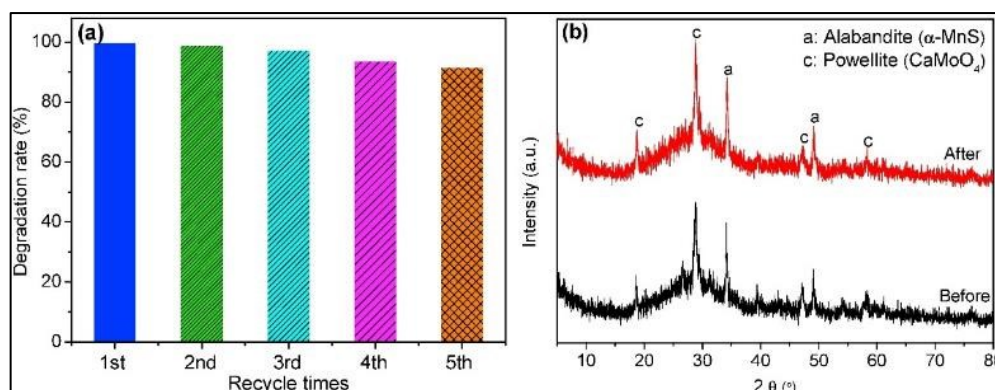
Synthesized CdS particles, drinking water treatment residue, and blast furnace slag were mixed with alkali activators, H₂O₂ as a foaming agent, and sodium dodecyl sulfate as a stabilizing agent by Ji et al. [49]. The hierarchically porous material was tested for photocatalytic degradation of organic dyes and polluted sediments collected from a lake in environment conditions to assess the material's stability and safety. Adsorption and photocatalysis were also compared and simultaneously tested. After

330 min, the contaminant concentrations decreased, and the humic-like substances transformed into protein-like substances under UV radiation [49].

Silicomanganese slag and carbon black were evaluated as alkali-activated alternatives to photocatalytic applications by Zhang et al. [55]. The photocatalytic degradation of basic violet 5BN dye was positively correlated to the electroconductivities, with the highest doping value (4.5 wt%) of carbon black presenting the greater degradation rates (88.3%) and electroconductivity (0.2976 S.m^{-1}). The team attributed the improved photocatalytic activity to the quick transfer of photo-generated electrons and holes to the network of carbon black [55].

Taking a step further with alkali-activated silicomanganese slag, He et al. [54] noticed that the reaction between a geopolymer composite formed an active phase of CaMoO_4 from silicomanganese slag, electroconductive black carbon, and NaOH after a NH_4^+ ion exchange process followed by impregnation by $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and calcination at 400°C . The team employed a response surface methodology with Box-Behnken experimental design to predict optimal conditions for photocatalytic degradation of basic violet 5BN and experimentally reached complete dye degradation at 3.78 wt% of CaMoO_4 loading and 5.64 mg/L dye concentration. After five cycling steps, the degradation fell from 99.6% to 91.6% with high structural stability – Figure 8 [54].

Figure 8 - Photocatalytic degradation of Basic Violet 5BN over 4CaMoO_4 /Electroconductive geopolymer composite: (a) Recycle tests; (b) Catalyst XRD pattern before and after photocatalytic removal. [54]



In another three-step process, Zhang et al. [21] activated granulated blast furnace slag with sodium silicate, ion-exchanged it to NH_4^+ and then loaded Fe_2O_3 onto the surface *via* wet impregnation with amounts from 0.5, 5, and 10 wt% of catalyst.

Congo red dye was degraded by photocatalysis, and the sample with 5 wt% of Fe_2O_3 showed the highest degradation efficiency, close to 100%, under UV irradiation [21].

Lei et al. [108] have introduced Fe_2O_3 into the geopolymer mix to increase the conductivity for electrocatalysis. Pre-treated stainless steel was dip-coated into the slurry to form a composite anode after curing for 8 h at 80 °C. The composite presented higher oxygen evolution potential, greater electrochemical activity area, and smaller impedance than the geopolymer without Fe_2O_3 . The cathode was pre-treated with stainless steel, and the electrocatalysis took place at 0.1 M N_2SO_4 . The degradation of indigo carmine was ~93%, with 10 wt% of the catalyst oxide after 90 min. In the 5th cycle, the degradation rate had fallen to values close to 80%, indicating a potential for long-term activity and reusability [108].

Blast furnace slag was also activated and subjected to NH_4^+ ion-exchange before wetness impregnation by ammonium metatungstate and calcination [103]. In the end, a nanocomposite with CaWO_4 was obtained, and the photocatalytic degradation of basic violet 5BN reached 90,3% with 5 wt% of catalyst. Zhang et al. [103] attributed the results to the synergistic effect between the catalyst and the material mesopore structure.

Magnesium slag-based nanostructured composite co-loaded with NiO and CuO were synthesized *via* the same three-step methodology. Zhang et al. [52] have found that 10 wt% of NiO + CuO showed the highest photocatalytic degradation (~100%) of indigo carmine dye. The team proposed a photocatalytic oxidation mechanism based on the band gap values of the semiconductor oxides [52].

Maiti et al. [64] synthesized TiO_2 rutile of different particle sizes (30, 50, and 100 nm) and mixed at 5 wt% with fly ash, alkaline activator ($\text{NaOH}:\text{Na}_2\text{SiO}_3 = 1:2$), and sand. Photocatalytic degradation of Methylene Blue was carried out under UV irradiation and TiO_2 particles of 30 nm degraded up to 96.4% of the contaminant in 90 min while reducing the porosity, roughness, and density of the geopolymer [64].

Hybrid behavior for wastewater treatment was explored with photocatalysis and membrane separation by Chen et al. [61]. Metakaolin, silica fume, and NaOH were mixed as a slurry to form the geopolymer membrane. $\text{Cr}(\text{NO}_3)_3$ aqueous solution simulating wastewater was then poured over the membrane fixed in a Buchner funnel sealed by a rubber ring. A negative pressure of 0.09 MPa was applied to accelerate the Cr(III) enrichment. Afterward, the membranes were calcinated at 550 °C to transform $\text{Cr}(\text{NO}_3)_3$ into Cr_2O_3 and employed in photocatalytic degradation of basic

green dye, reaching degradation rates close to 100% in 100 min for Cr_2O_3 5 wt% under static conditions and 50 min at 0.09 MPa due to the membrane-induced concentration of the dye [61].

Biochar and iron (Fe) as raw materials in geopolymer mix had synergistic effects on the removal of Methylene Blue from water investigated by Zhang et al. [22]. The team also investigated the efficiency of heavy metal immobilization according to the biochar content. Samples with and without either biochar or Fe_2O_3 were synthesized with circulating fluidized bed fly ash, bottom ash, metakaolin, NaOH, Na_2SO_3 , and water, and three groups were compared: 4 wt% biochar + Fe from raw materials, 4 wt% biochar – Fe from raw materials (removed using magnetic separation), 4 wt% biochar + equivalent Fe_2O_3 wt% analytically pure. The team also tested the influence of biochar contents, from 0 wt% to 8 wt%. The removal efficiency of methylene blue was highest at pH 8, with 8 wt% of biochar and Fe_2O_3 (84%). Without Iron in the mixture, removal efficiency decreased to 68%. With iron from raw materials but without biochar, the value fell to 65%. Heavy metals immobilization increased with the biochar content, reaching the highest immobilization values at a biochar content of 8 wt%. They concluded that biochar was instrumental in improving heavy metal immobilization whilst Fe improved the removal efficiency of dye contaminants, thus suggesting a synergistic effect from both materials in geopolymers used in wastewater treatment applications [22].

Saufi et al. [102] proposed geopolymers synthesized from perlite as a sorbent and photocatalyst for methylene blue (MB) degradation. The results indicated that the dye degradation efficiency by geopolymers without and with UV was up to ~89% and ~98% in 4 h, respectively. The general experimental results suggested that the new material elaborated with synergistic adsorption and photocatalytic activities has great potential for treating water contaminated by hazardous substances [102].

Falah et al. [62] also evaluated the use of geopolymers containing $\text{Cu}_2\text{O}/\text{TiO}_2$ nanoparticles and with a structure modified by tertiary ammonium (cetyltrimethylammonium bromide, CTAB). The MB removal mechanisms consist of adsorption and photodegradation. The results show that modification of the structure by CTAB increases dye removal performance, having the best result (97% removal in 60 min) with 5 wt% $\text{Cu}_2\text{O} / \text{TiO}_2$ [62].

Zhang et al. [29] evaluated a new cementitious catalyst based on Ni and Ca obtained by polymerization and ion exchange reactions using steel slag. During ion

exchange, first, there was an exchange with NH_4^+ and later an exchange with Ni^{2+} . The results showed that the ion exchange technique almost completely replaced Na^+ with Ni^{2+} . The product obtained was tested in photocatalytic degradation of methylene blue dye, showing an efficiency of 94.39% under UV irradiation. The high degradation is due to the synergistic effect of nickel ions with iron and calcium iron oxides [29]. Similarly, Zhang and Liu [109] evaluated geopolymers obtained from fly ash as a photocatalyst for methylene blue degradation in wastewater. The results showed that the efficiency of MB degradation by geopolymers was up to ~93% under UV irradiation due to the synergy of semiconductor adsorption and photocatalysis mechanisms [109].

A magnetic geopolymer composite prepared from biogenic rice husk silica, metakaolin, and magnetite with mesopores-structure derived from hydrogen peroxide and soybean oil was developed by Rossatto et al. [110]. The team evaluated the adsorbent dosage and initial pH at aqueous acid green 16 dye adsorption onto the composite. Removal of the dye was highest at low initial pH values (2.3), and the removal percentage was higher than 90% even after 3 usage cycles [110].

Iron ore tailing, a mining and mineral waste from the iron ore industry, replaced 30% of fly ash by mass in porous geopolymer for heavy metal removal from water. Duan et al. [111] have used a geopolymer with a total porosity of 74.6% from these raw materials to achieve a Cu^{2+} uptake efficiency of ~90%. They found higher removal efficiency at pH 5 and 40 °C and contact time over 70 min for 3 g/L of the contaminant. Their results suggest a spontaneous nature of Cu^{2+} adsorption and an endothermic behavior of the process, which is favorable at higher temperatures [111].

2.8.3 *Abatement of air pollutants*

The increase in the concentration of nitrogen oxides (NO_x) originating from burning fossil fuels has been one of the great environmental problems of our time, causing acid rain and respiratory issues, among others. One of the most promising solutions to reduce the amounts of NO_x in the atmosphere is its reduction in less problematic products. The most common technology is the selective catalytic reduction (SCR) of NO_x by NH_3 . For this application, iron-based catalysts are widely used due to their thermal stability, but new catalysts are important to increase selective oxidation at high temperatures and consequently increase NO_x conversion and N_2 selectivity [91]. Chen et al. [91] evaluated a composite of geopolymer and activated carbon produced to serve as catalytic support for iron. Above temperatures of 350 to 500 °C,

there was a NO conversion above 96.5% with N₂ selectivity above 94%. Furthermore, the catalysts obtained were durable and resistant to SO₂ and H₂O. It is suggested that the high efficiency of the catalyst is related to the synergistic effects of iron ions with the geopolymer matrix, having a greater redox capacity during the catalytic reaction [91].

Bedon et al. [11] studied a composite formed by coal fly ash-based geopolymer and perovskite (La_{0.6}Sr_{0.4}Ga_{0.3}Fe_{0.7}O₃) to be used as in general pollutants abatement applications. To assess the materials' performance, methane oxidation by perovskite is obtained at temperatures between 400 and 500 °C. The methodology consists of depositing the active phase (perovskite) on the surface of the geopolymer using a solid combustion synthesis and avoiding the usual wash coating method. Using one step, this method allows obtaining composites more easily and quickly when increasing the process scale. The results show that the composite obtained had a catalytic activity beginning at 400 °C and reached methane conversion of 5% at 600 °C and 75 % at 800 °C.

ZSM5 zeolites were used as filler in geopolymeric direct ink writing (DIW) by Cepollaro et al. [56]. Copper was later introduced to the material surface *via* ion-exchange. It presented efficiency up to 100% and above 100 °C for NO and NH₃ conversion and N₂ selectivity above 90% in a range of temperatures from 100 to 500 °C. The introduction of ZSM5 significantly impacts catalytic performance compared to geopolymer without any chemical treatment or with copper but without zeolites. They concluded that the ion-exchange method could be improved, but the results prove that the composite could be used for industrial selective catalytic reduction applications [56].

Dichloromethane (DCM, CH₂Cl₂) is a commercial chemical used in various applications, such as propellants in aerosols and pharmaceutical production. Catalytic oxidation has been an efficient technology for the abatement of DCM emissions [92]. Seelam et al. [92] evaluated metakaolin-based geopolymeric catalyst powders for the oxidation of dichloromethane. Hydrochloric acid treatment increased the specific surface area of the geopolymers due to the leaching of Na and Al. Higher specific surface areas (>500 m²/g) were obtained by calcining the obtained geopolymer. The best result of the dichloromethane oxidation was with the geopolymers treated with 1 M HCl with a maximum conversion of 90% of dichloromethane at 550 °C [92].

A summary of works regarding abatement of air pollutants is given on Table 5, with the type of catalyst process in which the material was tested, the raw materials employed in the geopolymer synthesis, the active phase (catalyst) and how the active phase was introduced into the material (catalyst processing).

Table 5 - Summary of applications of alkali-activated materials in pollutant abatement. GP = Geopolymer. SH = Sodium Hydroxide. SS = Sodium Silicate. KOH = Potassium Hydroxide. KS = Potassium Silicate.

Reaction	Activators and other raw materials	Catalyst	Catalyst Processing	Ref.
Adsorption	SH, H ₂ O ₂ , Soybean oil	Fe	From raw material	[110]
Adsorption	SH, SS	Fe, Biochar	From raw material	[22]
Adsorption	SH, SS, K12, H ₂ O ₂ , Alkali lignin	Biochar	GP-supported and as a composite	[105]
Adsorption, Photocatalysis	SH, SS	Fe	From raw material (aluminosilicate source)	[102]
Adsorption, Photocatalysis	SH, SS	Cd	From raw material as composite	[49]
Dichloromethane oxidation	SH, SS	Acid sites resultant from acid leaching treatment	From the synthesis process	[92]
Electrocatalysis	SH, SS, KH	Fe	From raw material	[108]
Photocatalysis	SH, PEG-4000	Ca, W	NH ₄ ⁺ ion exchange and then supported	[103]
Photocatalysis	SH	Ca, Ni	Ca: From raw material (aluminosilicate source), Ni: NH ₄ ⁺ ion exchange and then GP-supported	[29]
Photocatalysis	SS	Fe	NH ₄ ⁺ ion exchange and then GP-supported	[21]
Photocatalysis	SS	Ni, Cu	NH ₄ ⁺ ion exchange and then GP-supported (Ni, Cu)	[52]
Photocatalysis	SH, SS	Fe	From raw material	[111]
Photocatalysis	SH, SS	Ti	From raw material	[64]
Photocatalysis	SH, SS, H ₂ O ₂ , K12	Mn, Fe	From raw material (Fe) and ion exchange of Mn	[43]
Photocatalysis	SS	Ca, Fe, Ti	From raw material (aluminosilicate source)	[109]
Photocatalysis	SH	Cd, Graphene	From raw material and as a composite	[107]
Photocatalysis	SH	Electroconductive black carbon	From raw material as a composite	[55]

Photocatalysis	SH	Electroconductive black carbon, Ca, Mo	From raw material as a composite, NH_4^+ ion exchange and then GP-supported	[54]
Photocatalysis	SH	Cr	GP-supported	[61]
Photocatalysis	SH, SS, CTAB, Glucose	Cu, Ti	GP-supported and as a composite	[62]
Photocatalysis	SH, SS, H_2O_2 , Trixton X, SDS, CTAB, PEG-1000.	Cu, Ag	GP-supported, ion exchange with and without NH_4 step, as raw material	[63]
Photocatalysis, H_2 generation	SS	Graphene, Mn, Cu	From raw material (graphene), NH_4 ion exchange and then GP-supported as composite	[106]
Selective catalytic reduction (De-NO_x)	KH	Fe, C	NH_4^+ ion exchange and then GP-supported	[91]
Selective catalytic reduction (De-NO_x)	SH, SS	Cu, ZSM5	ZSM5 raw as composite, Cu for ion exchange	[56]
Selective catalytic reduction, Gas reform	SH, SS, KH	Co, Cu, Pt, Fe	NH_4^+ exchange, GP-supported	[37]

2.8.4 Miscellaneous applications

Alzeer et al. [59] used geopolymers as a new class of cost-effective and environmentally friendly acid catalysts. The catalysts obtained were tested in a liquid phase Beckmann rearrangement reaction model. Beckmann rearrangement is a vital reaction for many industrial organic syntheses. One such reaction is the production of ϵ -caprolactam, the precursor to polyamide-6 (nylon-6). The active phase inside the geopolymer was obtained by ion exchange reactions with NH_4^+ followed by heat treatment. The catalytic performance was improved after heat treatment and the results presented show that geopolymers have great potential for use as heterogeneous catalysts, being reused 5 times without losing efficiency [59].

The same authors later evaluated bifunctional heterogeneous catalysts derived from geopolymers obtained from coal ash with high Ca content in Friedel-Crafts and acylation reactions [58], [93]. The geopolymer materials were obtained with different porosity levels and a combination of acidic and redox-active sites. The acid sites were generated from ion exchange with NH_4^+ followed by heat treatment, while the redox sites originated from catalytically active ash components. The catalysts obtained

showed greater reactivity than other catalysts used, such as zeolites and mesoporous metallic silicates. The fact that the metallic oxide particles are inside the geopolymer matrix suggests that these catalysts demonstrate a high level of reuse and lifetime [58].

Satmon et al. [94] obtained new catalysts for isopropanol dehydrogenation using Cu and Ni supported on geopolymers. Catalysts containing 5 wt% Cu and 10 wt% Ni showed excellent performance in the conversion of isopropanol, reaching ~23% efficiency and ~88% selectivity for acetone under 90 °C conditions, 3 h reaction, and amount of catalyst 0.15 g/5 g of isopropanol. Regarding durability, the catalyst maintained its catalytic stability after five cycles [94].

The studies regarding miscellaneous applications are presented on Table 5, with the type of catalyst process in which the material was tested, the raw materials employed in the geopolymer synthesis, the active phase (catalyst) and how the active phase was introduced into the material (catalyst processing).

Table 6 - Summary of miscellaneous applications of alkali-activated materials in catalysis.

Reaction	Activators and other raw materials	Catalyst	Catalyst Processing	Ref.
Acylation of anisole and mesitylene	SH, SS	Fe	From raw material without addition, NH ₄ ⁺ ion-exchange	[58]
Beckmann rearrangement reaction	SH, KH, SS	As synthesized	NH ₄ ⁺ ion exchange	[59]
Friedel-Crafts benzylation reaction of benzene and other	SH, SS	NH ₄ ⁺	NH ₄ ⁺ ion exchange	[93]
Isopropanol Dehydrogenation	SH, SS, PVA	Cu, Ni	GP-supported	[94]

3 3D-PRINTED GEOPOLYMER-BASED CATALYST SUPPORTS²

In this chapter, the technology of additive manufacturing of geopolymers is explored from the basic theory, consisting mostly of the reaction kinetics and the relationship with the rheology, to the reasoning of the experimental plan adopted in the Thesis. This exploratory approach reviews the most important aspects of rheology and kinetics and explores the use of these fundamentals for the successful production of 3D-printed geopolymer monoliths.

3.1 *Fundamentals of the additive manufacturing of geopolymers*

Additive manufacturing is a group of emerging techniques to manufacture three-dimensional structures based on a digital model. With additive manufacturing, it is possible to reduce material consumption and achieve complex geometric shapes of higher surface area to volume due to the complex geometric shapes that are impossible or too expensive with other methods. In addition, other factors can be mentioned, such as reduced labor, construction time, and reduced waste generation due to production errors [112], [113]. Another possible benefit would be the construction in harsh environments such as space [114].

The additive manufacturing of geopolymers can be primarily categorized into two techniques: extrusion-based and binder-jet-based methods. In the extrusion-based approach, a paste is extruded through a nozzle in the form of filaments and then deposited layer by layer. This method is widely recognized and commonly employed due to its cost-effectiveness and relative simplicity. Conversely, the binder-jet-based technique involves a more intricate and relatively expensive setup. It consists of a powder bed comprising a one-part precursor made up of an aluminosilicate source and an alkaline activator. In this method, the powder bed is consolidated by applying a binding agent. Alternatively, an alkali activator may be applied to a powder bed consisting of an aluminosilicate source [115], [116].

Powder bed-based methods are inherently suboptimal for non-sintered materials like geopolymers, as they encounter challenges related to densification. These challenges manifest in the form of high porosity and inferior mechanical properties [116], [117].

² To be submitted as “3D-printed geopolymer-based catalyst supports” for international peer-reviewed journal.

Among the extrusion-based methods, Direct Ink Writing (DIW), also known as robocasting, is one of the most simple and versatile 3D-printing alternatives. The main DIW requirements are extrudability, buildability, and shape retention ability, all of which are related to the rheological behavior of the paste. In this regard, printing geopolymers represents a more intricate array of challenges compared to printing ceramics due to the setting time of the alkali-activation reaction that governs the hardening process of geopolymers [118].

Despite the endeavors of certain authors to gather and standardize printability parameters for geopolymers using DIW [115], [117]–[121], the process remains predominantly determined by a combination of setup, raw materials, and mixing procedures. The substantial variations in methodologies, equipment, and raw materials pose significant challenges in extrapolating results obtained from one research group to another. Therefore, to date, there are no standard methods for characterizing the printability of geopolymers [118].

Nevertheless, producing geopolymers by DIW is an interesting choice for catalysis due to the great range of properties that can be achieved according to the processing and raw materials employed. It is a great advantage that most ceramic raw materials can be introduced into the formulation to achieve composite products. Porosity, surface area, hydrophilic/hydrophobic behavior, and thermal and mechanical properties can be tuned, as can the effective electron transference, enabling geopolymers both as catalysts and catalysts supports in several applications [5], [14].

As aforementioned, the rheological behavior of the mixture is the most important characterization regarding DIW. Apart from the lack of standard methods to characterize the printability of geopolymer pastes and according to the literature, the most important properties of the paste/ink are defined by the dynamic yield stress, the static yield stress, the apparent viscosity, and the open time, since they are all related to rheology. From these four concepts, it is possible to assess most of the paste fresh properties and printability requirements.

3.1.1 Printability of geopolymers in Direct Ink Writing

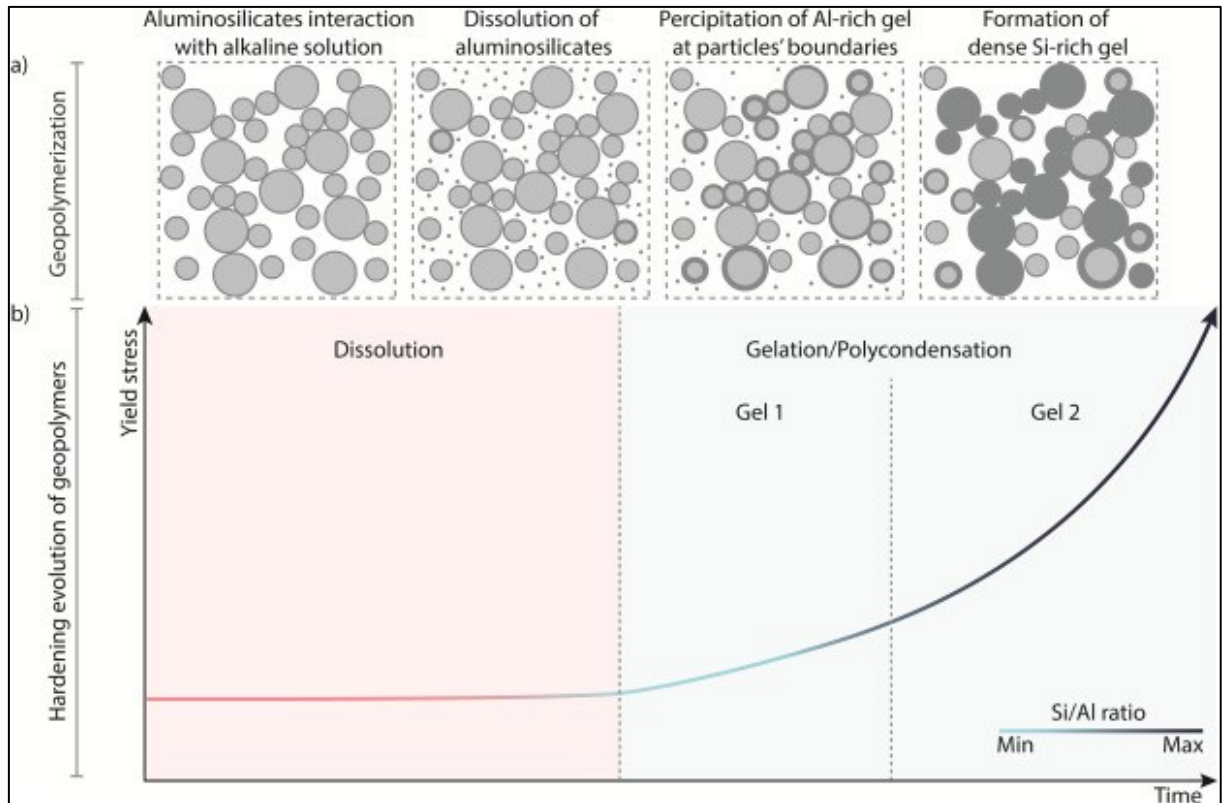
When comparing studies that employed Direct Ink Writing, translating the results presented in a random paper into the results given in some other random study is almost impossible due to the differences in paste composition and setup systems. Even so, for the sole purpose of relating the results obtained experimentally to the ones

found in the references, mixtures of similar raw materials might be used as a starting point to formulate 3D-printable paste. Practical printing tests are relatively quick and uncomplicated to perform. Additionally, a thorough rheology characterization may be carried out to assess the properties of a particular paste designed for DIW.

Considered mainly as a cementitious material, fresh geopolymers are suspensions undergoing physical and chemical changes. They present yield stress and thixotropy at the early stages of curing. Therefore, many methods to characterize geopolymer rheology have been adapted from the cement science and industry [122]. Also adapted from the cement industry and literature is the concept of structural build-up involving both reversible (thixotropic) and irreversible (rheopexy) processes for cements at rest state. Hence, methods that are useful to evaluate the additive manufacturing capabilities of cementitious are also valid for geopolymers. As mentioned before, comparing rheological parameters between different mixtures and equipment setups might be very difficult if not impossible. The characterization methods, however, might be suitable for different systems.

Being the product of the dissolution of aluminosilicates in an alkaline solution, in time, the development of the geopolymer microstructure undergoes two main gelation/polycondensation stages: Gel 1 and Gel 2. This leads to the hardening of the paste and consequent increase in yield stress and viscosity values [123]. Gel 1 is characterized as an Al-rich stage since Al-O bonds are easier to break at constant pH and low temperatures. The formation of Gel 1 leads to a fast development of mechanical properties but to a low degree. Gel 2 only begins to form when Si from the solid sources becomes available through diffusion mechanisms and corresponds to the main mechanical properties of the resulting material [124]. The mechanism is depicted in Figure 9.

Figure 9 - Early-stage hardening of geopolymers and reflex on the yield stress [123].

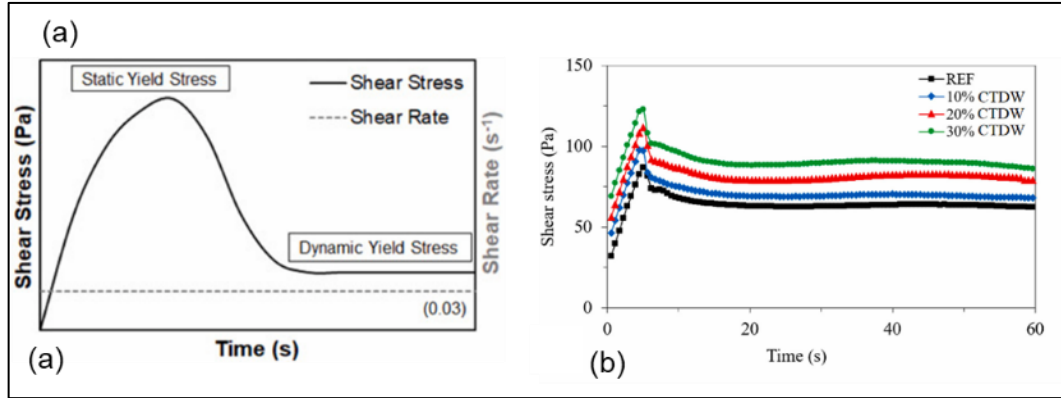


Gel 2 is characterized by the relevant development of yield stress and mechanical properties, being directly related to the buildability of the extruded filaments in 3D-printed structures. The yield stress, once defined as the minimum shear stress to start the flow has more recently been divided into two definitions: static and dynamic yield stress, the latter being the minimum shear stress required to keep the flow [125].

In the following, some testing protocols will be presented along with the pros and cons of each one.

The constant shear rate test protocol is applied to investigate the static and dynamic yield stresses and thixotropy. A constant shear rate of some low value, usually from 0.01 to 1 s^{-1} , is applied after the application of a high shear rate (from 60 to 100 s^{-1}) and some resting time [126], [127]. In this test protocol, the static yield stress is defined as the peak of the curve, and the dynamic yield stress as the relatively constant and lower shear stress required to keep the flow. In Figure 15, the expected result from the test and a practical representation of results obtained by Matos et al. [126] following such methodology are presented.

Figure 10 - (a) Graphical representation of results expected from the constant shear rate test protocol.
 (b) Results obtained by Matos et al. [126] following a similar protocol.



The thixotropy is a reversible, isothermal, time-dependent decrease in the apparent viscosity when a material is subjected to increased shear rate. It is associated with the difference between the static and dynamic stresses in results obtained by the constant shear rate test protocol. Hence, the bigger the difference between both values, the higher the thixotropy associated with the paste. The break-down percentage is defined by Equation 2 and the drop in apparent porosity by Equation 3, both adapted from Tuyan et al. [128]:

$$\text{Break - down percentage} = \frac{\text{static yield stress} - \text{dynamic yield stress}}{\text{dynamic yield stress}} \times 100 \quad (\text{Equation 2})$$

$$\text{Drop in apparent porosity} = \frac{\text{static yield stress} - \text{dynamic yield stress}}{\text{shear rate}} \quad (\text{Equation 3})$$

The tests may be repeated after giving some resting time to the paste to assess the development of structural build-up with time [128].

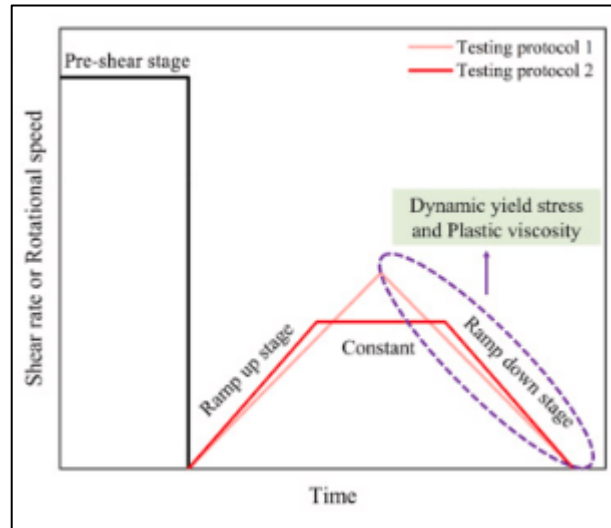
The flow curve test protocol consists of applying a high pre-shear stage to the paste and then an up curve and a down curve, that may or not have an intermediary constant shear rate step between both curves. From this method, structural build-up associated with dynamic yield stress and equivalent plastic viscosity are obtained by fitting the Herschel-Bulkley model (Equation 4) to the ramp-down stage. From Equation 4, the equivalent plastic viscosity (μ_{eq}) is given by Equation 5. A compilation of the testing protocol of flow curves is presented in Figure 11.

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (\text{Equation 4})$$

$$\mu_{eq} = \frac{3K}{n+2} \cdot (\dot{\gamma}_{max})^{n-1} \quad (\text{Equation 5})$$

where τ is the shear stress; τ_0 is the dynamic yield stress; K and n are the consistency and pseudoplastic parameters of the model and $\dot{\gamma}$ is the maximum shear rate applied.

Figure 11 – Flow curve testing protocols [118].



Both testing protocols, constant shear rate and flow curve, have been employed in the current work.

3.1.2 Reaction kinetics by isothermal calorimetry

Isothermal calorimetry is another methodology adapted from the cement industry; it provides information about the reaction kinetics from the reaction heat flow at a specific temperature. Calorimetric data can provide information about the whole geopolymerization process [129]. It can be used to virtually assess the influence of any mixture parameter in the reaction kinetics [130].

For the specific goal of finding parameters of printable pastes, only the initial hour may be assessed by isothermal calorimetry. The open time for most inks remains in the timetable of approximately 1 hour after the mixture process [118], [123]. It is in the first hour of reaction that dissolution takes place, and the most intense peaks of heat flow are usually observed before 10 min and are mostly related to the rapid dissolution of the aluminosilicate. This has been demonstrated by several authors and Figure 12 brings some results obtained by Zhang et al. [130] and Gonzáles-García et al. [131] at 25 °C for different mixtures at different time scales.

In Figure 12 (b), a second peak is observed after variable time. Its intensity and broadness are highly related to the silicate activator. The higher the modulus between alkaline and silicate activators, usually NaOH or KOH and Na₂SiO₃, the higher

and narrower the second peak, as it will also appear in a much shorter time. Figure 13 shows the results obtained by Zao et al. [129] for different alkaline/silicate ratios.

Figure 12 – Heat flow of geopolymerization reaction at 25 °C observed by isothermal calorimetry of NaOH + MK in the works of (a) Zhang et al. [130] and (b) González-García et al. [131].

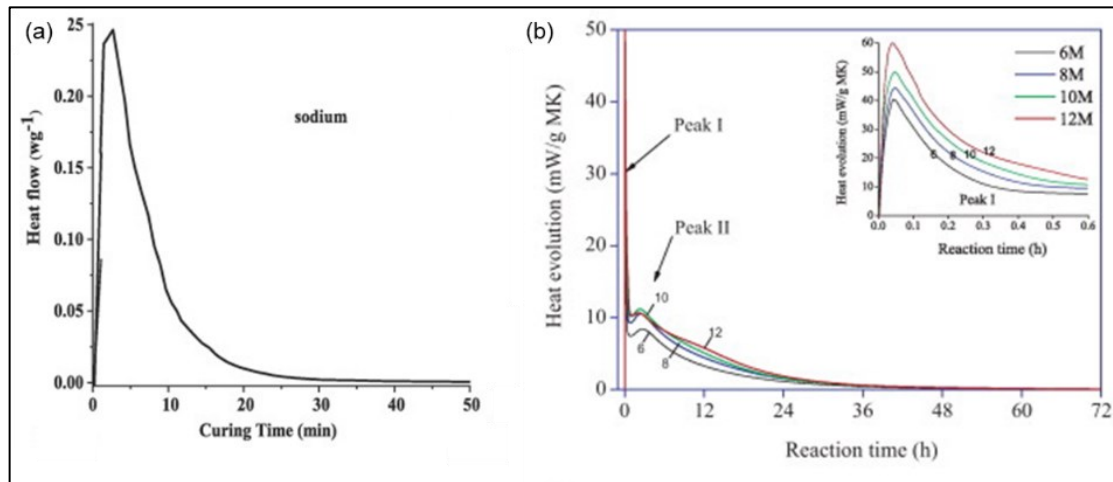
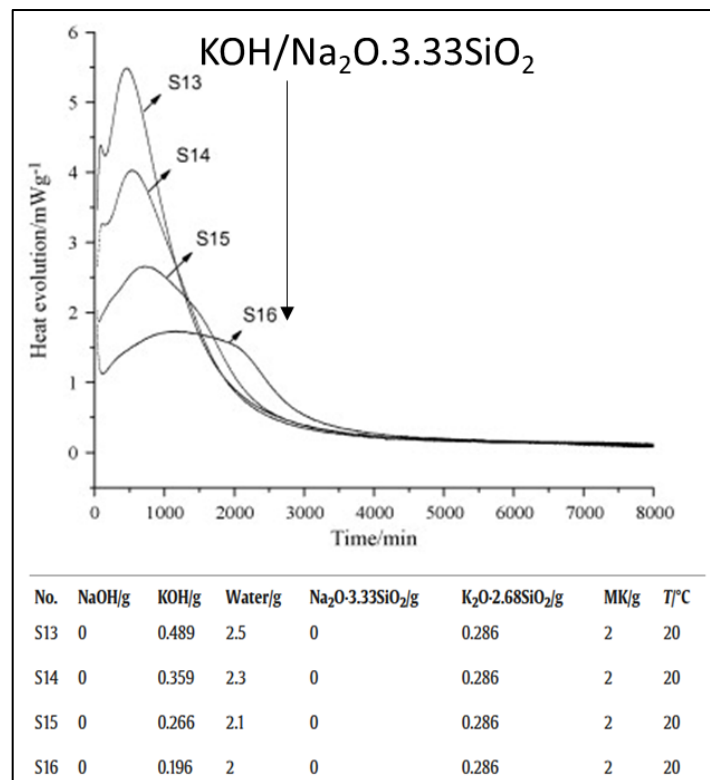


Figure 13 – Relationship between alkaline and silicate activators and geopolymerization heat flow in MK systems. The second peak is higher, narrower, and appears sooner as the modulus of $\text{KOH}/\text{Na}_2\text{O} \cdot 0.33\text{SiO}_2$ increases. Adapted [129].



3.2 *Experimental 3D-Printing of Geopolymer Monoliths*

Most parameters for the successful additive manufacturing of geopolymers can not be repeated from other studies since the raw materials are intrinsically different, as well as the mixture methodologies and 3D-printing devices. Nevertheless, it is possible to replicate the characterization methods to assess the systems in which a specific paste is to be printed. In this Section, two commercial metakaolins are used as the aluminosilicate source for printable inks. The raw materials, the pastes, and the products are characterized and discussed.

3.2.1 *Materials*

Two metakaolin samples were used as sources of reactive silica and alumina: MK-B (Ultra HP from Bentonita), a grey powder, and MK-I (Metacaulim from Imerys), a white powder. Both are available in the Brazilian market. The variation in metakaolin color serves as an indicator of differences in material composition. Choosing the raw materials followed the idea of increasing the chances of repeatability of results, therefore only commercially available materials were employed.

The liquid reagents used for alkali-activation were a mixture of sodium silicate (SS, Quimidrol, 10.8 wt.% Na_2O , 34.20 wt% SiO_2 , and 55.0 wt% H_2O) and a 10 M sodium hydroxide (NaOH) solution (SH, Neon, 99 wt%). Polyethylene glycol with an average molecular weight of 400 g/mol (PEG-400, Neon Comercial, 98 wt%) was added as a rheological agent in the mixture.

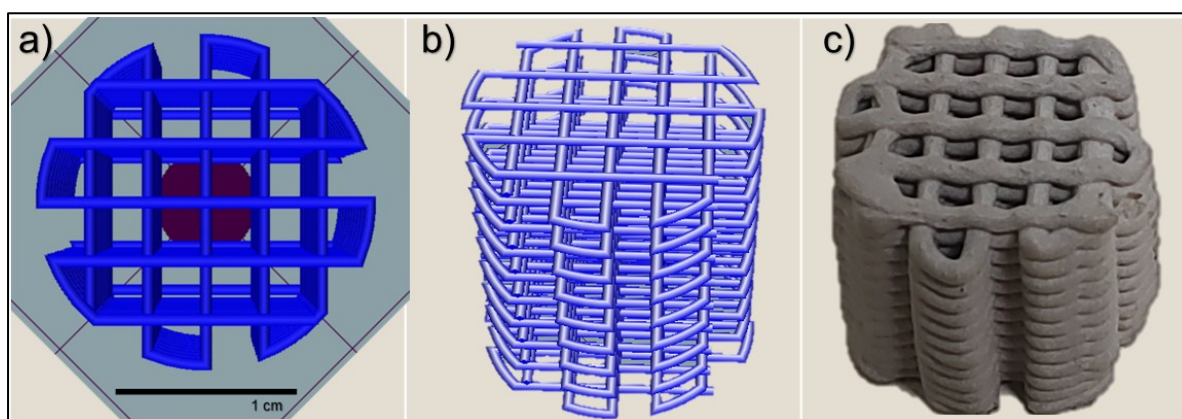
3.2.2 *Direct Ink Writing*

The mix design was inspired by compositions for pastes of high buildability and proper rheology for DIW, as investigated by our group in previous works [6,20], adding 3 wt% of PEG-400 to the mixture as a rheological agent. In a 70 g slurry, 40 g of metakaolin, 30 g of alkaline activators (50 wt% each), and 2.1 g of PEG-400 were added as raw materials. Samples comprising the mixture with only MK-B as the aluminosilicate source were named MKB-0. A second sample batch was made replacing 25 wt% of MK-B with MK-I and named MKI-0.

The MKB formulations have molar ratios of 3.25 for $\text{SiO}_2/\text{Al}_2\text{O}_3$, 0.19 for $\text{Na}_2\text{O}/\text{SiO}_2$, 0.62 for $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, and 12.22 for $\text{H}_2\text{O}/\text{Na}_2\text{O}$, while MKI formulations have molar ratios of 3.06 for $\text{SiO}_2/\text{Al}_2\text{O}_3$, 0.19 for $\text{Na}_2\text{O}/\text{SiO}_2$, 0.59 for $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, and 12.22 for $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

Sodium silicate was added to the NaOH solution. The alkaline activators and PEG-400 were stirred together for 10 min before being mixed with metakaolin for 6 minutes. The ink was then transferred to a 55 cm³ syringe. Printing was carried in a Duraprinter E-02 with a 0.84 mm-aperture nozzle. An open-source software, Slic3r, was employed to generate the G-Code from a CAD model of a cylinder measuring 13 mm in diameter and 11 mm in height as presented in Figure 14. The dimensions were defined according to the reactor diameter. This resulted in a total of 21 layers with a 30% volumetric filling density in a rectilinear pattern, leading to a porosity of 70%. The resulting geometry has 3 per centimeter (ppc) in the horizontal axis and 1.3 ppc in the vertical axis. The printing speed was set to 180 mm/s and the samples were printed in room conditions over biaxially-oriented polypropylene foils.

Figure 14 – a): Top view of the CAD model, b) CAD model and c) 3D-printed sample.



Due to polycondensation reactions [119], the ever-changing rheological properties of the paste during the printing process represent technical challenges for DIW of geopolymers. The pressure applied through the pneumatic system must vary accordingly to the increase in the dynamic yield stress over time. The pressure was manually varied from 0.1 to 5 bar to ensure a constant and uniform flow of paste. The whole printing process was carried out in ambient temperature and humidity conditions, which may also play a role in rheological conditions.

After printing, the geopolymers were cured at room temperature for 7 days and washed with distilled water until constant electrical conductivity and constant pH were reached. After the washing procedure, it is assumed that the samples are free of non-reacted sodium at room temperature. The washing procedure was arbitrarily defined according to previous unpublished results from the study group. These samples were called MKB-0 and MKI-0. The samples were then placed in the oven to be calcined at

800 °C for 5 h after a heating ramp of 10 °C/min – the calcined samples were named MKB-NiO and MKI-NiO.

3.2.3 *Raw materials characterization*

Metakaolin raw powder was characterized by X-ray fluorescence spectrometry (XRF; EDX-7000) and loss on ignition (LOI) at 950 °C. The particle size distribution was obtained by laser diffractometry (LUM Lumisizer analyzer). Ultrasonication was required since the particles are highly hydrophobic and aggregate during storage time.

Mineralogical compositions were investigated by X-ray diffraction (XRD; Rigaku MiniFlex600) - Cu K α radiation, from 5 to 80°, step of 0.02° and 0.5 s/step. Diffraction patterns were analyzed by X'pert Highscore Plus and Match3! Software using the ICDD database (International Center of Diffraction Data, PDF 4).

Simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) were carried out in N₂ atmosphere from ambient temperature to 1100 °C using a STA 449-F3 Jupiter (Netzsch).

3.2.4 *Paste characterization*

The rheological tests were conducted using a Haake MARS III (Thermo Fisher Scientific) rheometer with a vane geometry (16 mm in diameter x 22 mm in height) with four blades.

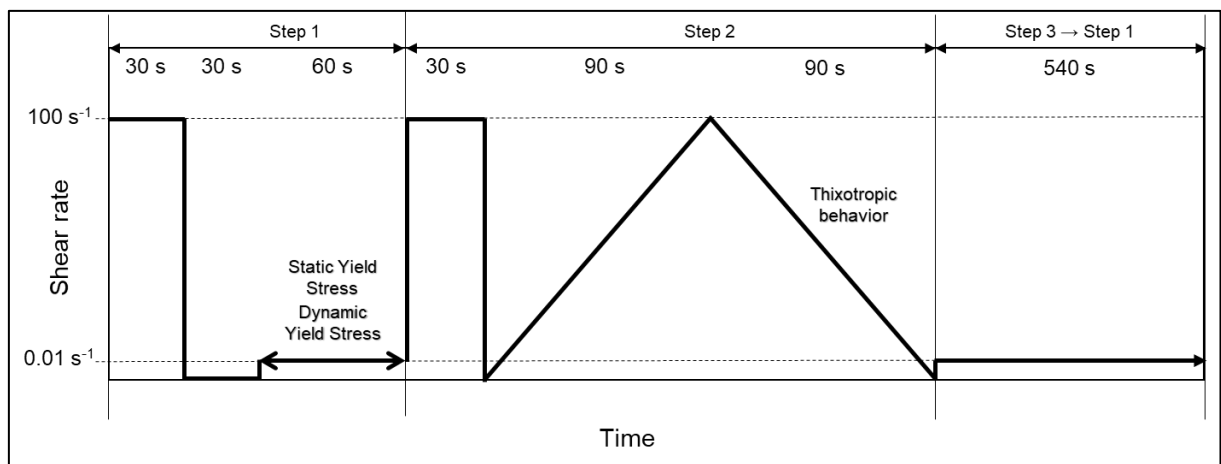
The hydration kinetics was evaluated using isothermal calorimetry (TAM Air calorimeter, TA Instruments). After the sample preparation, about 10 g of paste was placed in the calorimeter container. The temperature was kept at 23 °C and the measurements were recorded for 60 minutes. For the present research, PEG-400 was selected due to its relatively low molecular mass, and the percentage of this additive was determined using Isothermal calorimetry. The conducted experiments using pastes composed of MK-B and PEG-400 at concentrations of 0%, 3%, and 5% by weight, had their performance through isothermal calorimetry.

To assess the rheological behavior of geopolymer pastes, a testing protocol with three steps was designed to simulate an extrusion-based printing process as presented in Figure 15. This protocol comprises many testing methods into one single test and allows a wide overview of static and dynamic yield stress over time and the thixotropic behavior of the paste. The same test was repeated 5 times for each formulation to evaluate the early hardening evolution of the formulations and to assess

the real application in 3D printing, which might be not continuous in some printing setups.

In Step 1, the shearing history of the suspension subjected to 0.01 s^{-1} for 540 s is removed by a high shear rate (100 s^{-1}) for 30 s [132] and the suspension is left to rest for 30 s before going into a constant shear rate of 0.01 s^{-1} for 60 s. From Step 1, static and dynamic yield stress can be obtained. The static yield stress is found at the peak stress during constant shear rate at 0.01 s^{-1} and is the minimum required stress to start the flowing of material while the dynamic yield stress is defined as the required stress to maintain the flow [126].

Figure 15 – Rheology testing protocol.



Many authors have considered Step 2 as a single testing protocol [118], [133]. In the current work, it is employed as a tool to investigate the equivalent plastic viscosity. The choice was made based on the early-stage hardening of geopolymers depicted in Figure 9.

Thixotropy may be assessed both by Step 1 and Step 2, while Step 3 simulates a continuous printing process and the subsequent hardening evolution. The high shear and resting time from Steps 1 and 2 are supposed to simulate the sudden restart of the printing process.

The solidification of cement-like materials is irreversible and therefore is defined by rheopexy, but it might be reversible (thixotropic) in the early stages. The testing protocol is continuously repeated up to 5 times for each formulation to evaluate the gelation/polycondensation evolution over time, summing up to approximately 1 h of testing or less if the rheometer is unable to continue the test due to the high viscosity.

Equations 2 and 3 are used in Step 1 to evaluate the break-down percentage and the drop in apparent viscosity. Equations 4 and 5 are applied to the down ramp of Step 2.

3.2.5 *Monolith characterization*

The 3D-printed monolith microstructure was analyzed by SEM equipped with EDS and dedicated software (Hitachi TM3030). Apparent porosity and bulk density of the samples were determined according to ASTM C373 via the Archimedes method [134] and by using the relation among geometric measurements and weights with true densities. The true densities were determined with the gas pycnometer method using grounded samples (<75 μm). Geometric measurements and weights were obtained with the caliper and analytical balance in oven-dried samples.

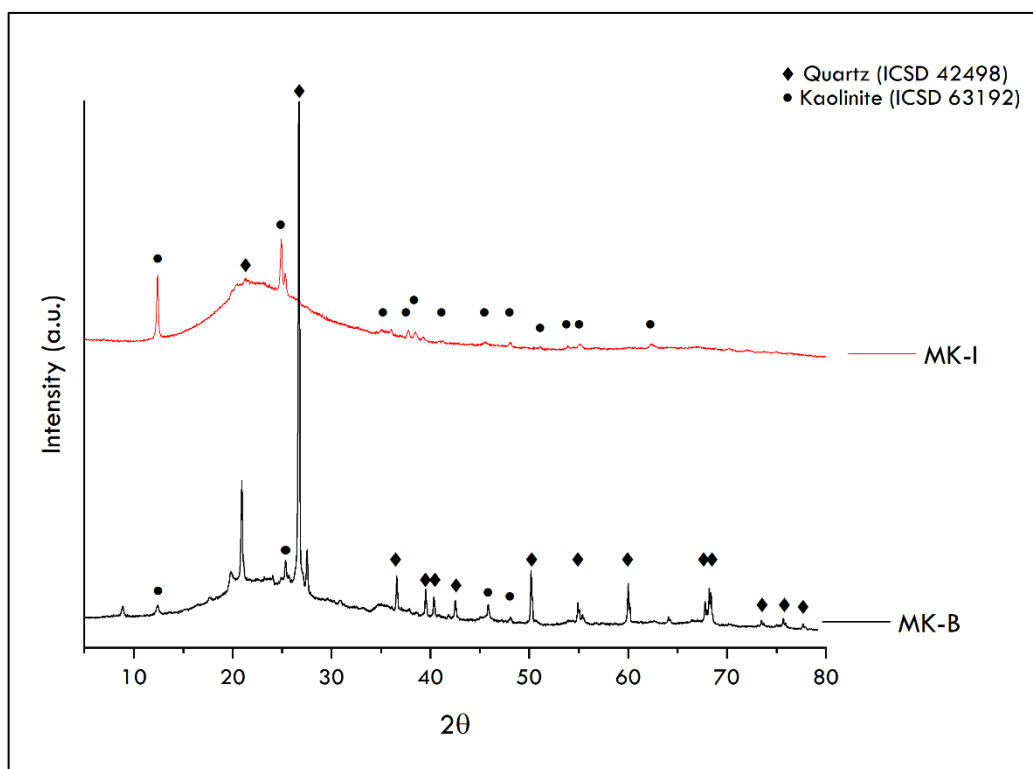
Specific surface area was calculated from N_2 adsorption-desorption isotherms and the Brunauer–Emmett–Teller (BET) theory. The measurements were carried out in a single-point ChemBET Pulsar TPR/TPD Automated Chemisorption Flow Analyzer (Quantachrome Instruments).

3.2.6 *Results and discussion*

3.2.6.1 Raw materials characterization

Figure 16 and Table 7 show the main crystalline phases and oxides present in the raw materials MK-I and MK-B. In MK-I we can see an amorphous diffractogram with some residual kaolinite peaks. This amorphous halo in the 10 and 30° region is typically found in these materials and represents their reactivity in geopolymerization. Kaolinite is a clay mineral base for the production of metakaolin with the chemical formula $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$. The processing of this clay mineral is carried out with calcination at temperatures of $\sim 750^\circ\text{C}$ to eliminate the combined water and consequent increase in reactivity. The XRF results (Table 7) confirm that this material is composed of aluminosilicates with few impurities in the composition.

Figure 16 - X-ray diffractogram (XRD) of MK-B and MK-I materials.



In the case of MK-B, the dominant crystalline phase observed is quartz, aligning with the findings from FRX analysis, which indicated a predominant presence of SiO_2 in the sample. Nevertheless, it's worth noting that there are several unidentified peaks stemming from other crystalline phases in MK-B's XRD pattern. In addition to these crystalline phases, an amorphous structure is also detected, characterized by a diffuse halo between 10 and 30°. However, this amorphous halo is notably less prominent than the one observed in MK-I.

Smaller peaks are present in both diffractograms, yet their identification remains challenging. These peaks are associated with phases found in both materials, but their intensity is often insufficient to distinguish them from background noise. Given the limited correspondence between these peaks and entries in the PDF-2 database, they have remained unidentified.

The average particle sizes (d_{50}) of MK-B and MK-I are 2.12 and 1.37 μm , respectively, as calculated from the particle size distribution presented in Figure 17. Considering that MK-I has a smaller particle size, lower crystallinity, and higher purity, it is possible to assume it as more reactive for geopolymerization. Likewise, from the lower number of unidentified peaks in its diffractogram, it is concluded that few contaminating elements can be found in this material, suggesting a product with better

quality, without possible interference in geopolymerization, and in the application suggested in this work (monolith for catalytic support).

Table 7 - Chemical composition (FRX, wt%) of MK-B and MK-I

Oxides	MK-B	MK-I
SiO₂	56.12	52.84
TiO₂	1.64	1.13
Al₂O₃	36.00	43.31
Fe₂O₃	2.27	0.85
K₂O	1.62	0.04
ZrO₂	0.07	0.02
CaO	0.00	0.04
V₂O₅	0.06	0.00
SrO	0.02	0.01
MnO	0.02	0.00
CuO	0.01	0.01
Cr₂O₃	0.01	0.02
ZnO	0.01	0.00
NbO	0.01	0.01
PbO	0.01	0.01
Ga₂O₃	0.01	0.01
Y₂O₃	0.01	0.00
LOI	2.11	1.71

It is also possible to assume from the particle size distribution that a suspension of MK-I will present higher viscosity than MK-B for the same amount of water [135]. This assumption was confirmed by preliminary tests and was also one of the reasons why MK-I only counts for 25 wt % of one of the mixtures. Besides requiring more water, a paste composed of MK-I, water, alkaline activators, and the rheology additive (PEG-400), presented a non-Newtonian behavior. It flowed under low shear stress but not under the required tensions for printing. The 25 wt % of MK-I was the threshold to apply approximately equal processing conditions for both pastes.

Figure 17 - Particle size distribution and density for MK-B and MK-I .

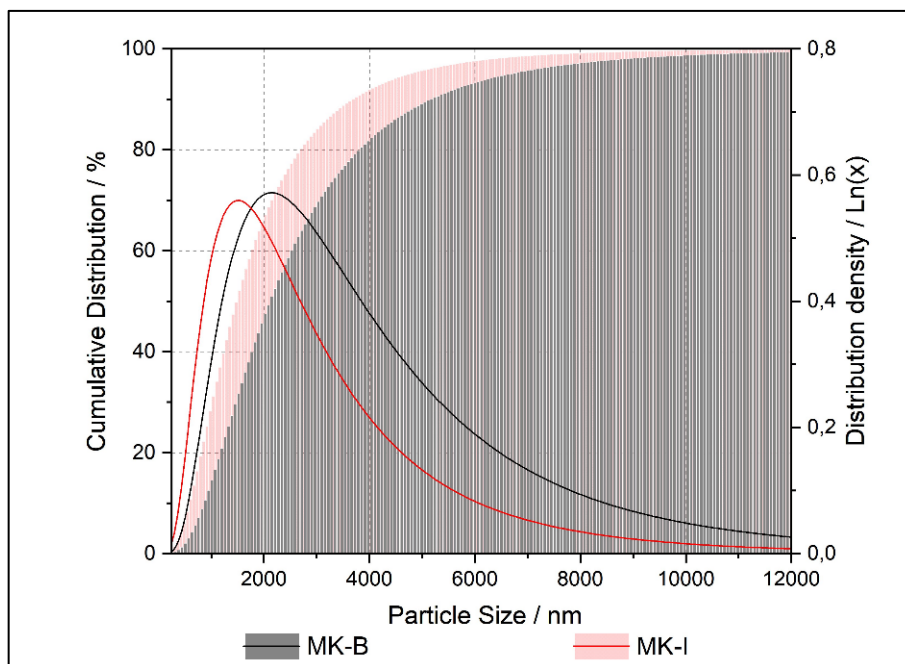
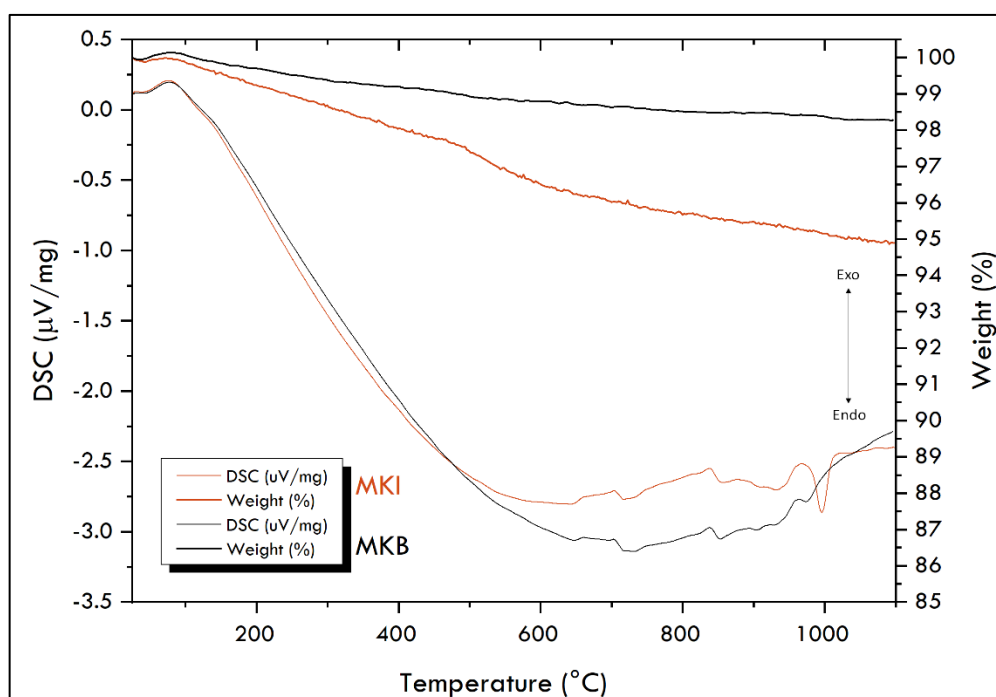


Figure 18 shows that both MK-B and MK-I do not present significant weight loss if heated up to 1100 °C, losing most of their masses up to 600 °C due to the loss of residual kaolinite and minor quantities of intrinsic water and impurities. Both present similar signals from 600 to ~1000 °C, probably due to minor phase transformations, and MK-I presents an endothermic peak close to 1000 °C related to the crystallization of a spinel phase leading to mullite formation [42].

Figure 18 – DSC/TGA analysis of MK-I and MK-B.



3.2.6.2 Paste characterization

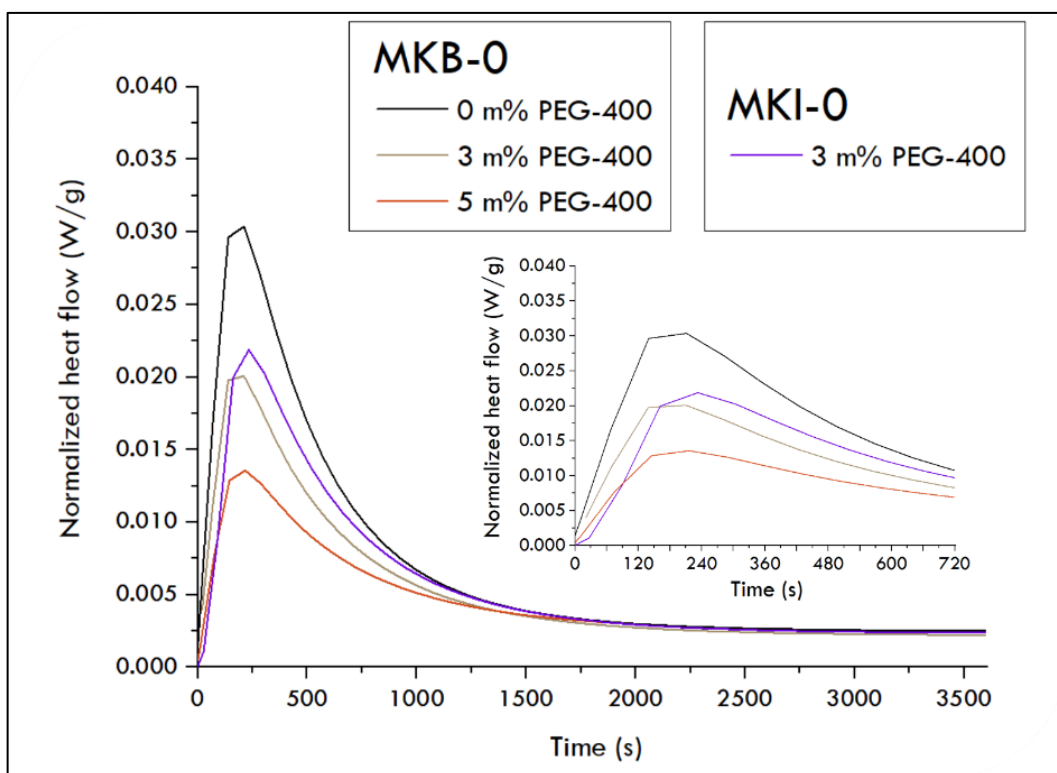
Several studies by different authors [63, 121, 130, 131] have explored the use of polyethylene glycol (PEG) with varying molecular weights as a rheology additive. PEG, a water-soluble polymer, is well-known for enhancing the self-curing properties of concrete, reducing water evaporation, improving water retention, and preventing early-age cracking [132]. The specific mechanism through which PEG enhances the rheological characteristics of geopolymer pastes for extrusion has not yet been reported. With other materials as ceramic mass, PEG is employed as a water retention agent and is used as a plasticizer.

Notably, when PEG-400 was incorporated at a concentration of 5 wt%, the normalized heat flow peak was observed to be less than half of that in pastes without the additive. However, it is essential to highlight that practical printing tests conducted with 5% PEG-400 were unsuccessful, as the printing process proved to be unstable. On the other hand, when 3 wt% PEG-400 was employed in both MKB-0 and MKI-0 pastes, the normalized heat flow values remained similar, and the practical printability had acceptable results.

As mentioned before, it is important to note that the first heat flow peak occurs within 10 min. This holds for all paste compositions, as they all reach their peaks within this timeframe. It's worth mentioning that a second peak was not observed because the test lasted for a full 60 min and that MKI-0 presents a larger area under the curve, meaning it has a higher reaction rate.

The introduction of PEG-400 leads to a reduction in the initial heat flow peak, subsequently decreasing the reaction rate, which is directly linked to an increase in the reaction extent, thus extending the duration for which the paste remains workable – even if not noticeable in Figure 19 due to the lack of the second peak. In simpler terms, the additive provides a longer timeframe for printing before the paste reaches a point of excessive viscosity, rendering it unsuitable for extrusion through the 0.84 mm nozzle.

Figure 19 - Isothermal calorimetry results for MKB-0 and MKI-O pastes with PEG-400.



The rheological characteristics of MKI-0 and MKB-0 were evaluated using the testing procedure depicted in Figure 15. The key properties crucial for the printability of inks intended for extrusion/printing include static and dynamic yield stress, as well as plastic viscosity. These properties collectively play a main role in buildability.

The testing protocol is continually repeated 5 times, each repetition will be here called a “run”, and each step is analyzed separately without ignoring the pre-shearing history induced by the other steps.

From the data obtained in Step 1, both the static and dynamic yield stresses can be derived. In Figure 20 and Figure 21, one can observe a discernible pattern in the evolution of the yield stress for MKB-0 and MKI-0 after each run, despite the non-constant nature of the increase in these values – as compiled in Figure 23 for both pastes.

Figure 20 - Step 1 of the rheology testing protocol applied to MKB-0.

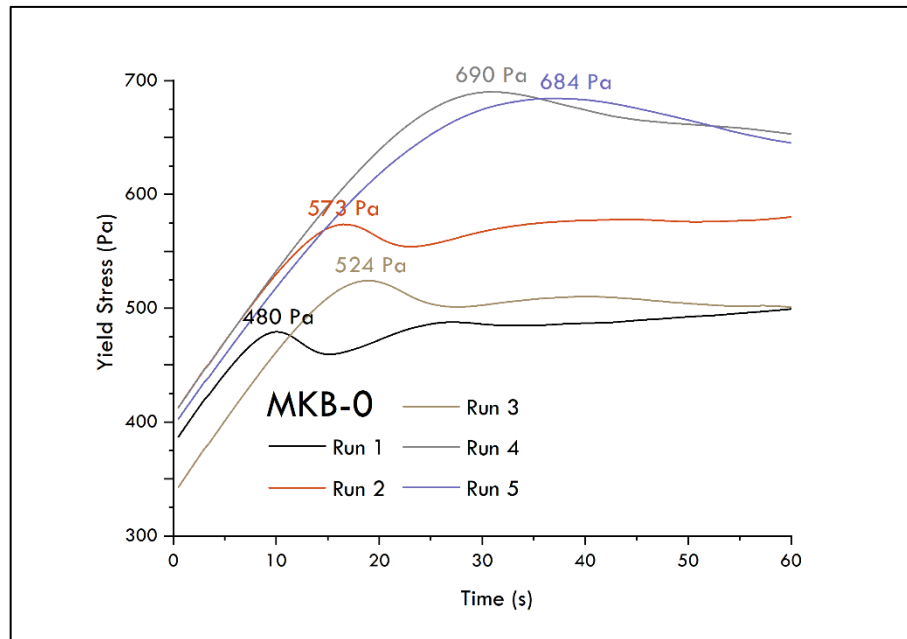
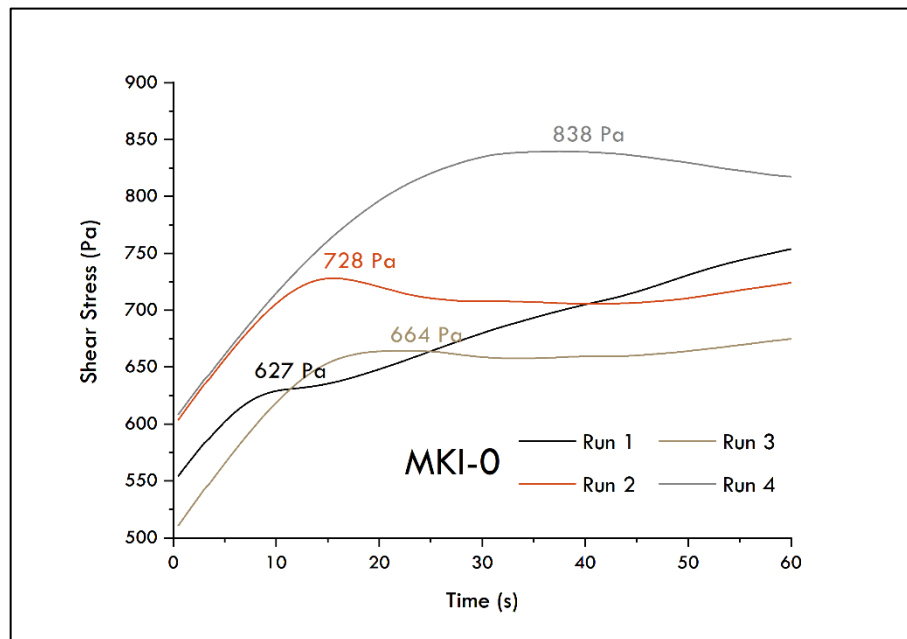


Figure 21 - Step 1 of the rheology testing protocol applied to MKI-0.



It should be noted in Figure 21 that Run 5 was excluded from MKI-0 results due to the impossibility of the equipment to carry on the measurement after the paste reached very high viscosity values.

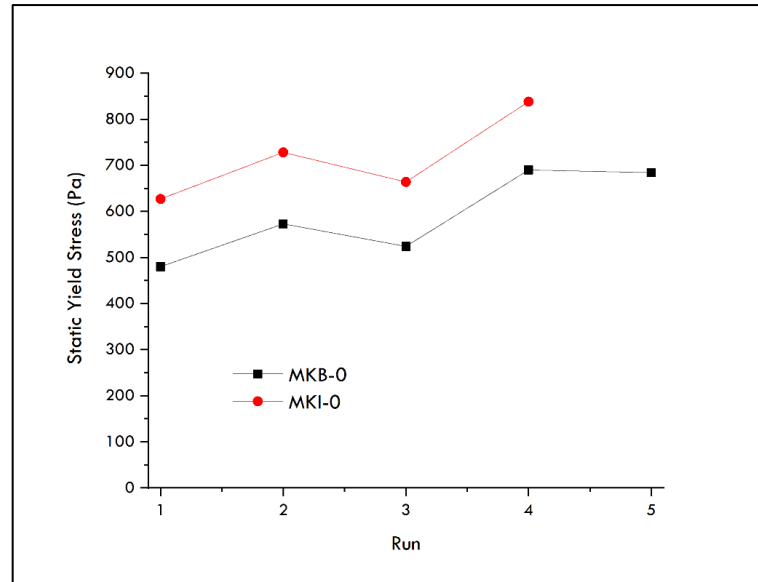
Both the gel development and the pre-shearing history must be considered when analyzing the results. In Step 3, which precedes Step 1 after the first Run, the paste is subjected to a shear rate of 0.01 s^{-1} for 9 min. As depicted in Figure 21 and

Figure 22, the shear stress does not remain constant once it reaches the static yield stress level, meaning that the shear rate is not sufficiently high to avoid gelation.

As seen in the isothermal calorimetry results, there is not a second heat flow peak within the timeframe of ~60 min and the development of Gel 2 polycondensation is limited. Thus, the results are most probably related to the first stages of geopolymerization.

The structural build-up that occurred in Step 3 is broken by the high shear rate at the beginning of Step 1. This condition simulates the material's condition before, during, and after printing. Therefore, the difference between static yield stresses in each Run is also a measure of the material's thixotropy.

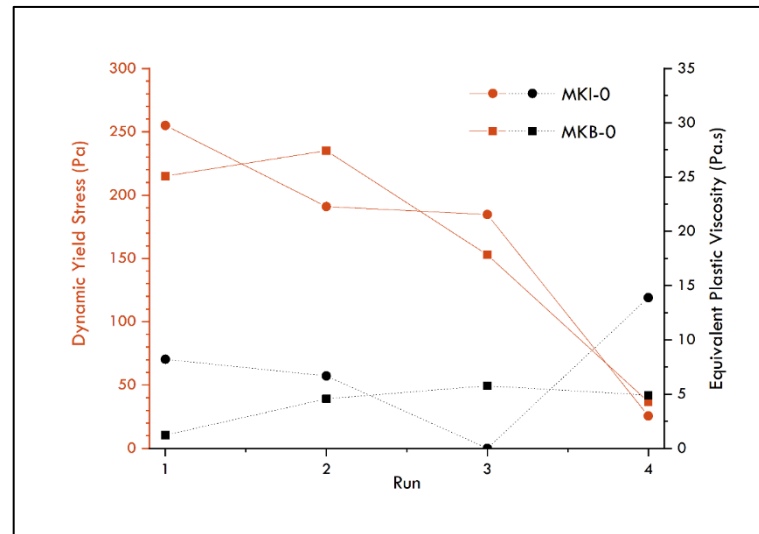
Figure 22 - Static yield stress for MKB-0 and MKI-0 in each Step 1 run.



In Ordinary Portland Cement concretes, there is a common assumption that a high shear rate erases all the shearing history, bringing the material to a reference state [136]. The destruction of the structured network that leads to the geopolymers' hardening is also reflected in the decrease of dynamic yield stress after applying a high shear rate [123]. This was also observed in both MKB-0 and MKI-0 pastes.

In Step 2, the dynamic yield stress and plastic viscosity values are obtained by fitting the Herschel-Bulkley equation to the descent part of the ramp. The results are seen in Figure 23. After the brief structural build-up occurred in Step 1, the paste is subject to 100 s^{-1} and then to an up-and-down ramp from 0 to 100 s^{-1} for 180 s.

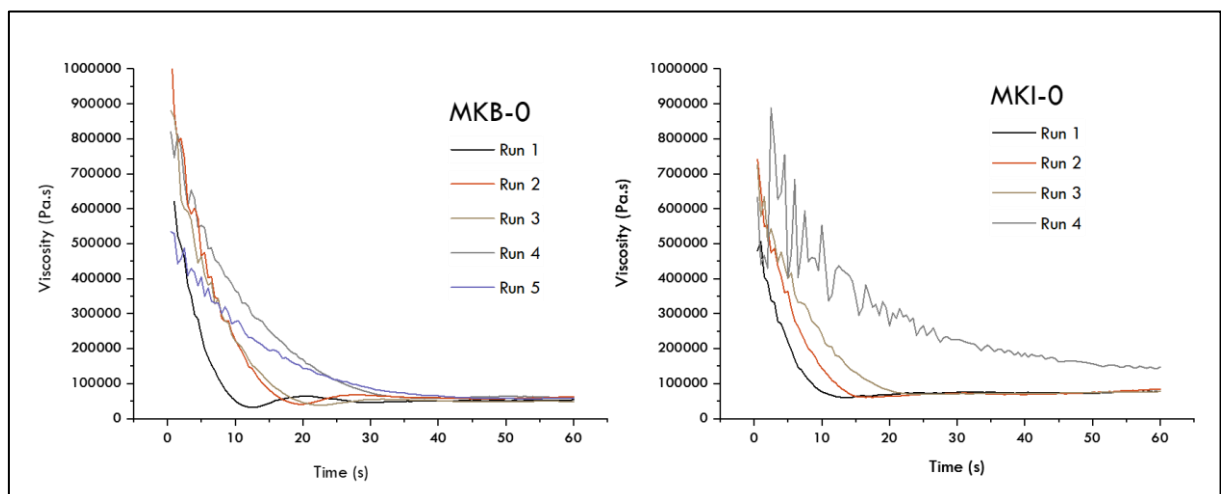
Figure 23 - Dynamic yield stress and equivalent plastic viscosity as derived from Step 2.



The hardening of the geopolymer mixture increases over time (Figure 9). The dynamic yield stress continuously decreases in each run due to the breakage of the pastes' structure, which at each run requires more stress as seen in Step 1 results.

As the Gel forms, the network of gel domains plays a major role in the material's rheology. That is reflected in the plastic viscosity values (Figure 23) from the down ramp in Step 2. MKB-0 presents a consistent behavior, while MKI-0 values deviate without any trend. Evidence of flocculation is also found in Step 1, under constant low-shear stress, through the variation of the apparent viscosity shown in Figure 24.

Figure 24 - Apparent viscosity of MKB-0 (left) and MKI-0 under constant shear rate (0.01 s^{-1}). In the fourth run, viscosity values vary drastically for MKI-0 as the paste presents a higher reaction rate.



The metakaolin MKI has a narrower particle size distribution and a smaller average particle size. This characteristic leads to higher water requirements and higher reactivity [137]. Incorporating MKI into the mixture results in a shorter open-time window and reduced workability due to flocculation, as seen in Figure 24. Its smaller average particle size also leads to higher static yield stress values - Figure 22 – as expected [135]. MKI-0 pastes' plastic viscosity kept decreasing until the third run and increased drastically to the fourth run, indicating that the pre-shearing was insufficient to hold the gelation. Since MKB-0 has a slower reaction rate, the same behavior is not observed for it.

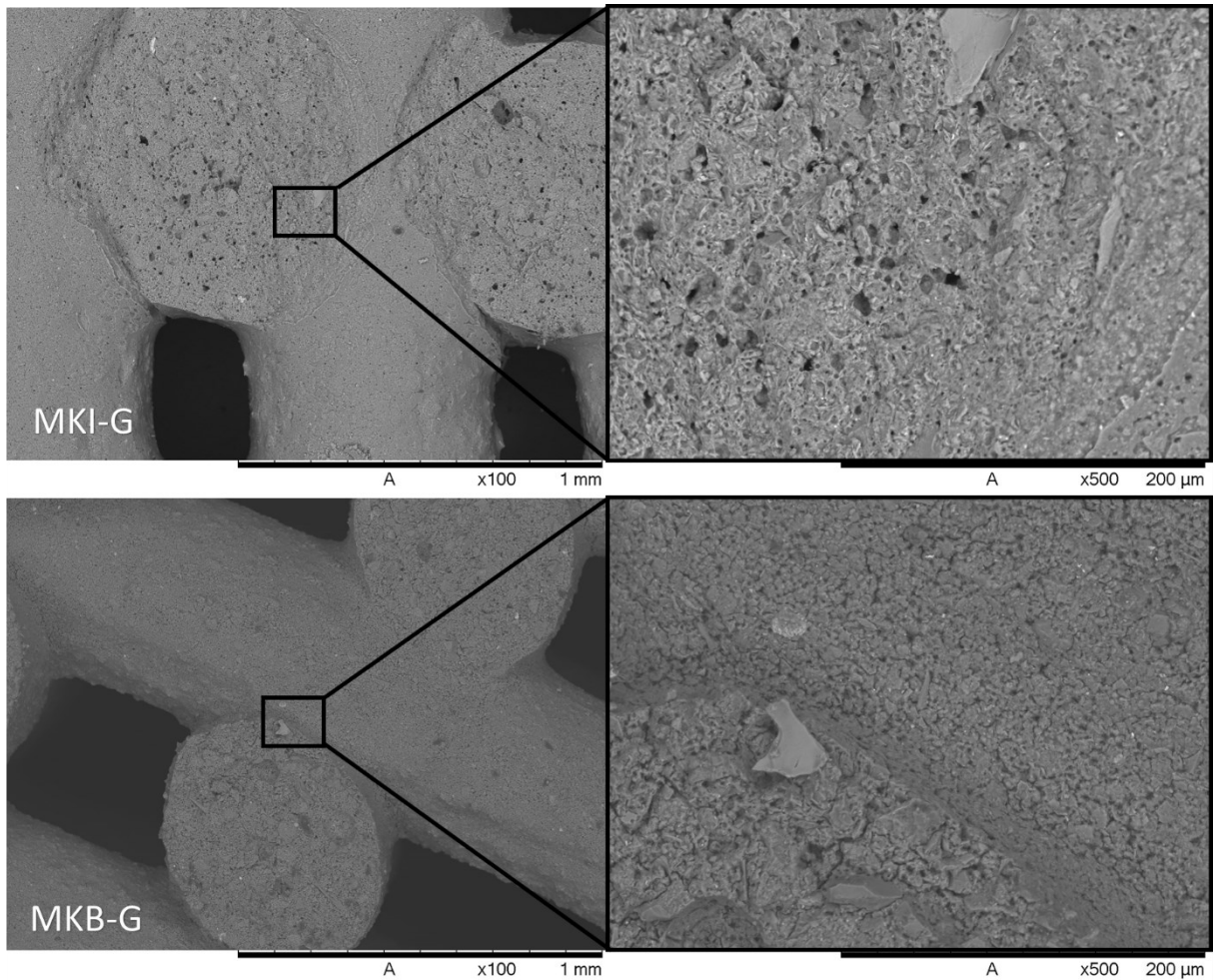
From the rheological measurements and practical tests, it can be concluded that MKB-0 is a more stable ink since it presents similar buildability and longer open-time than MKI-0.

3.2.6.3 Monolith characterization

The ambient-conditions cured and washed 3D-printed monoliths were named MKB-G and MKI-G. They were analyzed by SEM coupled with EDS to confirm the layer adhesion and strut shape and quality.

MKI-G and MKB-G monoliths were cut in half and the longitudinal axe was analyzed in SEM image (Figure 25). The struts present an ellipsoid shape with an average length of $171 \pm 3 \mu\text{m}$ in the longer axe and $132 \pm 4 \mu\text{m}$ in the shorter axe for 3 measurements in the MKB-G sample. This was attributed to a defect in the plastic nozzle. A good match between the layers is observed, meaning that the viscosity of the lower layer was low enough to interact with the upper layer and high enough to retain the strut's shape.

Figure 25 - SEM images of MKI-G and MKB-G monolith. Detail: intrinsic porosity of the geopolymer matrix and interface of struts.



The monoliths presented higher porosity than the designed value of 70%. This was expected since the designed value is based only on the CAD model. It is noticeable in

Figure 25 that both samples present intrinsic porosity. The specific surface area (BET), the total porosity, and true densities are presented in Table 8.

Table 8 - 3D-printed monoliths MKI-G and MKB-G specific surface area, total porosity, and true density.

Sample	Specific surface area (m ² /g)	Total porosity (%)	True density (g/cm ³)
MKI-G	27.86	71 ± 3	2.87
MKB-G	31.18	74 ± 2	2.89

The values presented in Table 8 should be interpreted with consideration for the margin of error associated with the measurements. For instance, the specific surface area determined through single-point BET testing can exhibit deviations of 2 to 3 points according to preliminary comparisons made obtained by the research group. The standard deviation observed in total porosity aligns both values within each other's range. However, it is essential to note that the true density, as obtained via gas pycnometer measurements, typically exhibits errors no greater than 0.1%. Nevertheless, it would be inappropriate to conclude that MKB-G possesses a denser matrix than MKI-G based on the true density measurement alone. True density is primarily a reflection of the density of the grounded powder rather than the monolith structure itself.

In contrast to previous studies, it's worth highlighting that the specific surface areas observed for both samples in our work are notably higher than those reported by Luukkonen et al. ($6 \text{ m}^2/\text{g}$) [63] and Botti et al. (ranging from 5.9 to $11.3 \text{ m}^2/\text{g}$) [84]. Both prior studies utilized 3D-printed monoliths as filters for water treatment and as heterogeneous catalysts for biodiesel production, respectively, incorporating geopolymer powder as a filler in their ink formulations. In contrast, the monoliths MKB-0 and MKI-0 do not incorporate any fillers, which makes the findings particularly noteworthy as they indicate the substantial surface area achieved without the use of additional materials.

3.3 Conclusions

This chapter addresses the challenging process of 3D-printing geopolymers by Direct Ink Writing. The research includes a comprehensive characterization process to elucidate the impact of two distinct types of Metakaolin, possessing varied compositional and crystallographic properties, on the rheological properties of the geopolymer pastes. Subsequently, monoliths with open porosity were 3D printed, and their characteristics were thoroughly examined in terms of porosity, specific surface area, and true density.

The findings indicate that both the average particle size and distribution significantly influence rheological properties and the temporal window available for the printing process. Isothermal calorimetry results demonstrate that the incorporation of a rheology additive, specifically PEG-400, leads to a reduction in the reaction rate, thereby prolonging the working time during the printing procedure.

The suggested rheology testing protocol facilitates the evaluation of structural build-up over time, revealing that a reduction in both average particle size and distribution results in an elevated initial static yield stress and a more pronounced decay of dynamic yield stress following each repetition of the testing for the same paste, a strong indicative of faster structural build up and therefore elevated reactivity.

Two types of commercial metakaolin, MKB and MKI, have been tested. The former exhibits a broader particle size distribution, a larger average particle size, and higher quantities of elements other than Al and Si. The characteristics of MKI poses difficulties to printability, limiting its use to 25 wt% in the paste. MKB characteristics are more adequate for adequate printability – even so, the paste containing MKI was named MKI-0.

Still regarding printability, the maximum printable static yield stress is below 900 MPa with the tested setup of printer and nozzle diameter. The higher the static yield stress, the lower the dynamic yield stress due to the breakage of the reacted gel.

The total porosity of the 3D-printed monoliths slightly exceeded the initially designed due to their intrinsic porosity. The monoliths were named MKB-G and MKI-G. Notably, without the incorporation of any additives intended to enhance specific surface area, the printed material exhibited relatively high specific surface area values compared to those reported in the existing literature - $\sim 27 \text{ m}^2/\text{g}$ for MKI-G and $\sim 31 \text{ m}^2/\text{g}$ for MKB-G. This favorable property makes the material well-suited for its intended application in catalysis.

4 Thermal behavior of 3D-printed geopolymer monoliths³

Geopolymer are known for their high-temperature resistance [1]. In terms of their thermal behavior, Duan et al. [138] have reported that the microstructures of geopolymers become denser as the temperature increases, particularly up to 400°C. This densification is likely a result of additional sintering and geopolymerization processes involving the raw materials used [138].

Similarly, Kantarci *et al.* [139] have noted an increase in compressive strength up to 300°C, regardless of the type of additive employed. However, temperatures exceeding 300°C can lead to a decrease in compressive strength values. They argue that the rise in compressive strength is attributed to the promotion of polycondensation reactions among the tetrahedral aluminosilicate gels. Conversely, significant drops in compressive strength at higher temperatures can be attributed to the formation of micro-cracks in the interface regions and thermal incompatibility between the geopolymer matrix and the aggregates.

Furthermore, the authors have successfully explored the incorporation of additives such as nano-silica and micro-silica to enhance the compressive strength of geopolymers when exposed to elevated temperatures. The results of their research demonstrate that these additives can interrupt crack formation and facilitate a binding effect between sliding surfaces [139].

Hossan et al. [140] corroborate these findings, providing an explanation for the remarkable thermal stability and minimal structural degradation of the geopolymer up to temperatures ranging from 700 to 800°C. They attribute this exceptional performance to the inherently inorganic structure of the resulting product. Moreover, the same authors assessed geopolymer pastes incorporating activators based on potassium and sodium. Notably, potassium geopolymers exhibited higher residual compressive strengths across the tested temperatures ranges. This increased strength is linked to the observation that potassium geopolymers had fewer microcracks when compared to their sodium-based counterparts [140].

In addition to their high-temperature resistance, geopolymers are known for their adsorption capabilities, facilitated by a substantial surface area achieved through

³ To be submitted as "High-temperature catalysis with novel 3D-printed geopolymer monoliths" for international peer-reviewed journal.

diverse procedural approaches [5], [8], [10], alongside their highly adaptable processing potential. Yet, the development of catalytic geopolymers intended for high-temperature processes remains at a nascent stage. As far as the current knowledge extends, two published works are investigating this facet of geopolymers. The first one by Candamano et al. [17] assessed the viability of an active nickel phase supported within geopolymeric samples for employment in ethanol reforming reactions. The second, from Botti et al. [98], evaluated sodium and potassium geopolymer as heterogeneous catalysts for biodiesel processing at temperatures ranging from 300 to 700 °C. None have used geopolymer monoliths at high temperatures. Even though promising, there is a lack of literature employing geopolymers for high-temperature catalytic processes.

In the previous Section, monoliths MKB-G and MKI-G have been presented and discussed. Here, the viability of geopolymers as catalysts for high-temperature catalytic methane steam reforming.

4.1.1 Methodology

Samples of geopolymer monoliths (MKB-G and MKI-G) were heated up to 800 °C (5h, 10 °C/min). This procedure was called calcination. The calcined samples are supposed to be used as supports for Nickel, as will be presented in Section 3.4, therefore they were named MKB-NiO and MKI-NiO.

Mineralogical changes after calcination were investigated by X-ray diffraction (XRD; Rigaku MiniFlex600) - Cu K α radiation, from 5 to 80°, step of 0.02° and 0.5 s/step. Diffraction patterns were analyzed by X'pert Highscore Plus and Match3! software using the ICDD database (International Center of Diffraction Data, PDF 4).

Dilatometry tests (Expert System Solution Misura ODHT) were performed with solid and powder samples. With these tests, it was possible to understand the behavior of the samples with increasing temperature. Solid samples were tested with the formulations MKB-NiO and MKI-NiO up to 800 °C at a heating rate of 10 °C/min. With the MKB-G and MKI-G samples, tests were carried out with the powder at temperatures of up to 1200 °C and a heating rate of 10 °C/min.

Changes in true density and porosity were evaluated by gas pycnometry using grounded samples (<75 μ m) and total porosities were obtained using the relation among geometric measurements and weights with true densities in accordance with

the ASTM C373 [134] standard test method. Geometric measurements and weights were obtained with the caliper and analytical balance in oven-dried samples.

The compressive strength of the 3D-printed monoliths before and after thermal treatment was measured in a universal testing machine (INSTRON 5569) with a loading rate of 0.50 MPa/s according to ASTM C-1231 [141].

Specific surface area was calculated from N₂ adsorption-desorption isotherms and the Brunauer–Emmett–Teller (BET) theory. The measurements were carried out in a single-point ChemBET Pulsar TPR/TPD Automated Chemisorption Flow Analyzer (Quantachrome Instruments).

4.1.2 Results and discussion

In Figure 26 and Figure 27, the raw materials MK-B and MK-I are compared to the geopolymer before (MKB-G and MKI-G) and after (MKB-NiO and MKI-NiO) calcination.

Figure 26 - XRD profiles of MK-B (metakaolin), MKB-G (geopolymer) and MKB-NiO (calcined monolith).

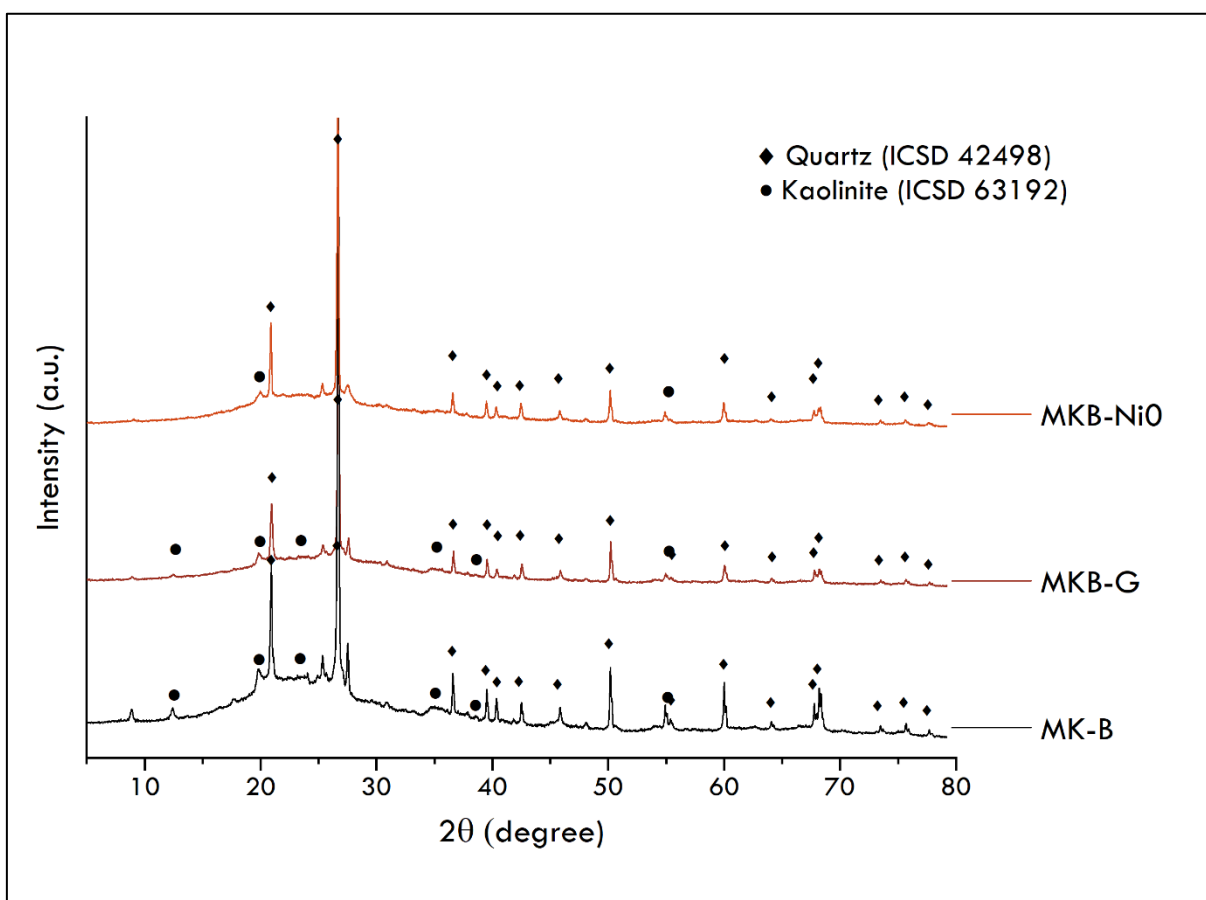
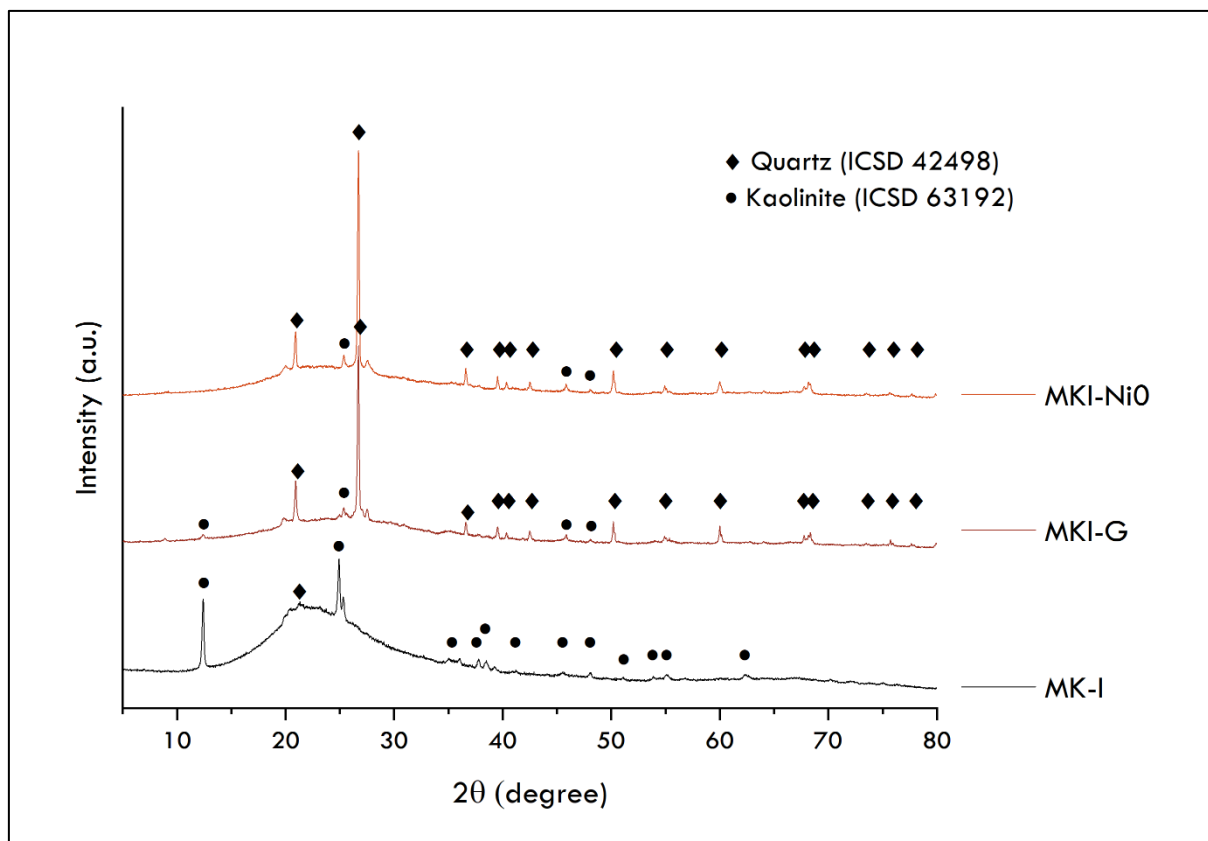


Figure 27 - XRD profiles of MK-I (metakaolin), MKI-G (geopolymer), and MKI-NiO (calcined monolith).



The most notable changes in the crystallographic profiles after geopolymerization and calcination are the disappearance of peaks associated with kaolinite and the reduction of the amorphous halo from 15° to 45° (2θ angles) in both samples, as expected.

After the thermal treatment, the geopolymer acquires crystallographic stability, with quartz and some minor peaks of kaolinite being identifiable. While the amorphous content was not quantified, it also appears to be preserved.

Figure 28, the shrinkage at 800°C is relatively modest for both geopolymer formulations. However, as the temperature reaches 1100 °C, MKB-G experiences an approximate 20% shrinkage, while MKI-G contracts by approximately 25%. This suggests that subjecting the samples to 5 h at 800 °C would likely induce further shrinkage beyond the levels observed in Figure 29 for the same temperature. Interestingly, when thinking in high-temperature applications, by exposing the samples once more to 800°C after calcination, they exhibit minimal expansion.

Figure 28 – Shrinkage of non-thermally treated geopolymer powder samples (MKB-G and MKI-G) and expansion of calcined monolith samples (MKB-NiO and MKI-NiO)

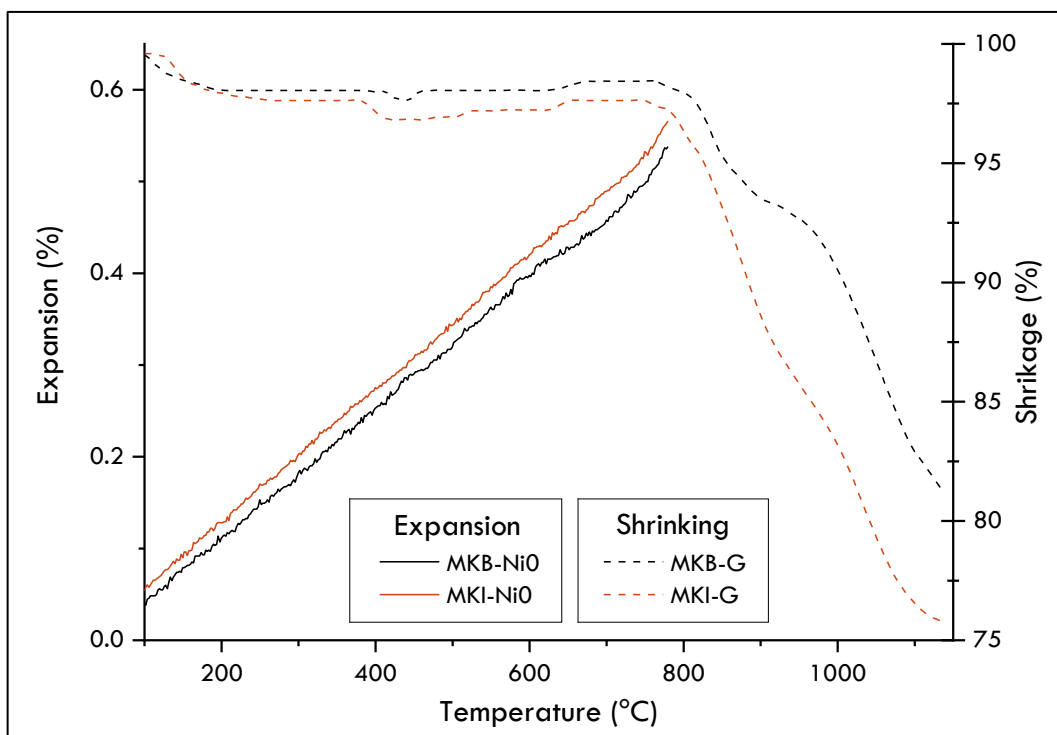
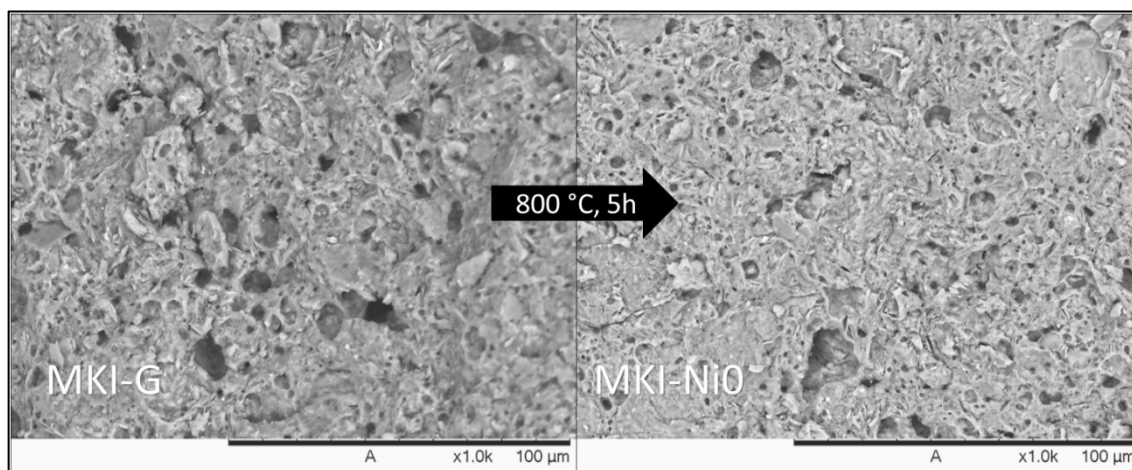


Table 9 - Total porosity and specific surface area of the samples before and after calcination.

Sample	Total porosity (monolith - %)	Specific surface area (grounded samples - m ² /g)
MKB-G	74 ± 2	31.18
MKB-NiO	70 ± 2	6.93
MKI-G	71 ± 3	27.86
MKI-NiO	68 ± 2	5.28

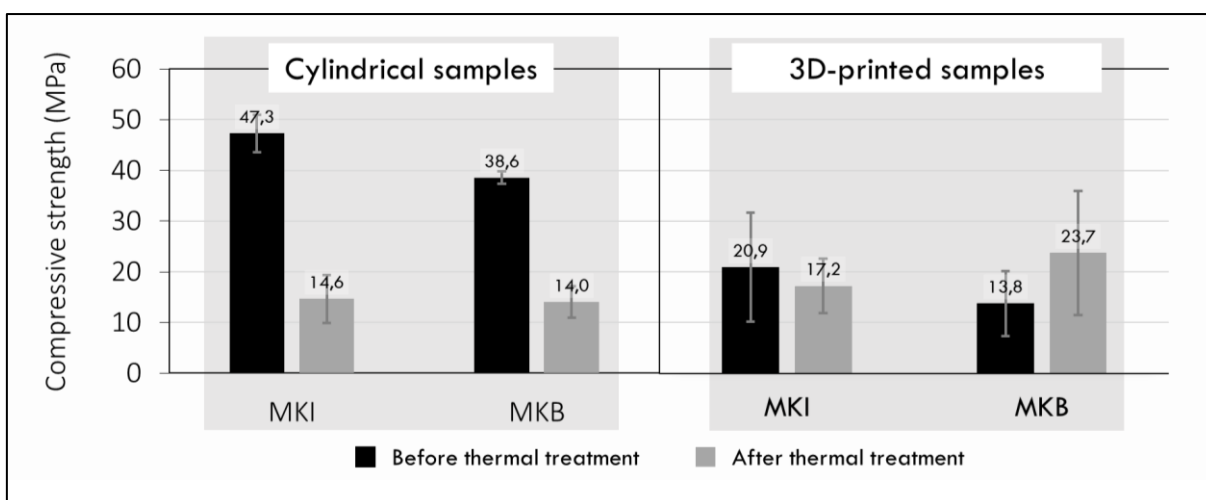
Figure 29 - SEM images of MKI monolith before and after calcination.



Due to shrinkage, the specific surface area decreases from 74% to 70% in MKB samples and from 71% to 68% in MKI. This is reflected in the total porosity, which decreases for both samples. Shrinkage, however, does not play a major role in the compressive strength of the 3D-printed samples, as shown in Figure 30. The thermal treatment strongly influences cylindrical samples obtained through traditional geopolymer production methods since the solid sample tends to crack during the shrinking. For the additively manufactured samples, it appears that design and printing quality play a far more significant role than the consequences of thermal treatment noticed in the traditional cylindrical solid samples without designed porosity.

Despite the presence of longitudinal and transversal macro pores in the samples, which reduce their overall mechanical properties when compared to traditional monoliths, they still exhibit commendable compressive strength in comparison to most reported ceramic monoliths. For instance, traditional alumina foams with an apparent porosity close to 85% and sintered at 1560 °C achieve maximum compressive strengths lower than 7 MPa [136], while 3D-printed cordierite honeycomb structures, sintered at 1390 °C, exhibit compressive strengths ranging from 20 to 5 MPa, depending on the cell geometry [137]. It is important to note, however, that the mechanical properties of monoliths used in catalysis are not evaluated in the majority of published works.

Figure 30 - Compressive strength of cylindrical and 3D-printed samples before and after thermal treatment (800 °C - 5h).



One possible outcome of shrinkage during calcination would be that it limits the potential for catalyst dispersion. However, the porosity values remain close to the designed while the specific surface area is close to the ones found by the groups of

Luukkonen et al. [63] ($6 \text{ m}^2/\text{g}$) and Botti et al. [84] (ranging from 5.9 to $11.3 \text{ m}^2/\text{g}$) and successfully employed for adsorption and catalysis respectively.

These findings strongly support the feasibility of utilizing 3D-printed geopolymer monoliths as catalysts in high-temperature processes. These monoliths offer a substantial specific surface area suitable for various applications and exhibit minimal thermal expansion following calcination. These characteristics make them a promising choice for catalytic purposes.

In the next Section, the Methane Steam Reforming (MSR) for hydrogen production is adopted as the testing procedure to assess the geopolymer monoliths viability for a high-temperature process.

4.2 *Application of geopolymer-supported catalysts in methane steam reforming*

In the second chapter of this Thesis, a comprehensive overview of geopolymers for catalytic applications was provided. Their inherent composition, containing alkali elements and minor quantities of different metals, was highlighted as a promising characteristic that makes them suitable candidates for use as supports for active metals in the steam reforming of hydrocarbons. In Chapter 3, the production of 3D-printed geopolymer monoliths was explored, from processing to the resulting physical properties. Now, these 3D-printed geopolymer monoliths are effectively tested as supports for Ni catalysts for methane steam reforming.

4.2.1 *Catalysis of Methane Steam Reforming*

Catalytic processes are considered the driving force of the chemical industry, and more than 80% of chemical products have some catalytic process in their production. Most of them use heterogeneous catalysts, where the catalyst is in a physical phase, e.g. solid, different from the product to be processed, liquid or gaseous. Heterogeneous catalysts usually consist of an active component supported over a substrate, in a composite phase or as the main solid phase. Their processing routes vary from simple impregnation of noble and non-noble transition metals onto cheap high-surface-area supports to nanostructured materials [142]. Operation temperatures are usually in the range of 100 to 600 °C, and there may still be some processes that require temperatures as high as 800 °C, such as Methane Steam Reforming (MSR) for hydrogen production [143], [144].

In the last decade, the interest in hydrogen as an alternative to the energy decarbonization economy has grown exponentially [145]. Even though most hydrogen still produced worldwide from non-renewable sources [146], it is considered a promising clean energy vector for the future, with greater calorific value and a lower carbon footprint if produced from renewable resources [147]. Hydrogen gas can be used as fuel in internal combustion engines [148], gas turbines [149], and fuel cells [147] with high efficiency and ultra-low local carbon footprint since the final product is water [150].

There are storage safety drawbacks that limit the Hydrogen-related infrastructure. To overcome this challenge, hydrogen may be stored in a Power-to-Gas strategy, chemically or physiochemically in various solid or liquid compounds, and

converted *in situ* during application. [150], [151]. Catalysts play a crucial role in hydrogen production. The most common are transition metals such as Cu, Co, Ni, and Fe for their low cost and availability [146].

According to the International Renewable Energy Agency's classification, the sustainability and environmental friendliness of hydrogen production are contingent upon the source from which it is derived. The predominant method of hydrogen production involves the steam reforming of natural gas, categorizing it as "gray hydrogen" due to its origin from a non-renewable source. When the resultant CO and CO₂ are captured and only H₂ is exploited, the production is classified as "blue", even though with strong disagreements among environmentalists [152].

Many other forms have been explored in recent years to reach a cleaner production of hydrogen from methane, but these alternatives are still only applied at the research level [153].

The non-catalytic thermal cracking of methane requires temperatures higher than 1200 °C due to the strong C-H bonds. However, methane can be decomposed at lower temperatures can be reached by using a catalyst [153]. Methane steam reforming is a well-established and economically viable process that operates at high temperatures involving an endothermic reaction. This process generates Syngas (a mixture of H₂ and CO), which finds utility in various applications such as ammonia synthesis, serving as an intermediate product for other chemical reactions, or as a fuel source for fuel cells [146].

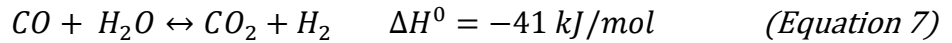
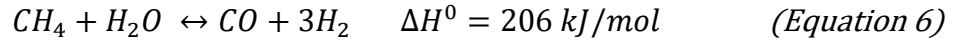
Although not seen as a "green" alternative, since natural gas is a non-renewable feedstock and CO and CO₂ are byproducts of the reaction, it has found support on incipient technologies based on biomass to become a more environmentally friendly process in the coming years [150].

It's important to emphasize that in this Section, the focus is not on discussing or questioning the sustainability of Methane Steam Reforming itself. Instead, the choice of this process is driven by the high operational temperatures it entails. The primary objective is to assess the potential of geopolymer monoliths as alternative catalytic materials capable of withstanding the rigorous demands of such high-temperature operating conditions.

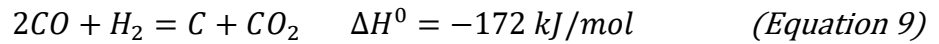
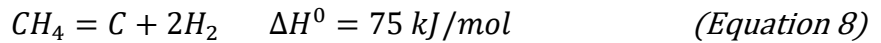
However, it is worth noting that methane can be sourced from biomass using various thermochemical and biological processes. While this technology is still in its early stages, the production of hydrogen from biomass is regarded as a highly efficient

and clean alternative for large-scale energy production, offering a sustainable and eco-friendly alternative to fossil fuels [150].

The main chemical reactions in Methane Steam Reforming are the reforming (Equation 6) and the water-gas shift (WGS) Equation 7.



As an endothermic process, high reaction temperatures, over 700 °C, are required to achieve high methane conversion [154]. Besides the two main reactions, many others may occur simultaneously, some of which lead to coke generation – carbon deposition - on the catalyst surface, and the main two paths are given by Equations 8 and 9 [155].



There is a high thermodynamic potential for coke formation on the catalyst surface, especially through the mechanism described by Equation 8, as MSR is performed at high temperatures [156]. As metals, usually nickel, are employed as catalysts, there is also a high probability of metal sintering with the process' high temperatures or even the formation of nickel carbide [157]. Independently of which mechanism takes place, all of them will lead to the deactivation of the catalyst by decreasing the available active sites [39], [158].

When designing macro-structured catalyst supports for MSR, the requirements are effective heat and mass transfer, low-pressure drop, and good mechanical strength. Meaning that the main physical characteristic of importance is the channel size for the passage of reactants and products [159].

Considerable research efforts have been dedicated to the advancement of highly thermally conductive materials for hydrocarbon steam reforming. This focus on enhancing heat transfer properties has been driven by the aim to improve the overall efficiency of the process and to mitigate or minimize the formation of coke, a carbonaceous byproduct. In parallel, research has also explored the use of bi-metallic catalysts to optimize process efficiency [155], [160].

The group of Ashraf et al. [161] have compared the performance of Ru/La-Al₂O₃ monoliths in MSR with monoliths of two different cells per square inch (CPSI) –

100 and 170 cpsi. They concluded that the geometric parameters are closely related to the catalyst loading – according to their results, higher cell densities allow for thinner catalytic layers and the highest methane conversion [161]. More works have explored experimental and numerical methods for methane conversion intensification [154], [162], [163].

However, it's worth to note that relatively less attention has been given to the development of support materials with the specific capability to prevent coke formation. This aspect has been underscored by the findings of Meloni et al. [144] in their review on Ni-based catalysts for Methane Steam Reforming (MSR). Addressing this gap in research is crucial for advancing the efficiency and sustainability of the MSR process.

As seen in Chapter 2, alkali and alkali earth metals are recognized as promoters that enhance the reactivity of steam or CO₂ with carbon, thereby improving the catalyst's resistance to coke formation. Additionally, these metals play a role in strengthening the interaction between nickel and the catalyst support, which in turn helps to minimize nickel sintering and further enhances the catalyst's resistance to coke formation [34], [155].

These previous works did not utilize 3D-printed monoliths with pores in both the horizontal and vertical axes, like the ones adopted for the current thesis as described in Section 3.2.2. As a result, the extrapolation of results from other studies to the unique 3D-printed geopolymer monoliths examined in this thesis remains challenging due to the specific characteristics of these structures.

Surprisingly, there has been limited research into producing geopolymer catalysts for reforming reactions, given the compelling factors supporting their potential. Geopolymers offer several advantages: they are relatively cost-effective, their processing is straightforward akin to cement, their primary raw materials are abundant globally, and they inherently contain alkali and other metals in their composition that may improve the promoters' efficiency and durability. These attributes make geopolymers a promising candidate for catalyst development in steam reforming and related reactions. To the best of the author's knowledge, only Candamano et. al. [17] have explored this latent potential, even if their team limited the study to powdered geopolymer in a packed bed configuration [17]. Further exploration of this research avenue could unlock valuable insights and innovations in the field.

It is crucial to emphasize that the primary objective of this work does not involve optimizing design parameters, catalytic loading, the quality of Nickel deposition, or methane reforming efficiency. Instead, the main goal is to assess the suitability of geopolymers for high-temperature catalytic processes, particularly MSR. The focus lies in evaluating the feasibility and overall performance of geopolymer-based materials in this challenging application. Once it is established that geopolymers are indeed viable as catalytic materials, further in-depth research on the topic can be pursued.

In the upcoming sections, a structured 3D-printed geopolymer monolith is employed as a Ni-based catalyst for the first time. The pioneering approach holds the potential to open new possibilities for geopolymers in catalytic applications.

4.2.2 *Materials*

The materials employed in the production of the 3D-printed geopolymer monoliths have been described in Section 3.2.1. To obtain Ni-based geopolymer catalysts, Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Neon, 99 wt%) was used for geopolymer impregnation.

4.2.3 *Catalytic geopolymer preparation*

The 3D-printed geopolymer monoliths were produced according to the described in Section 3.2.2. After printed, cured, and washed until reaching constant electrical conductivity and constant pH, the samples were heated up to 800 °C (5h, 10 °C/min) to remove impurities and residual water. The printed samples were afterward impregnated using an aqueous solution employing nickel nitrate hexadydrate and the amounts of salt (m_{sal} , nickel nitrate hexahydrate) were known according to Equation 10 [164], where $\%_{\text{met}}$ is the amount required of metal; m_{sup} is the mass of the catalytic support to be impregnated (g); MM_{sal} is the molar mass of salt (g/mol) and MM_{met} is the molar mass of metal (g/mol). As there is no wash coating layer, the value of m_{sal} is multiplied by 1.5 to ensure an effective impregnated mass close to the originally calculated value.

$$m_{\text{sal}} = \frac{\%_{\text{met}} \times m_{\text{sup}} \times \text{MM}_{\text{sal}}}{\text{MM}_{\text{met}} \times (100 - \%_{\text{met}})} \times 1.5 \quad (\text{Equation 10})$$

After impregnation, the catalysts are calcined once more at 800 °C (5 h, 10 °C/min) to remove nitrate and other impurities.

Duplicates of each formulation were evaluated at 800 and 900 °C. Each sample of a given formulation received a number from 1 to 4 to facilitate the reading and the discussion of the results. Duplicates of MKB-Ni20 samples were renamed as MKB1 and MKB2 for testing at 800 °C and as MKB3 and MKB4 for testing at 900 °C. Samples MKI-Ni20 followed the same logic.

4.2.4 *Catalytic geopolymers characterization*

The samples were characterized by SEM equipped with EDS and dedicated software (TM3030, Hitachi Ltd.). Mineralogical compositions were investigated by X-ray diffraction (XRD; MiniFlex600, Rigaku Corporation) - Cu K α radiation, from 5 to 80°, step of 0.02° and 0.5 s/step. Diffraction patterns were analyzed by X'pert Highscore Plus and Match3! Software using the ICDD database (International Center of Diffraction Data, PDF 4).

Specific surface area was automatically calculated from N₂ adsorption-desorption isotherms and based on the Brunauer–Emmett–Teller (BET) theory, according to the procedure descibre in details elsewhere [165]. Hydrogen temperature programmed reduction (H₂-TPR) was performed from ambient temperature to 1100 °C with a heating rate of 10 °C/min by using a reducing stream of 75 ml/min of 5% H₂/N₂. Both measurements were carried out and calculated by single-point ChemBET Pulsar TPR/TPD Automated Chemisorption Flow Analyzer (Anton Paar QuantaTec Inc.).

4.2.5 *Apparatus and procedures for methane steam reforming*

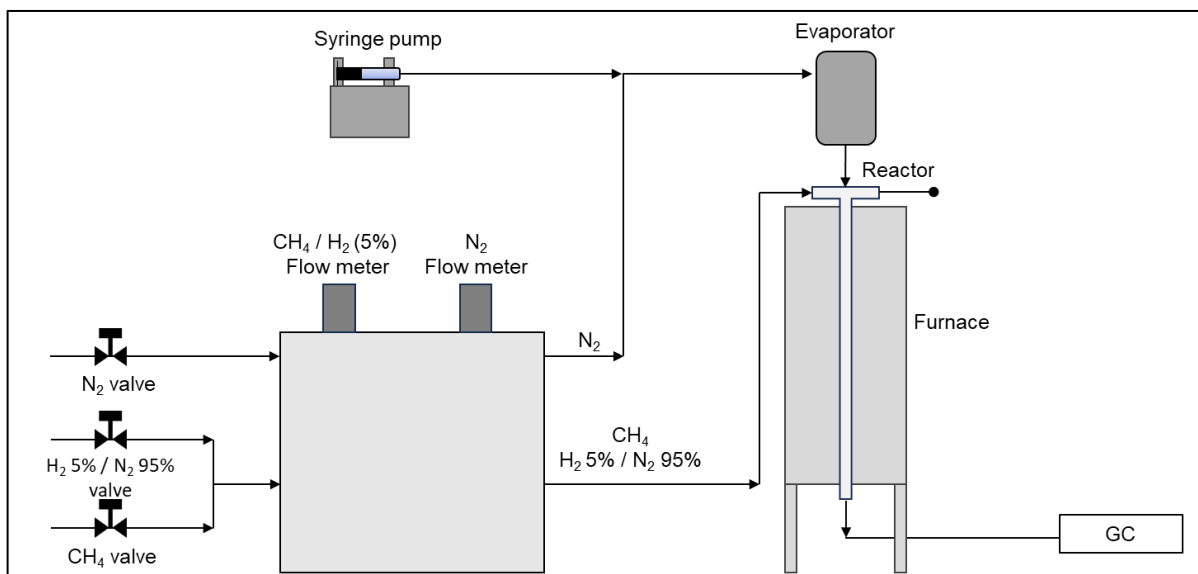
The thermal behavior and stability of the 3D-printed catalyst geopolymers was tested under Methane Steam Reforming (MSR) conditions at 800 and 900 °C with a steam/methane ratio of 3:1.

The experiments were conducted using a quartz tubular reactor, featuring an inner diameter of 16 mm and a length of 473 mm. Quartz wool as used to close the gap between the reactor walls and the sample, forcing the flow through the internal structure of the monolith. The reactor was positioned inside a temperature controlled furnace. Figure 31 provides a schematic representation of the experimental apparatus. Various components of the lab-scale system are interconnected using Teflon piping and secured with Swagelok-type locks. The different parts of the lab-scale plant are connected using Teflon piping and fastened by *Swagelok*-type locks.

The feed mixture consisted of N₂ (99,999%, pure) for reaction dilution, H₂ (diluted to 5 wt% in N₂ 99,999%, pure) for catalyst reduction, and CH₄ (99,99%, pure). Volumetric flow meters and needle valves were employed to regulate the flow rates of these gases. Additionally, a programmable syringe pump was utilized to introduce deionized H₂O into an evaporator, where N₂ served as the carrier gas for water vapor. The evaporator temperature is maintained at 105 °C and is regulated by a digital controller, with feedback provided by a thermocouple placed near the steam outlet.

The products generated in the reactor were analyzed by a Gas Chromatography device (GC), specifically a Clarus® 580 (PerkinElmer, Inc) equipped with a sampling loop of 2 mL, a thermal conductivity detector (TCD) and Flame ionization detector (FID). The columns Rt-U-BOND e Elite GC GS-Molesieve, 30 m long and 0.53 mm of internal diameter (by Restek), were used. Quantitative calibration was performed using samples from the species that were to be detected in the tests. Argon (99.999% pure) was used as the carrier gas.

Figure 31 – Schematic representation of a laboratory-scale MSR setup.



The activation of the catalyst is conducted in situ. The heating process involves raising the temperature from ambient conditions to the desired reaction temperature, either 800 or 900 °C, at a controlled heating rate of 10 °C per minute. During this heating phase, a flow of 100 ml/min of a 5% H₂/N₂ mixture is passed through the system. Once the target reaction temperature is reached, the flow of the activating gas is sustained for 1 h.

After the activation process, a flow of N_2 and water vapor is introduced for 20 min to thoroughly purge any residual activating gas from the system. Following this purging period, the introduction of CH_4 marks the initiation of the reaction.

The experimental parameters for samples of the designed dimensions presented in Section 3.2 are given in Table 10.

Table 10 - Samples and respective experimental parameters for Methane Steam Reforming tests.

Samples parameters		
Sample height (cm)	Sample diameter (cm)	Sample mass (g)
1.3	1.1	1.2
Experimental parameters		
Weight Hourly Space Velocity (WHSV)/h	Gas Hourly Space Velocity (GHSV)/h	Space velocity (NL/(h.g _{cat}))
20	62,225 – 68,024	17.8
Temperature (°C)	H ₂ O _{steam} : CH ₄	Residence time (ms)
800 - 900	3	58 (800 °C) – 53 (900 °C)

The parameters were set in intermediary values compiled by Meloni et al. [144] for catalysts supported on ceramic carriers and according to the capability of the experimental setup.

The initial gas sampling is obtained in the GC 10 min after the start of the reaction just to ensure that the reaction has started. It is assumed that the reaction rate and gas flow are still not stabilized at this point, hence the results of the first point are not presented. Subsequent data points are acquired following the time needed for the equipment to prepare itself for a new data point acquisition – usually a period ranging from 23 to 30 min. Five to six points are acquired for each sample, summing up approximately 2 h and a half of data acquisition.

The chromatography device presents the results in terms of product concentration in $\mu\text{mol/mol}$, based on the area under the curve of the sensor's response signal (μV) *versus* the retention time of the gas in the column(s). The conversion from the area under the curve ($\mu\text{V}\cdot\text{sec}$) to $\mu\text{mol/mol}$ is done through a calibration curve obtained from a standard gas.

According to the calibration curves used for the presented tests, the reason between $(\mu\text{V}\cdot\text{sec})/(\mu\text{mol}/\text{mol})$ for CH_4 is only 1.8% of that for CO_2 . In other words, whereas 76 $\mu\text{V}\cdot\text{sec}$ detected by the FID should represent 1 $\mu\text{mol}/\text{mol}$ of CO_2 , it is interpreted as 55.4 $\mu\text{mol}/\text{mol}$ of CH_4 by the TCD. Another way of looking at the data is to understand that 1 $\mu\text{mol}/\text{mol}$ of CH_4 is read as 1.38 $\mu\text{V}\cdot\text{sec}$ by the TCD.

The methane conversion rate (X_{CH_4}) is hereby presented as the minimum methane conversion and is calculated by Equation 11 and the hydrogen yield (Y_{H_2}) by Equation 12. All the values are in moles.

$$X_{\text{CH}_4} = \frac{n_{\text{CH}_4\text{in}} - n_{\text{CH}_4\text{out}}}{n_{\text{CH}_4\text{in}}} \times 100 \quad (\text{Equation 11})$$

$$Y_{\text{H}_2} = \frac{n_{\text{H}_2\text{out}}}{n_{\text{H}_2\text{out}} + n_{\text{CH}_4\text{out}} + n_{\text{COout}}} \times 100 \quad (\text{Equation 12})$$

For limitations of the GC system, the CO_2 concentration in the experiments were below the detection threshold, making its detection difficult under the conditions employed. Another essential observation to be made is that the detection threshold for CO was below 1900 $\mu\text{mol}/\text{mol}$. As a result, the calculated Hydrogen Yield (Y_{H_2}) is wrongfully increased when CO is not accounted for. With the observed limit detection of CO, the overall deviation in X_{H_2} is equal to 6%.

Both equations must be carefully analyzed for a proper discussion. The influence of CO_2 being accounted as CH_4 and CO, sometimes not being detected at all, strongly influences the carbon balance and other aspects of the results.

4.2.6 Results and discussion

The Ni-impregnated geopolymer monoliths' metal content is presented in Table 11, calculated based on the weight difference before and after impregnation.

Table 11 - Nickel impregnated into 3D-printed geopolymer monoliths.

Formulation	Nickel (wt%)
MKB- Ni20	14 $\pm$ 3
MKI- Ni20	12 $\pm$ 3

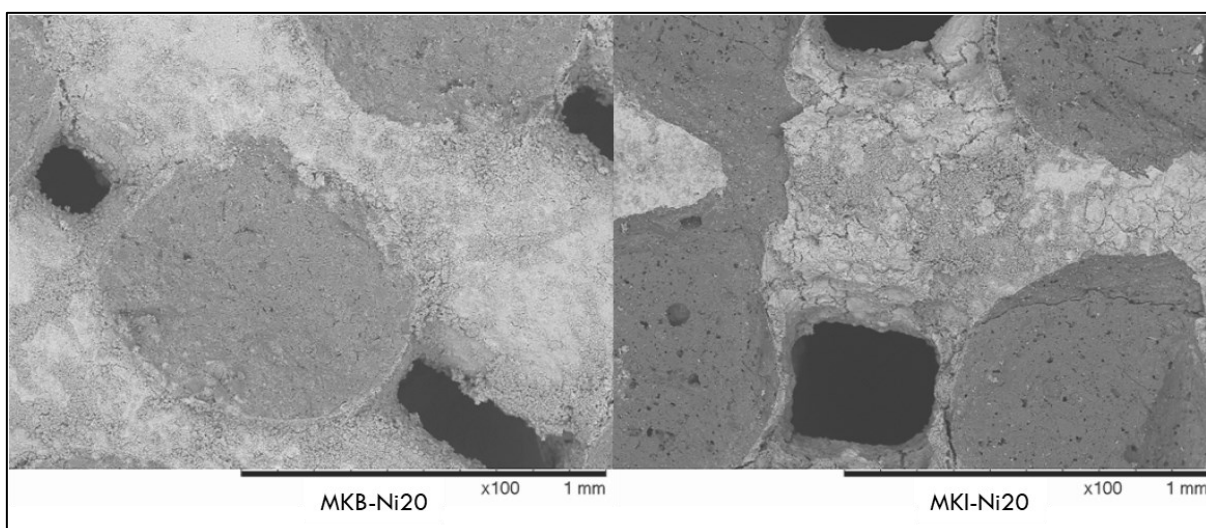
Subsequent discussions concerning the results presented in the following sections should include the disparities between MKB-Ni20 and MKI-Ni20 in terms of effective catalyst content. Many of the previously referenced studies in this thesis have

not paid careful attention to this aspect. Wet-impregnation is a tricky method to obtain Ni-impregnated catalytic supports. It is often poorly described in the literature [17], [88], [144] and remains largely dependent on the researcher's skills during the experimental procedure. Consequently, the cross-comparisons between results often become a challenging aspect of this work.

3.4.6.1 Characterization by SEM

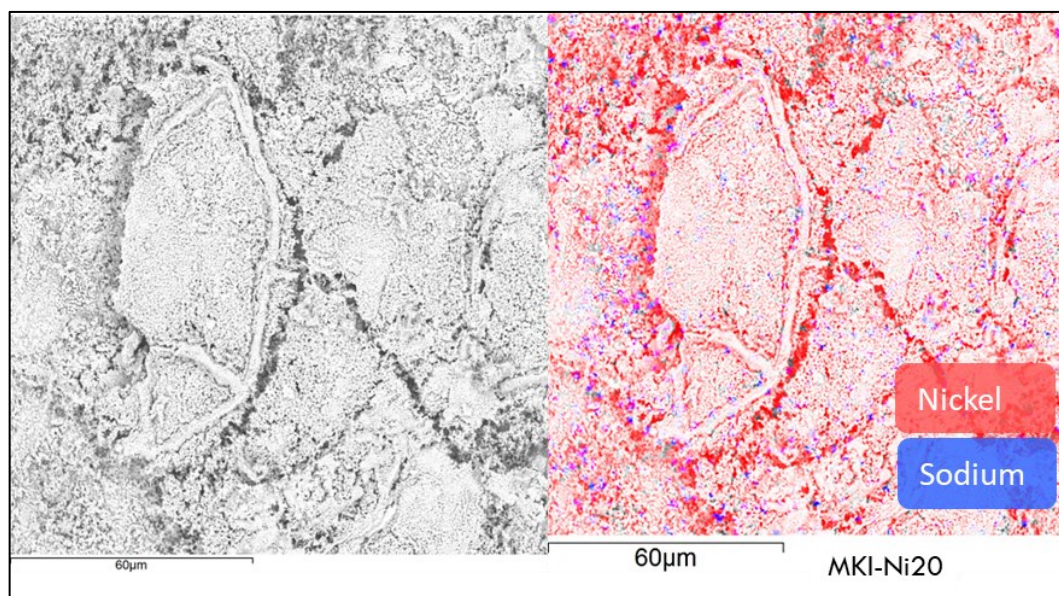
Ni-impregnated samples MKB-Ni20 and MKI-Ni20 presented a large deposition of catalyst in their surface. In Figure 32, Ni deposited on the support surface is visible as a white coating, even presenting a crackled aspect from possible excess (nickel over nickel). The cracked film behavior is usual for systems with large amounts of metal loading [165].

Figure 32 – SEM images of MKB-Ni20 (left) and MKI-Ni20 (right) at magnification = x100.



In Figure 33, EDS analysis confirms the coating of nickel (red) on the monolith's surface. It is known that not only the weight percentage of the catalyst but also its morphology and dispersion significantly influence catalytic activity and, consequently, the efficiency of catalysis. However, it must be remembered to the reader that the focus of the current work is not on catalytic efficiency, but rather on assessing geopolymers' suitability for high-temperature catalysis. Efficiency largely depends on the monoliths' design, composition, processing parameters, and catalysis conditions [64], [159], [166], [167].

Figure 33 – EDS elemental mapping detail of MKI-Ni20 sample. Deposited nickel is seen in the color red, and sodium from the support is blue.



3.4.6.2 Crystallography

From the results shown in Figure 34 and Figure 35, the crystallographic profile of both samples MKI-Ni20 and MKB-Ni20 are very similar, with minor differences in intensity for some peaks that do not interfere with the phase identification, which is identical for both materials.

Peaks related to nickel oxide are present in the data. Some are close or overlapped with peaks related to quartz, but some are quite characteristic of the metal catalyst phase.

Some minor peaks not identified previously in Figure 16, Figure 26, and Figure 27, which show the characterization of raw metakaolin and subsequent geopolymers, are still present in the nickel-impregnated samples. During the identification process conducted using the X'Pert HighScore software, there was a high likelihood (identification score > 50) of the presence of a $\text{Ni}_2\text{Al}_2\text{SiO}_8$ spinel phase. However, due to significant differences in intensity patterns and substantial overlap with existing peaks, this phase was excluded from the graphical data presented in Figure 34 and in Figure 35. For more information related to the software please refer to the methodology in Section 3.2.3. Further findings from the TPR analysis, shown in the next topic, strongly suggest that such phases might be present in both geopolymers.

Figure 34 – Crystallographic profiles of MKB-NiO and MKB-Ni2O.

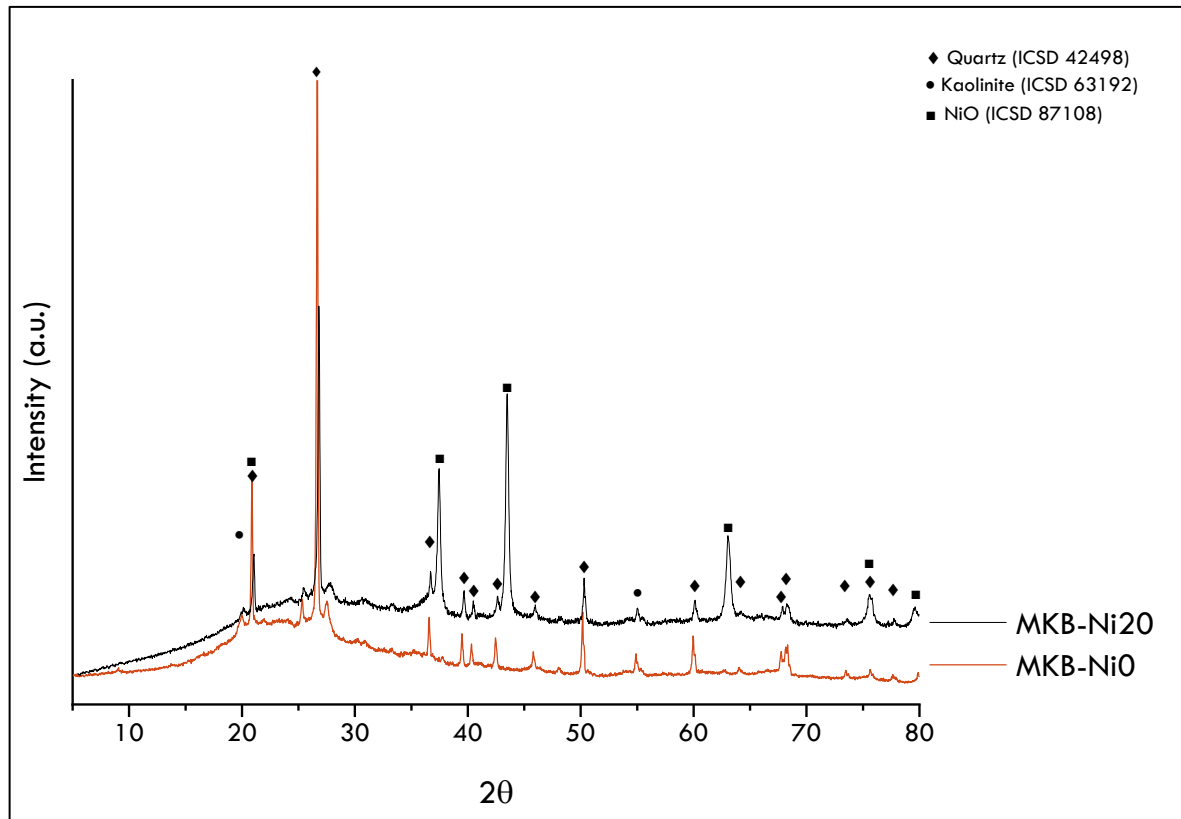
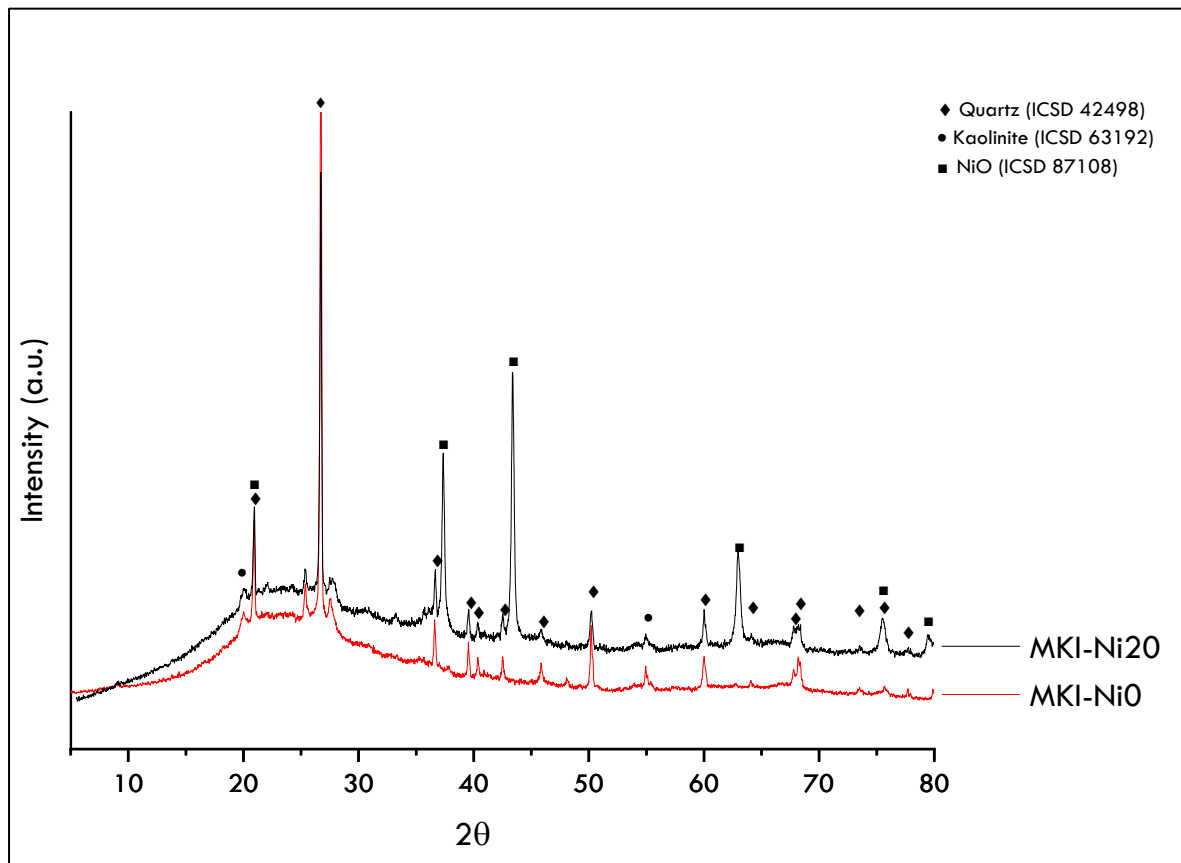


Figure 35 - Crystallography profile of MKI-NiO and MKI-Ni2O sample.



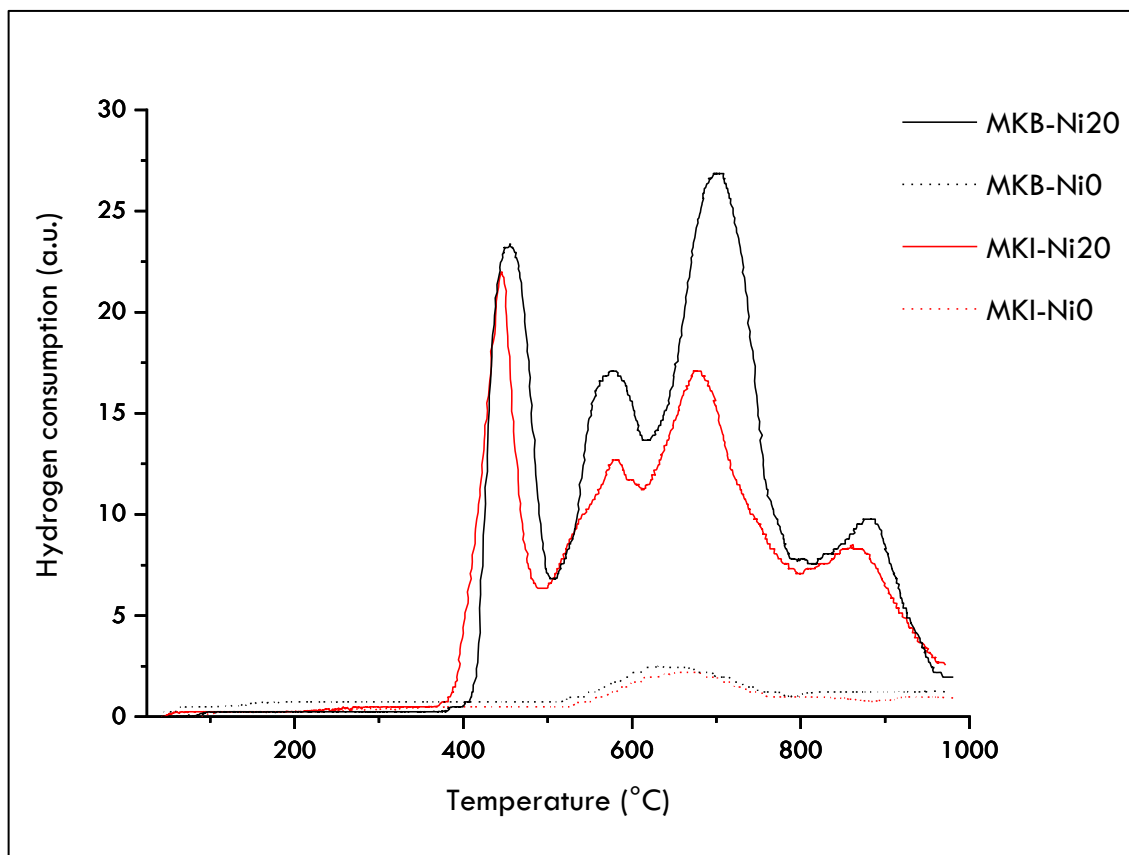
3.4.6.3 Temperature programmed reduction (TPR-H₂) and BET area

The reducibility of the catalysts can be evaluated through temperature-programmed reduction analysis (TPR-H₂), which measures the hydrogen consumption at different temperatures. TPR-H₂ not only allows the identification of NiO species but also provides insights into the interaction between the support and catalyst. This interaction often plays a crucial role in suppressing the sintering of the catalyst and reducing crystalline phases containing the catalyst that may have formed during the analysis or previous thermal treatments [168].

Limited research has been dedicated to Ni-geopolymers, particularly with regard to conducting temperature-programmed reduction with hydrogen (TPR-H₂) analyses on these specific samples. Consequently, the specific literature directly supporting the findings in this study is notably scarce. To compensate for this gap, the discussion draws upon studies involving nickel supported on alumina and aluminosilicates containing alkali elements as promoters. This broader analysis provides essential context and insights into the observed behaviors of the 3D-printed monolith geopolymer catalysts here reported.

The influence of alkali and alkaline earth metals on nickel reduction has been extensively investigated in the literature, spanning various supports and catalytic processes. Alumina and aluminosilicate supports were specifically selected as a comparative basis for geopolymers, primarily due to their widespread availability in literature and partial compositional resemblance, despite significant crystalline disparities. Across numerous investigations, these studies consistently affirm that the presence of alkali and alkaline earth metals strengthens the interaction between the catalyst and the ceramic support [89], [168]–[177] – the same result reported by Zhang et al. [34] for Ni supported on perovskite.

The 3D-printed geopolymer monoliths were evaluated by TPR-H₂ analysis both with and without impregnated nickel. The hydrogen consumption profiles are shown in Figure 36.

Figure 36 – TPR-H₂ profiles of 3D-printed geopolymer monoliths.

The specific surface area (BET) does not present effective change from non-impregnated to impregnated samples since the values fall within the equipment margin of error of ± 1 , which is considered insignificant for BET single-point measurements – from 7.2 m²/g to 6.9 m²/g after impregnation and thermal treatment for MKB-Ni20 and from 5.2 to 5.5 m²/g for MKI-Ni20.

It is possible to notice that MKB-Ni20 samples exhibited greater H₂ consumption, which is evident from the larger area under their respective curves. The area under the curve for MKB-Ni20 was 22% larger than MKI-Ni20. While that could be attributed to differences in surface area, resulting in a greater catalyst dispersion and, consequently, a higher metallic surface area, it could be also the result of catalyst weight percentage differences derived from the impregnation method as seen in Table 11. Nonetheless, non-impregnated MKB-NiO samples also presented larger H₂ consumption than MKI-NiO, which could be attributed not only to the larger surface area but also to compositional distinction. This assumption becomes more acceptable when the temperature peaks of impregnated samples are compared, and other characterization results are considered.

From the consumption profiles shown in Figure 36, the raw materials composition, the crystallography results, and the available literature, some conclusions may be drawn about the Ni-impregnated geopolymer monoliths. First and foremost, besides the peaks close to 400 °C, which are related to nickel oxide of weak interaction with the support [17], it is crucial to note the three main peaks of hydrogen consumption that are common to both formulations despite presenting temperature peaks deviations.

From the XRD results shown in section 4.2.4, it was noticed the possibility of the presence of a $\text{Ni}_2\text{Al}_2\text{SiO}_8$ spinel phase. This possibility is reinforced by the TPR- H_2 results, since the peaks above 400 °C are all related to strong interactions between catalyst and support. Even if the XRD results were inconclusive about which crystalline phases were formed by the interaction of nickel with the support, it must be remembered that geopolymers are essentially amorphous, turning the characterization of the interaction catalyst-support even more difficult.

The displacement of peaks to lower temperatures is commonly associated with lower content of alkali and alkaline earth metals and weaker interaction of NiO with the support [168]. As seen in Table 7, Section 3.2.3, metakaolin MK-I presents a lower content of K and other metals, which could lead to a weaker interaction between support and catalyst. Caution must be paid to the XRF results, as the measurements for Na, Mn, K, and Ca might exhibit inaccurate weight percentages. The predominance of Si and Al in the metakaolin samples can potentially obscure the accurate measurement of other elements with lower atomic numbers.

Despite all the uncertainty regarding each characterization result individually, an overall conclusion about the materials is possible once these results are analyzed combined. When the weight percentage of impregnated Nickel, the composition of the supports, the specific surface areas, and TPR- H_2 profiles are analyzed together, it is possible to assume that MKB-Ni20 samples might be better catalysts than MKI-Ni20. This assumption has been tested in Methane Steam Reforming as follows in the next Section.

3.4.6.4 Methane Steam Reforming enhanced catalysis

Samples MKB-Ni20 and MKI-Ni20 were tested as catalysts for Methane Steam Reforming (MSR). The products of steam reforming of hydrocarbons are controlled

mainly by thermodynamics, in an endothermic process that leads to process temperatures above 700 °C [163].

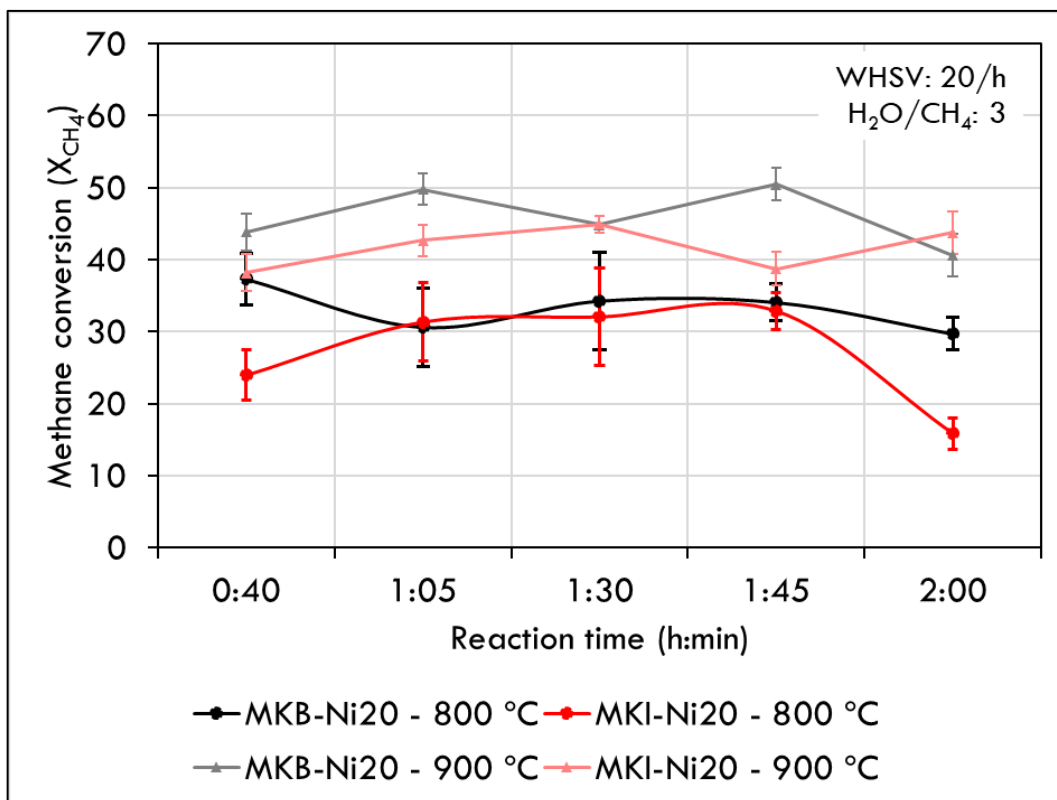
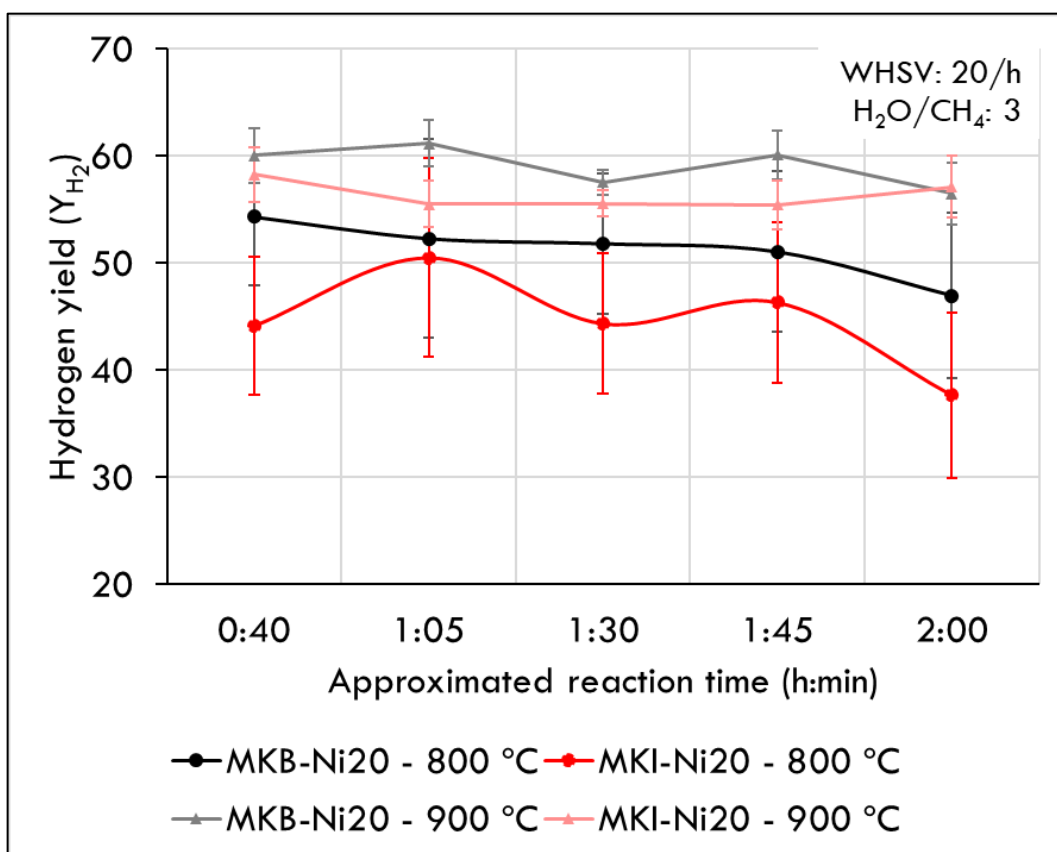
A limiting parameter in the MSR reforming process is the heat transfer towards the reaction volume, from which a thermal profile is derived, imposing a constraint on the reaction efficiency [178]. The issue may be overcome by using high thermal conductivity carriers such as monoliths and foams [144].

The results of Section 4 by themselves and the existing literature would be enough to support the idea of geopolymers as viable materials for catalysis processes at high temperatures like steam reforming. However, this idea has been scarcely explored up to date - 2023. One of the reasons for that could be the reported low thermal conductivity of geopolymers, generally lower than 1 W/(m.K) at 25 °C for Na-metakaolin-based materials [179]. For instance, the typically reported thermal conductivity of widely applied support materials like alumina and cordierite are 30 W/(m.K) and 3 W/(m.K), respectively, at 25 °C [154], [159].

The idea of using additive manufacturing to obtain geopolymer monoliths with pore structures in both longitudinal and transversal axes is to take advantage of low pressure drop, good mechanical properties, high surface area, and increased heat transfer, all of which are directly related to the monolith design [159]. As a consequence, this feature also allows for the material to endure harsher conditions than it would with other geometries, as evidenced by the results of thermal behavior in Section 4, more specifically those of compressive strength of bulky and 3D-printed samples after thermal treatment presented in Figure 30.

To assess the thermal resistance of the geopolymer samples, the process conditions were set at 800 and 900 °C, which are the highest temperatures employed in MSR. The value of WHSV (Weight Hourly Space Velocity), 20/h must be optimized to achieve the highest possible methane conversion. However, this optimization is not necessary to evaluate the material's viability as a catalyst.

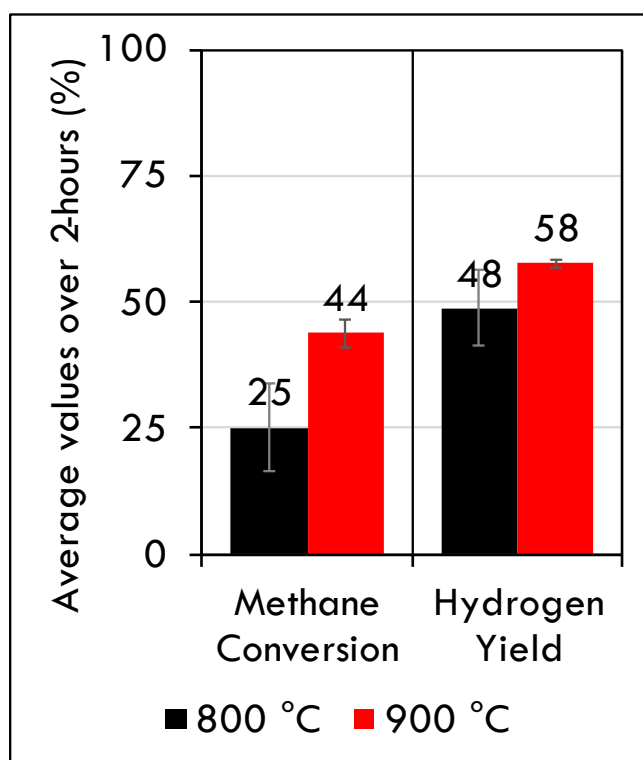
The results were compiled in terms of methane conversion (X_{CH_4}) and hydrogen yield (Y_{H_2}) as aforementioned. The results for methane conversion are presented in Figure 37 and hydrogen yield in Figure 38. The standard error was calculated from the average deviation between all samples tested at the same temperature – 2 samples of each type for each temperature.

Figure 37 – Average methane conversion (X_{CH_4}). Please note the Y axis range.Figure 38 – Average hydrogen yield (Y_{H_2}). Please note the Y axis range.

No pattern of catalyst deactivation was observed throughout the length of the experiment, suggesting the viability of the geopolymer monoliths as catalyst supports for high temperature catalysis processes such as MSR. The deviations presented along the 2 hours of reaction seem random and related to the experimental setup.

It is possible to conclude from Figure 39 that the reaction at 900 °C presented higher average methane conversion and hydrogen yield for both formulations, as expected. Even with the standard deviation values for X_{CH_4} at 800 °C, the hydrogen yield is strong evidence of higher catalytic activity at 900 °C. The larger values of standard deviation values for MSR at 800 °C are attributed to the experiment limitations.

Figure 39 – Methane conversion and hydrogen yield average performance of MKB-Ni20 and MKI-Ni20 samples over 2 h of MSR.

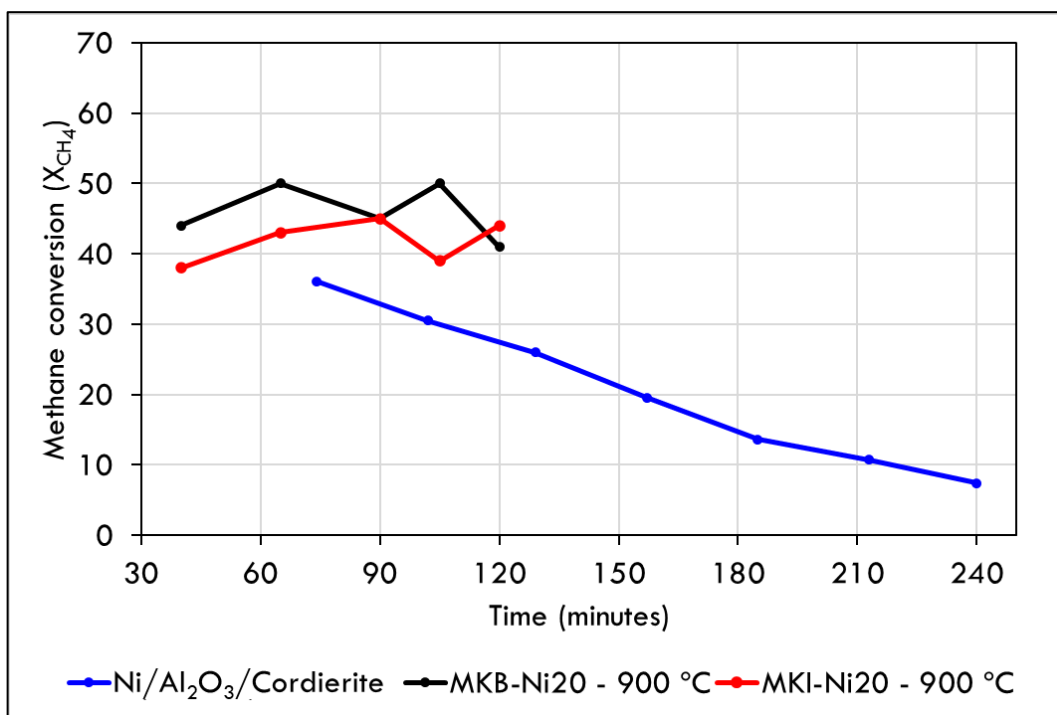


Most importantly, the graph in Figure 39 shows the low general standard deviation at 900 °C for both methane conversion and hydrogen yield, demonstrating the stability of the geopolymer catalyst for the highest possible operating temperature of a Methane Steam Reforming plant, enabling the material as a candidate for other catalytic processes that require higher temperatures, even if the conversion values are not as high as the reported in the literature for conventional materials [180].

MSR is highly dependent of the experimental conditions and monolith design [159], [162], [181]–[183]. While the observed conversion values with geopolymer monoliths were not as elevated as those achieved with most papers published about MSR with cordierite and Al_2O_3 , which approached conversion values close to 99%, it must be noted that optimizing experimental parameters such as the WHSV and the metallic dispersion was not between the objectives of the Thesis. The primary aim of these results is to establish the proof of concept: geopolymers can serve as catalyst supports for high-temperature catalytic reactions.

In comparison to conventional ceramic catalysts such as $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{cordierite}$, which are widely available in the market and documented in the existing literature, the studied Ni-geopolymers exhibit distinctive qualities. In a study by Hou and Hughes [184] on the kinetics of methane steam reforming (MSR) with $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ supported on cordierite, a significant decrease in methane conversion (X_{CH_4}) was observed after 120 minutes under reaction conditions close to the ones tested with the geopolymer monoliths, but at temperatures of 525 °C and 550 °C. Figure 40 compares their findings with the ones reported in this Thesis, although direct comparisons are challenging due to differing values. Their MSR tests were conducted at lower temperatures and different WHSV and pressure, making it difficult to effectively compare conversion values.

Figure 40 – Comparison of X_{CH_4} over time on the stream for Ni/ α -Al₂O₃/Cordierite reported by Hou and Hughes [184] and the geopolymer monoliths MKB-Ni20 and MKI-Ni20. Please note the different operating conditions. For Ni/ α -Al₂O₃/Cordierite, consider these parameters: Temperature = 550 °C, Reaction pressure = 120 kPa, H₂O:CH₄ = 3, WHSV $\approx$ 160/h.



Wet-impregnated Ni/Al₂O₃ supported on commercial cordierite monoliths have been tested by Pereira et. al [180] at experimental conditions closer (Pressure = 1 atm; Temperature = 800 °C; H₂O:CH₄ = 3, GHSV = 225, WHSV = 223/h similar to those employed in this thesis, albeit with a 11x higher WHSV. Their monoliths presented high X_{CH_4} ($\approx$ 98%) and stability over the course of 24 hours on stream. They have noticed, however, that the impregnation method plays a major role over the conversion efficiency [180].

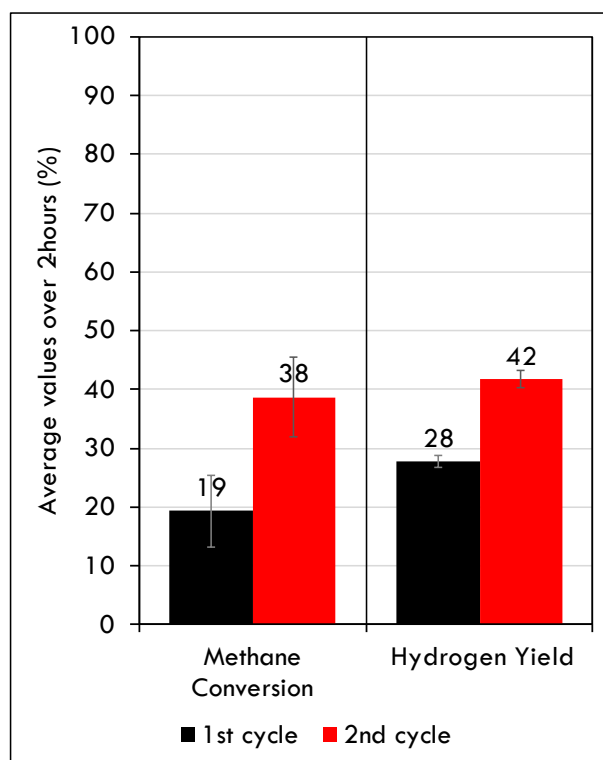
The Ni-geopolymer behavior during MSR at high temperatures is mostly attributed to the strong interaction of nickel with the geopolymer matrix during calcination and activation steps, with the formation of some complex crystalline structures that were not reliably characterized by the XRD results, as one possible Ni₂Al₂SiO₈ spinel phase. Even if precisely identifying which crystalline phases are formed by the interaction of nickel with the support, the existence of such phases is confirmed by TPR-H₂, Figure 36, with multiple peaks of hydrogen consumption appearing after the typical peaks related to NiO.

As an attempt to confirm that the existence of nickel-containing crystalline phases increases the materials' lifetime, one spent geopolymer catalyst was regenerated via oxidation in air at 800 °C and tested once more for MSR. After regeneration, the testing procedure followed the methodology previously applied to all samples. The sample MKI2, which presented the lowest methane conversion and hydrogen yield of all samples, was chosen for this experiment.

As seen in Figure 41, the catalytic activity of the sample increased after regeneration. That might be due to several reasons. The activation before the first cycle might not have been as successful due to some experimental error, for example, or the catalyst might have been rearranged during the first cycle and regeneration in such a way that the second activation was more effective. Also, Na may be significantly less present in the materials' surface after the first reaction since it might be leaching and being carried by water vapor. Excess Na may hinder the catalytic activity [30].

More characterization would be necessary to correctly describe the verified reaction rates. Nonetheless, the behavior of the regenerated catalyst reassures the positive interaction between nickel and the geopolymer matrix.

Figure 41 - Average values of methane conversion and hydrogen yield in MSR for sample MKI2 for 2 h at 800 °C during the first cycle and after catalyst regeneration.



Such strong interaction of nickel with the geopolymer support leads to a lower tendency to catalyst sintering and coking, both of which lead to catalyst deactivation [34], [155], [160]. The geopolymer catalyst is able to withstand the process' high temperatures and keep a stable performance for the reaction as better evidenced by the MSR data at 900 °C. These findings were confirmed by the regeneration test even if assessed by only one sample.

MKB-Ni20 samples presented both higher nickel-impregnation rates, higher specific surface area, and larger hydrogen consumption during TPR-H₂. These results were confirmed during MSR, particularly at 900 °C, when the standard deviation values allowed for a more accurate evaluation. Through XRD characterization and TPR-H₂, strong evidence of crystalline phases containing nickel was built, and a regeneration test in a sample even increased the methane conversion rate and hydrogen yield, allowing for a conclusion that sintering and consequent deactivation of the catalyst have been successfully prevented during the first cycle of reaction. All the hereby reported findings regarding methane steam reforming with 3D-printed geopolymer samples are positively correlated to the materials characterization, providing a systematic methodology to further improve future works.

5 CONCLUSION AND PERSPECTIVES

From a concise yet thorough literature review to an extensive exploration of product processing development, materials characterization, and performance evaluation, this research convincingly demonstrates that geopolymer catalysts hold substantial promise for high-temperature catalysis processes. This conclusion is drawn from the wealth of findings documented in the existing literature, as outlined in Chapter 2, and the experimental results presented in Chapter 3.

All the main and specific objectives have been met successfully, representing a milestone for geopolymers as catalyst materials. This work not only solidifies a new paradigm for the future applications of geopolymers in catalysis but also paves the way for an array of high-temperature applications that have been relatively unexplored for these materials. The main conclusions are presented point by point as follows:

- Following the existing literature and adapting it for the intended specific application, a new rheology testing protocol has been proposed and successfully employed as a characterization method for geopolymer pastes composed only of metakaolin, alkaline activators, and a rheology additive, without fillers.
- Only commercially available feedstock materials, including two types of metakaolin, were used as raw materials to produce the geopolymer catalysts.
- The rheology is mainly affected by particle size and distribution. Metakaolin with larger particles and broader particle size distribution presented better workability.
- In contrast to the usual applications for which it is intended, the more reactive metakaolin, characterized by its pure composition, smaller particle size, narrower particle size distribution, and larger amorphous content, posed increased processing challenges. These challenges arose due to the shorter time available for 3D printing and the complex rheological behavior exhibited by this material.
- PEG-400 is an effective rheological additive and decreases the geopolymerization rate, increasing the open time available for additive manufacturing of geopolymers.
- Despite compositional and crystallographic differences between the raw metakaolin used, the two geopolymer formulations (MKB and MKI) presented very similar results for most characterizations.
- After printing, the proposed geopolymer formulations present a specific surface area close to 30 m²/g. The value dropped to around 6 m²/g, following the massive shrinkage resulting from the first calcination.

- The designed porosity of 70% is successfully achieved by the proposed methodology.
- After calcining, the monoliths porosity decreases by 4 to 5% on average. The calcined geopolymers present low thermal expansion and insignificant crystallographic changes.
- The thermal behavior of 3D-printed porous samples significantly differs from that of bulkier samples obtained through traditional methods. Post-thermal treatment, the compressive strength of 3D-printed samples does not decrease. In these samples, mechanical properties are more closely associated with the design of the monolith and the quality of the printing, rather than the calcination process.
- The 3D-printed geopolymers have been successfully impregnated with nickel as a catalyst. The impregnation method demands optimization since it presented a lower weight percentage of catalyst impregnated than the projected.
- For both MKB and MKI formulations, 20 wt% was the goal for nickel impregnation. The obtained values were both lower than 15 wt%, with MKB presenting ~14 wt% and MKI ~12 wt% of catalyst on average. The standard value deviation was also considerable, although equal to both formulations: ~3 wt%.
- Joining the XRD characterization of the geopolymer catalysts to the results of TPR-H₂, it is possible to conclude that the nickel catalyst strongly interacts with the geopolymer support, with the formation of different crystalline structures composed of nickel, aluminum, and silicon.
- The peaks related to the crystalline structures composed of nickel and the support composition are not evident by XRD since most of them are interposed with the peaks of the pre-existing crystalline structure, but the existence of such structures is evidenced by the TPR-H₂ results showing at least three major peaks of reduction by hydrogen at temperatures higher than the ones required by NiO, which is usually related to weak interaction with the support.
- The existing crystalline structures resulting from the strong interaction of nickel with the geopolymer support provide high stability to the catalyst at high temperatures, preventing sintering and coke formation that would lead to the catalyst deactivation.
- Both geopolymer catalyst formulations have presented high stability for Methane Steam Reforming at 800 °C and 900 °C.

- As expected, the results for methane conversion and hydrogen yield were higher for MSR at 900 °C.
- At 900 °C, the results of MSR presented a lower value deviation. That is mainly attributed to equipment and experimental limitations.
- The prevention of catalyst deactivation by the interaction catalyst-support has been tested with one sample. A regeneration treatment by oxidation in air followed by a second cycle of catalyst activation led to higher methane conversion and hydrogen yield in the tested sample.

All the results strongly suggest that 3D-printed geopolymers have the potential to become significant candidates for high-temperature catalysis processes in the near future. There remains a vast unexplored territory in this emerging field.

It is important to highlight that both methane conversion and hydrogen yield values depend not only on the support material but also on the experimental conditions and the design of the monolith. Varying these parameters were not relevant to the proof of concept.

Future works should focus on refining design parameters, enhancing post-processing techniques, and optimizing compositions, searching for ways to boost catalysis efficiency while minimizing alkali leachability. Improving the material's thermal conductivity, for instance, can be achieved through simple composition adjustments.

Researchers venturing into this challenge should bear in mind that this study did not explore fillers, varying design parameters, experimenting with bi-metallic catalysts, exploring diverse reaction conditions, and numerous other options. These unexplored pathways hold the potential for exciting new prospects concerning geopolymers as catalyst materials for high-temperature processes, not only for gas reforming but also for catalytic combustion. There is not one major challenge ahead to be met anymore, but many. That is the good news.

ACADEMIC PRODUCTION DERIVED FROM THE DOCTORATE PERIOD

Over the course of the doctorate, the student was involved in or was directly responsible for the academic production of 2 published/accepted for publication papers in international peer-reviewed journals, 5 works presented in Brazilian and international congresses and conferences and 2 highly innovative papers to be submitted for publication in international peer-reviewed journals.

Published/accepted in international peer-reviewed:

- R. V. Eleutério, L. Simão, and D. Hotza, “Alkali-activated materials for catalytic applications: A state-of-the-art review”, *Materials Science & Engineering B*, accepted in November 2023.
 - *Qualis: A1; Impact factor: 3.6; CiteScore: 4.7.*
- R. V. Eleutério, L. Simão, P. Lemes, and D. Hotza, “Evaluation of As-Received Green Liquor Dregs and Biomass Ash Residues from a Pulp and Paper Industry as Raw Materials for Geopolymers,” *Minerals*, vol. 13, no. 9, p. 1158, Aug. 2023, doi: 10.3390/min13091158.
 - *Qualis: A3; Impact factor: 2.5; CiteScore: 3.9.*

Published in congress' annals:

- R. V. Eleutério, F. T. Albino, L. Simão, L. Senff, D. Hotza, “Thermal behavior of geopolymers for new catalytic applications”. In: Pan American Ceramics Congress and Ferroelectrics Meeting of Americas, 2022, Panama City. Annals of Pan American Ceramics Congress and Ferroelectrics Meeting of Americas, 2022. p. 60.
- R.V. Eleutério, F.T. Albino, E. Pietschmann, A.P. Cambunda, L. Simão, R.C. Catapan, D. Hotza, “Impressão 3D de catalisadores geopoliméricos para aplicações em reforma gasosa a alta temperatura”. In: 67º Congresso Brasileiro de Cerâmica, 2022, Florianópolis, Annals of 67º CBC, 2023, p. 29.
- Y. A. Vieira, V.C. Cordova, R.V. Eleutério, M. Kelbert, D. de Oliveira, A. F. Junior, “Imobilização de lacase de trametes versicolor em suportes de montmorilonita ativada com cobre”. In: Anais do 24º Congresso Brasileiro de Engenharia Química, 2023.

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To be submitted:

- R. V. Eleutério, F. T. Albino, E. Pietschmann, , M. O. Palm, L. Simão, R.C. Catapan, D. Hotza, “3D-printed geopolymer-based catalyst supports”. Based on Chapter 3 of the Thesis.
- R. V. Eleutério, F. T. Albino, E. Pietschmann, A. P. Cambunda, , M. O. Palm, L. Simão, R.C. Catapan, D. Hotza, “High-temperature catalysis with novel 3D-printed geopolymer monoliths”. Based on Chapter 4 of the Thesis.

DISCLOSURES

During the preparation of this work the author used CHAT GPT 3.5 / OPEN AI to improve readability and grammar of the text. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

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