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Fabrication Challenges in Synthesizing Porous Ceramic Membrane to Effective Flue Gas Treatment

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ABSTRACT

Global warming is a serious concern worldwide, and many sources contribute to the rise in the temperature of Earth. One major source is air pollution. It is of utmost importance to apply the necessary remedial actions to address the contaminants in outdoor and indoor environments. In this research, a step is taken to treat flue gases, for which membrane technology is introduced. A porous ceramic membrane is synthesised from calcined porous alumina (Al_2O_3) and activated washed fly ash. Some other additives such as starch $(C_6H_{10}O_5)$ n, binder solution along with ethyl silicate ($C_8H_2O_4Si$) and a deflocculating agent carbonic acid (H_2CO_3) are employed. Some of the issues faced during the fabrication of a porous ceramic membrane are discussed, i.e., cracks in membrane sample, nonactive reactant issue, uneven rise or fall during demoisturisation or sintering steps. The membrane sample is characterised through different tests, including thermogravimetric analysis and DTG. Satisfactory results are obtained, with a negligible percentage weight loss after 750 °C. X-ray fluorescence for fly ash portrayal and X-ray diffraction analysis for structure assessment are conducted, which describe that the fabricated membrane has a crystalline structure similar to ceramic. Archimedes' principle is used to determine the bulk density and porosity of the membrane sample, and the values are 4.484 g/cm^3 and 62.5%, respectively. An average pore size of 7.6 µm is identified through optical microscopy, and the mechanical strength is determined to be 2.7 MPa. Furthermore, a pilot-scale visual permeability test is performed for flue gas treatment of combustion fuel containing tyre and coal powder. The results show the compatibility of the fabricated porous ceramic membrane to be utilised for the treatment of flue gases.

1. Introduction

The rapid growth of the population has triggered industrial and infrastructure development. In response, it has caused many environmental catastrophes, including global warming, air pollution, water crisis and waste disposal issues [1]. WHO statistics show that almost all (99%) of the population breathes unhealthy air, contaminated with various levels of pollutants, in which the exposure in low- and middle-income countries is much higher than in other countries [2]. For instance, Pakistan is ranked 3rd amongst 118 countries with the worst air quality in 2021, with an average US air quality index of 156. Most Pakistani cities are amongst the worst polluted cities in the world due to air contamination with PM2.5 and PM10,

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having average yearly readings of 65.81 µg/m^3 [3]. Specifically, Peshawar is ranked 6th amongst all cities in Pakistan in 2019 and 37th worldwide with an average particulate matter concentration of 63.9 µg/m^3 yearly. The sources of pollution are emissions from transport and factories, including brick kilns, using tyres, wood and coal for fuel purposes [3]. Air pollution imposes various environmental and health problems, i.e. global warming, decreased production of crops, reduction in animal reproduction and diseases such as respiratory ailments with chronic obstructive pulmonary diseases, skin irritation and cancer [3]. The most alarming is the death ratio; according to a WHO report, 4.2 million deaths every year occur as a result of exposure to contaminated ambient air [2]. These statistics force researchers and different firms to cope with the situation and reduce future threats to the environment and human lives.

Many techniques are used to control air pollution, which are energy-efficient and optimised processes [4,5]. Amongst them, ceramic membrane technology is considered the most common, reliable and effective control technique, with inbuilt features, including a lesser thermal expansion coefficient, high-level corrosion stability, high mechanical strength, enough specific surface area provision, excellent permeability and lightweight compared with metals [6]. To have a maximum transport rate, porous membrane layers must be synthesised with thin layers [7].

Many commercial porous ceramic materials, including alumina, zirconia and silica, are used for the fabrication of membranes [8,9] Amongst them, alumina is considered the most widely used porous material owing to its high chemical and mechanical stability and good structure [1]. However, the sintering difficulty increases because these oxides' high-level lattice energy, which forces them to have a sintering temperature of more than 1500 °C, and pure powdered oxides are expensive [10]. To reduce the fabrication cost of porous ceramic membranes and yield comparable mechanical and chemical properties, researchers are working on by-products or wastes, including fly ash. Fly ash mainly consists of alumina and silica [11]. It has been widely used to prepare ceramic membranes, such as porous flat ceramic membranes synthesised with dolomite [12] and highly porous whisker-structured mullite ceramic membranes [13]. Different additives are added to the base material to enhance the properties; for example, starch is used as a binder and a consolidator or pore-forming agent, carbonic acid is adopted as an antiflocculant agent, and ethyl silicate is utilised as a binder [14,15]. Many applications of polymeric and metallic membranes for CO_2 and H_2S capture [16] and water recovery from flue gas [17] have been reported. However, wide-ranging studies on porous ceramic membranes made of alumina and fly ash mixtures for flue gas treatment are limited. Therefore, this study is conducted to fill the gap.

The aim of this work is to fabricate a porous ceramic membrane. The characterisation and the application of the synthesised membrane for flue gas treatment are discussed. The problems that have been mentioned are faced during the membrane fabrication. Fly ash and alumina are used as supports to reduce membrane costs whilst increasing the mechanical strength and yielding a uniform pore structure. These materials are chosen because of their thermal stability and availability. Therefore, the purpose of this study is to create high-quality and reasonably priced ceramic membrane supports by using the physical and chemical features of the base material. The fabricated membrane is utilised on a pilot-scale flue gas treatment.

2. Methodology

2.1 Starting materials

As base materials, alumina and fly ash were selected for the fabrication of the ceramic membrane support. The fly ash addition will reduce the cost of the base material, and fly ash contains mostly silica and alumina; porous alumina will react with silica oxide and produce mullite, which will increase the mechanical strength and create a uniform pore structure [18]. The chemical compounds used for the preparation of the ceramic membrane are summarised in Table 1.

2.2 Membrane fabrication

To prepare the membrane sample, this study mixed 5 g of calcined porous alumina (as base material) with 5 g of activated washed fly ash manually. Two solutions were prepared: 30vol% solution of starch and 1 M solution of NaOH and Na_2SiO_3. Afterwards, 5 ml of each solution was mixed and ball milled with the base material with a ratio of 2.3 g of base material/ml of solution. The process is shown in Figure 1. Drops of carbonic acid and 3 ml of ethyl silicate were added to the base mixture. The sample paste was finally poured into a polyethylene mould with 0.06 m diameter. The sample was covered fully and placed in a water bath at 60 °C for 1 h to prevent uneven shrinkage.

Table 1: Composition of chemicals used for the fabrication of a porous ceramic membrane

Chemicals	Formula	Purity (%)	Supplier
Ethyle Silicate	Na_2SiO_3	99	Haq Chemicals Peshawar
Sodium Hydroxide	NaOH	99	Haq Chemicals Peshawar
Carbonic Acid	H_2CO_3	99	Haq Chemicals Peshawar
Alumina	Al_2O_3	99	Daejung Chemicals and Metals Co., Ltd.
Fly Ash	Contains many oxides, determined through XRF analysis	63%SiO_2 22% Al_2O_3	Lakhra Coal-Fired Power Plant, Sindh, Pakistan
Starch	$(C_6H_{10}O_5)_n$	99	Daejung Chemicals and Metals Co., Ltd.

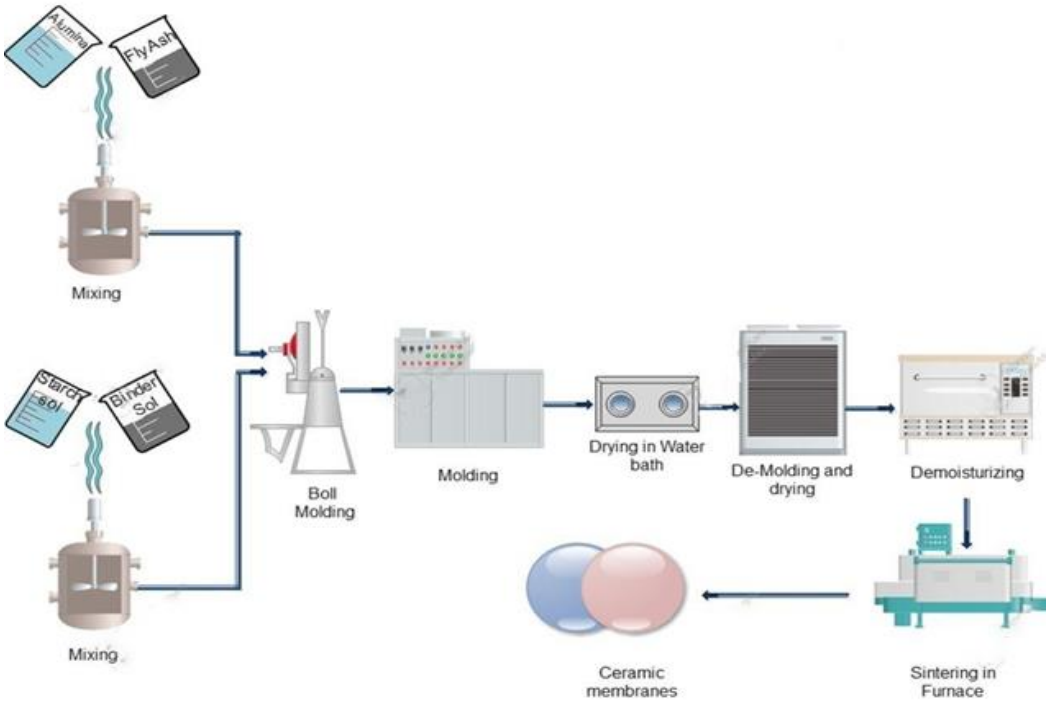

Figure 1. Process flow diagram for synthesis of porous ceramic membrane using porous alumina

Then, the sample was quenched for a few minutes at 13 °C and dried in ambient air at 22 °C. The demoulded membrane sample was placed in an oven for 20 h at 105 °C for the removal of moisture content. The sample was passed through stepwise sintering at 1250° C in a furnace. The final prepared porous ceramic membrane is depicted in Figure 2.

Figure 2. Membrane sample top view after sintering at 1250 °C in furnace

2.3 Tackling the fabrication obstacles

The fabrication of a membrane requires extreme attention at each step. If the procedures are not followed as described by the researchers, each step will lead to failure, and achieving the desired results will be difficult. Some of problems that may be faced during research are explained here.

1. The base material must be properly activated, i.e. the alumina must be calcined, and the fly ash must be washed and activated. The starch solution and the binder solution must be made reactive; if the material is not activated properly, membrane sample will not be formed. Upon demoulding, fracture will appear, as shown in Figure 3.

Figure 3. Breakdown of membrane sample upon de-moulding as the alumina was not calcined and starch solution was not prepared properly.

2. Care must be taken during demoisturising in the oven. The temperature must be maintained at 105 °C for 20 h. Any sudden decrease in the temperature will lead to cracks, as shown in Figure 4. Such cracks happened because of a stoppage of the power supply to the oven (due to an electrical shutdown in the lab) when demoisturisation was in progress.

Figure 4. Crack in membrane sample when power supply was stopped to oven during de-moisturization at 105°C for 20 hours.

3. Sintering must be carried out in a stepwise manner, e.g. proper heat rate, which should be maintained for specific time at a specific temperature before the required temperature is reached. Any uneven rise or fall in temperature will deform the shape of the membrane sample, as shown in Figure 5.

Figure 5. Swallowing of membrane during sintering, the root cause was uneven rise in temperature during fabrication.

2.4 Characterisation methods

The elemental compositions of the principal raw materials, fly ash, were determined using the X-ray fluorescence (XRF) technique at the Material Characterization Laboratory, U.S.-Pakistan Center for Advanced Studies in Energy, UET Peshawar. For measurement purposes in X-ray diffraction (XRD) analysis, Cu-kα radiation was applied. The specimens were fabricated through a backloading mechanism. A solar (2.5° and 0.6 mm) antiscatter slit, including a diffracted beam, was supplied. For the reduction of air scattering, the scattering screen was placed above the sample with a length of 2 mm. For the operation of the X-ray tube, the generator position was fixed at 30 kV and 10 mA. Measurements were conducted in a vertical Bragg–Brentano geometry in between 10° and 70° for 2Θ angles having a shape size of 0.02° with a rate of 0.6 s per step. The specific measurement time for each scan was 30 min. The paste of the formulation was subjected to thermogravimetric analysis (TGA, SII 6300, EXSTAR) to identify weight loss patterns. In this test, a powdered membrane sample of 8.5 mg was considered, and nitrogen was passed through the apparatus at a flow rate of 30 ml/min for 30 min. A heat rate of 20 °C/min was set until 1250 °C to remove the volatile organic components. Afterwards, atmospheric ambient air was introduced. The powdered membrane sample must be dried first for 2 h at 100 °C.

3. Results and discussions

3.1 Bulk density, porosity and pore size

The bulk density, porosity and pore size of the synthesised membrane sample were determined at the Material Characterization Lab, Renewable Energy Section, U.S.-Pakistan Center for Advanced Studies in Energy, University of Engineering and Technology Peshawar to determine its feasibility. The bulk density of the membrane was found to be 4.484 g/cm^3, which was measured through Archimedes' principle.

The fly ash ceramic membranes had theoretical densities of 3.16 and 3.98 g/cm^3 [19]. Only clay was present as the main crystalline phase in the proppants produced for this investigation. Thus, the proppants made from fly ash had a greater apparent density of 4.48 g/cm^3 [20], in comparison with the majority of ceramic proppants in the Chinese market and those produced by Carbo Company, whose density ranges between 2.80 and 3.40 g/cm^3. To sum up, fly ash was used to create high-density ceramic proppants on the basis of the superiority of the single crystalline phase. The percentage porosity for the sintered membrane sample was 62.5% according to Archimedes' principle. The average pore size of the membrane was determined by optical microscopy, as shown in Figure 6, with a value of 7.6 µm.

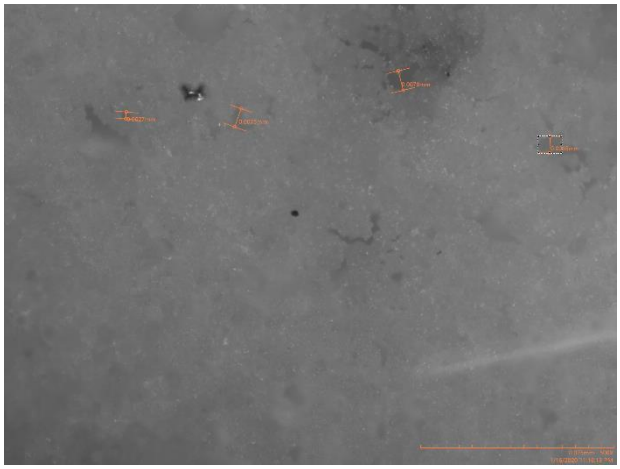

Figure 6. Average pore size of the sintered membrane sample (500X resolution).

3.2 Mechanical strength

The mechanical strength was measured at UTM Lab, USPCAS-E, UET Peshawar through a graph of force versus deflection shown in Figure 7. The recorded bending strength value was 2.7 MPa for the sintered membrane sample. The same patent has been mentioned in the literature [21]. The high sintering temperature of 1250 ℃ resulted in high mechanical strength. This result was mostly due to the formation of a neck because the higher sintering temperature gradually eliminated considerable grain expansion or contraction and increased the membrane's strength [22].

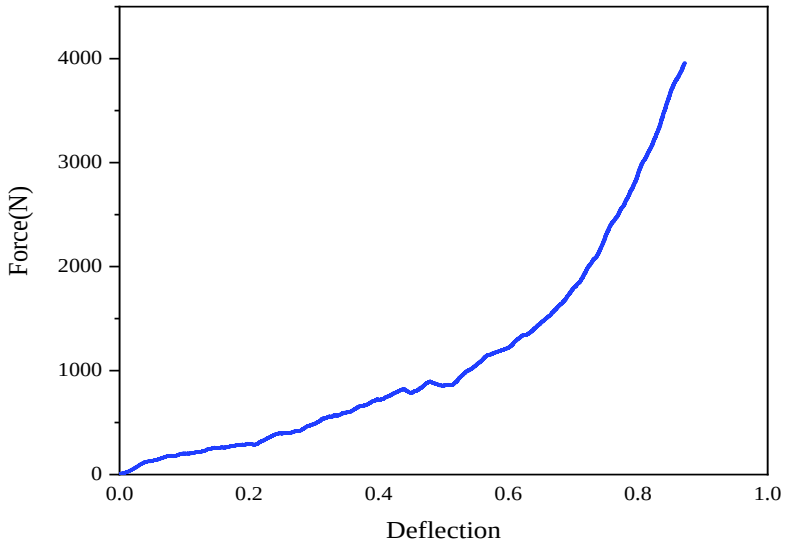

Figure 7. Mechanical strength found 2700 KPa, a fracture is found in the sample at 4000 N force.

3.3 X-ray diffraction (XRD)

The XRD results showed the crystallinity and total reactivity of the membrane determined at different peaks values, as depicted in Figure 8. The powdered sample had many phases, where considerable constructive interferences can be seen as the peak showed in detail in Figure 8. Dehua et al. also obtained close results whilst studying the effect of sintering temperature on the membrane pattern at different temperatures [23].

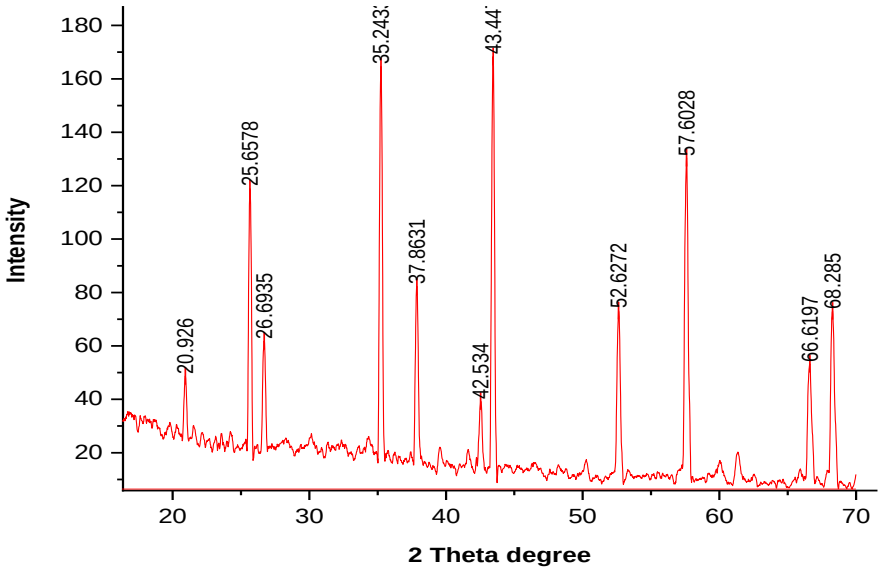

Figure 8. XRD patterns of porous ceramic membrane sintered at temperature of 1250℃.

3.4 Thermal gravimetric analysis (TGA)

TGA was performed at Material Characterization Laboratory, U.S.-Pakistan Center for Advanced Studies in Energy, UET Peshawar for the nonsintered membrane sample powder (i.e. the slurry powder which contains starch and other volatile oxides and moisture content). The result showed that the ceramic membrane endured the high temperature and, thus, could be utilised for the treatment of exhaust gases. With the increase in temperature,

the mass loss decreased. The total mass change was 28.96%. Initially, the sample was not sintered, due to which demoisturisation and burning of starch occurred. Afterwards, a negligible amount of loss in mass was found in the sample. The percentage weight loss is shown in Figure 9. This weight loss was due to the presence of either moisture or starch which worked as a pore forming agent; during sintering, the starch burnt and left pores behind. Furthermore, some volatile oxides can withstand high temperatures up to 750 °C. TGA was carried out until 1200 °C. From Figure 9, no loss in percentage weight occurred after 750 °C. That is, the ceramic membrane obtained is thermally stable and is ideal to be used for flue gas treatment.

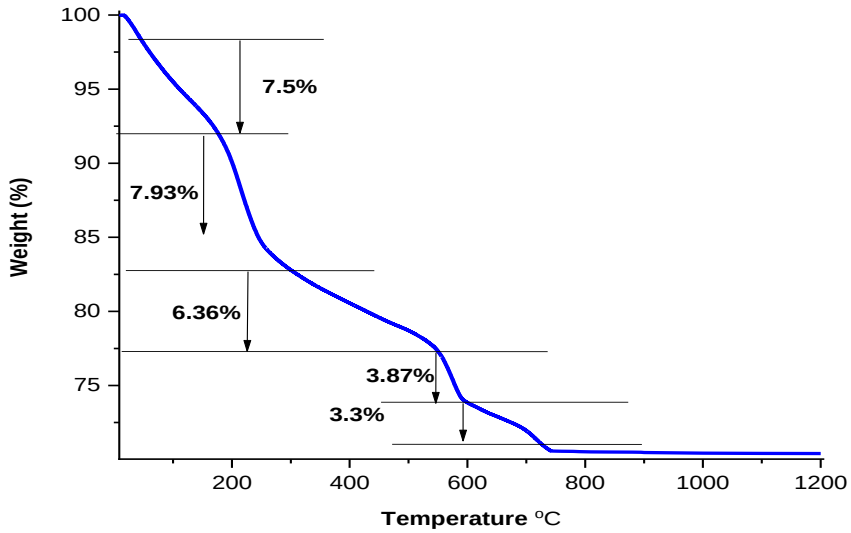

Figure 9. Thermal gravimetric analysis (TGA) result of non-sintered membrane powder

The first derivative of mass percent versus temperature is also displayed to make the graph easy to comprehend. The first derivative was applied to the original picture to determine the maximum temperature peak of each mass loss, which is known as inflection point. Figure 10 shows the highest temperatures at which the ceramic membrane lost some weight: at 212.85 °C because of demoisturisation and starch combustion and at 576.47 °C because of the removal of volatile oxides.

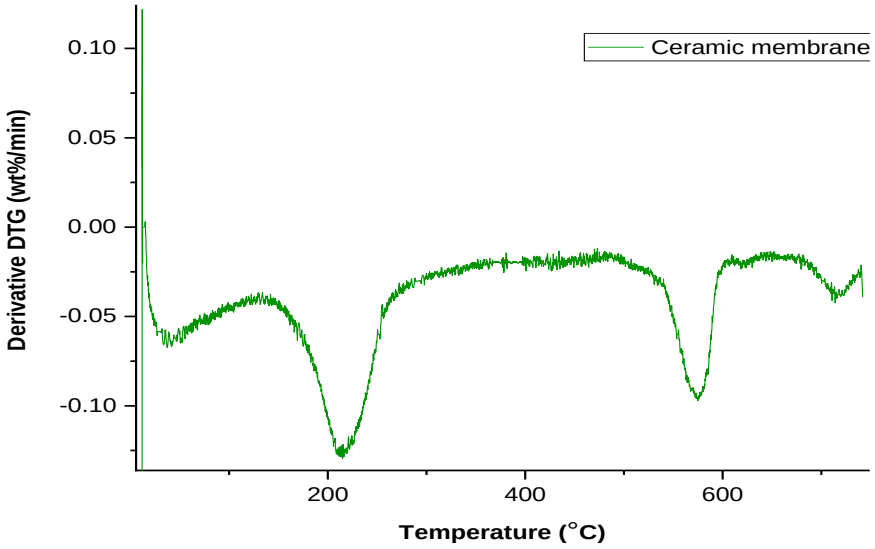

Figure 10. The first derivative DTG of ceramic membrane

4. Visual test

The pilot-scale setup included two parts, as shown in Figure 13. One was a combustion chamber with a chimney. The other was a glass tube containing the membrane sample and a suction pump at the top end (full description: a two-portion glass tube having upper and lower parts containing a porous ceramic membrane in the middle). The lower part was exposed to the flue gases coming out of the combustion chimney. The upper portion was connected with a vacuum pump through a tube. The pump created a vacuum with the suction facility, where the exhaust gases of the chimney were induced through the tube-containing membrane in the middle. The fuel used for combustion was a mixture of tyre and coal powder. The flue gas went through the chimney and then passed through the glass tube, where the membrane was fixed in the middle by the force of vacuum pressure. The results were very satisfactory, i.e. the black smoky particle was stuck on the membrane surface exposed directly to the chimney. The cake produced and the lower part of the tube are shown in Figures 11 and 12, which are comparatively blackish. Hence, a porous ceramic membrane must be used for flue gas treatment.

Figure 11. The Cake of black smoky particle produced at the surface of membrane exposed to chimney flue gases passage, the test took 2 mints.

Figure 12. The glass tube where the bottom end is directly connected with chimney, and upper end is connected with vacuum pump. The membrane is placed at the middle of glass tube. Upper part of the glass tube is less blackish compare to lower part as the flue gas is filtered to some extent.

Figure 13. Pilot scale visual permeability test experimental setup

5. Conclusions

This research article highlights the importance of addressing air pollution as a major contributor to global warming. The study focuses on the treatment of flue gases using a porous ceramic membrane synthesised from calcined Al_2O_3 and activated washed fly ash, along with other additives. The fabrication process of the membrane encountered some challenges, such as cracks, nonactive reactants

and uneven rise or fall during demoisturisation or sintering steps. Nevertheless, the membrane sample exhibited satisfactory results in various characterisation tests, including TGA and DTG; it showed a negligible weight loss after 750 °C. The XRF and XRD results confirmed the ceramic-like crystalline structure of the fabricated membrane. The membrane demonstrated a bulk density of 4.484 g/cm^3, a porosity of 62.5%, an average pore size of 7.6 µm and a mechanical strength of 2.7 MPa. A pilot-scale visual permeability test was conducted for flue gas treatment, involving combusting fuel containing tyre and coal powder. The result showed the compatibility of the fabricated porous ceramic membrane for such applications. Overall, the findings indicate the potential of membrane technology for addressing air pollution and treating flue gases, contributing to efforts in combating global warming.

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