Synthesis of Coal Fly Ash-Based Zeolites for Carbon Capture

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Abstract

In the growing interest of creating novel technologies to combat the rise of CO_2 in the atmosphere, zeolites have emerged as a sustainable solution for carbon sequestration. Zeolites are aluminosilicate-based material that are highly porous, low cost, and highly stable. This research focuses on the production and utilization of hydrothermally-synthesized coal fly ash (CFA)-based zeolites. The CFA type utilised in this study is categorised as Class F, it had a total percentage of SiO_2, Al_2O_3, and Fe_2O_3 as 86.23%. The CFA used in this study was 90-125µm. Loss on Ignition (LOI) for the CFA was also conducted and the median LOI for the samples was 3.95%. During pre-treatment using a permanent magnet, an average of 48.232% of magnetics were removed from the CFA. After synthesis of the zeolites, the samples were analysed and the results showed that the addition of NaOH gradually increased the concentration of sodium oxide (Na_2O) in CFA from an average of 6.34% to an average of 7.23%. The results also revealed a significant reduction in SiO_2 and Al_2O_3 percentage by an average of 43.26% and 40.10% respectively, and the concentration of SiO_2 was always higher than that of Al_2O_3 in all the samples.

The compositions of $SiO_2$and Al_2O_3 gradually increased with an increase in the four controlled variables but started to decrease at higher values of each variable. The zeolites were subjected to a carbon capture test and the highest carbon capture was at 4M NaOH, hydrothermal treatment time of 30 hours, hydrothermal treatment temperature of 120°C and CFA: NaOH ratio of 1:12.5. It was also observed that there was a rapid increase of the adsorption capacity of CO_2 from 10 minutes to 30 minutes followed by a progressively slow increase with the increase in contact time. The adsorption of $CO2$ approached equilibrium within 30 min. The carbon capture test for CFA-based zeolites was then compared with that for the commercial zeolites and the carbon capture capacity of the commercial zeolites was approximately twice that of the CFA-based zeolites.

Key Words: zeolite synthesis, carbon capture, fly ash utilization

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1.0 Introduction

Rapid population and economic growth have led to an increase in energy usage. This has made it necessary to build more sizable coal-fired thermal power plants to meet the demand for the production of electricity. The world's needs for the production of power are largely met by fossil fuels [1].For this reason, it is critical to regulate emissions of gaseous pollutants that are produced during the burning of coal. Consequently, the generation of waste streams and the release of gaseous pollutants continue to be major environmental and economic issues that have led to a global waste disposal catastrophe [2]. The use of less expensive and more efficient adsorbent materials for the CO_2 capture processes has garnered attention in recent years and is acknowledged as a crucial technology for the production of sustainable energy. Recently, there has been a lot of interest in coal fly ash (CFA), a cheap solid substance that makes up roughly 80% of the remaining solid coal combustion [3]. The management of coal fly ash (CFA) presents a formidable challenge in developing countries such as Zimbabwe. Millions of tonnes of coal fly ash are produced annually in Zimbabwe and only less than 5% of this fly ash is used primarily in the cement and building sectors [4]. Too the best of the authors knowledge limited research has been done on the reuse of coal fly ash generated from power stations in Zimbabwe. In this regard, this study explores a way of beneficiating from CFA generated at Hwange power station which is the biggest power station in Zimbabwe. One potential use of coal fly ash is adsorption, although its capabilities are restricted, it can be altered in several ways to improve performance depending on the quality of the CFA. This primarily entails converting fly ash carbons or their derivative materials into derivative porous materials like zeolites and silica, as well as impregnating or grafting them with amine solvents. As adsorption materials, zeolites show great potential in reducing air pollution [5]. Furthermore, air and solid waste pollution can be treated simultaneously.

Compounds containing Si and Al, which resemble zeolite, make up the majority of CFA. Therefore, CFA promotes the synthesis of zeolites [6]. Fly ash can be either classified as Type F or Type C. Alumino-silicate glass, which includes silica, alumina, iron, and calcium, makes up the majority of fly ash. Carbon, magnesium, sulfur, sodium, and potassium are minor components. Fly ash's chemical makeup varies depending on where the coal comes from. For example, fly ashes from softer lignite of sub-bituminous coals give higher calcium content (greater than 10% to greater than 30% CaO) and are lower in silica and alumina (Type C) than ashes from hard bituminous or anthracitic coals, which tend to produce ashes high in silica and alumina but low in calcium (Type F) [7]. Zeolites are crystalline hydrated aluminosilicates of alkali earth cations that are referred to as molecular sieves. Their three-dimensional structure is made up of tetrahedral frameworks that are joined by oxygen atoms [8]. The synthesis process and the final zeolite structure can also be influenced by the characteristics and makeup of the fly ash

The synthesis of CFA-based zeolites involves several factors that can influence the resulting zeolite properties. These factors can affect the adsorption capacity, selectivity and kinetics of CO_2 capture by the zeolites and some of these factors were investigated in this study such as NaOH concentration, hydrothermal treatment time, hydrothermal treatment temperature and CFA: NaOH ratio. Therefore, this project focuses on the synthesis of coal fly ash-based zeolites for carbon capture to mitigate environmental impacts caused by the release of carbon dioxide into the atmosphere and simultaneously reduces land pollution caused by the disposal of coal fly ash. The captured carbon dioxide can be released from the adsorbents, that is, the zeolites, and used for various purposes.

2.0 Materials and methods

In this study, coal fly ash samples collected from Hwange Thermal Power Station, Zimbabwe, were used in synthesis of zeolites. The method of direct hydrothermal treatment with sodium hydroxide of varying concentrations (2.0, 2.5, 3.0 and 4.0 and 5.0 M) at different temperatures (80°C to 160°C), CFA: NaOH ratios (1:5, 1:7.5, 1:10, 1:12.5 1:15) and activation time (18hours to 42hours) was applied [9]. Sieving was carried out to determine particle size distribution. Characterisation of the zeolite material was performed using a XRF machine. The experiments were performed according to the equation,

$$FlyAsh + xNaOH \quad \xrightarrow[temperature]{time} \quad zeolite + radiuum$$

Where x is the concentration of NaOH solutions. The coal fly ash samples were subjected to pre- treatment first before synthesis of the zeolites and their loss on ignition (LOI) was also determined. The effects of alkali concentration, reaction temperature and CFA: NaOH ratio and hydration time on the synthesis of the zeolites and subsequent carbon capture were studied in detail. Figure 1 summarises the steps followed in the synthesis of the zeolites.

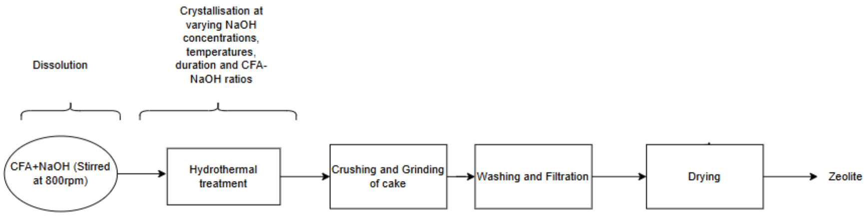

Figure 1: Flowsheet diagram of zeolite synthesis

3.0 Results and Discussion

3.1 Characterisation of Raw CFA

Table 2 shows the XRF results for raw CFA.

Table 2: Raw CFA XRF Results

Components	% Composition
SiO_2	47.95
Al_2O_3	28.23
Fe_2O_3	10.05
CaO	4.97
MgO	0.25
SO_3	2.14
Na_2O	0.34
K_2O	1.18
TiO_2	2.07
P_2O_5	1.78
MnO	1.04

The CFA utilised can is categorised in Class F, it contains a total percentage of SiO_2, Al_2O_3, Fe_2O_3 of 86.23%.

3.2 Particle Size Analysis

Figure 3 shows the particle size distribution curve. Three fractions of CFA were obtained as shown in the figure.

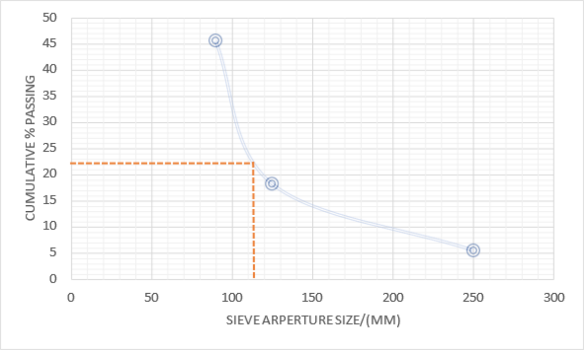

Figure 3: Particle size distribution curve

The percentage passing through between 90µm and 125µm, equates to 63.70%. However, the percentage retained, that is above 125µm is 36.30%. The median particle size (d_{50}) for the CFA is 113.5µm as shown by the dotted line

3.3 CFA Loss on Ignition

ASTM C 618 limits LOI of both Class F and Class C fly ash to 6%. The median LOI for the samples was 3.95%. There are less organic and carbonaceous elements in the fly ash, as shown by the low LOI value. Because organic contaminants might obstruct the development of zeolite phases during the hydrothermal synthesis process, a lower LOI value is typically recommended.

3.4 CFA Pre-treatment

From the pre-treatment process, it was observed that the CFA had a greater proportion of magnetic particles. An average of 48.232% of magnetics were removed from the CFA before the zeolite synthesis procedure. Their inclusion in fly ash has the potential to introduce impurities into the zeolite synthesis process, hence compromising the ultimate product's quality and purity.

3.5 Effect of Synthesis Parameters on Zeolite Formation and CO_2 Capture

3.5.1 Effect of NaOH Concentration

According to Verrecchia *et al.* [10] the optimum NaOH concentration varies between 3.5M and 4M NaOH which is consistent with the results in this research. The addition of NaOH gradually increased the concentration of sodium oxide (Na_2O) in CFA from 6.34% to 7.23% with the increase in NaOH concentration from 2M NaOH to 5M NaOH. The NaOH concentration affects the extent of dissolution and the formation of Na_2SiO_3 and Na_2AlO_2. Additionally, the concentrations of $Si^{4+}$and Al^{3+} were high at 3M and 4M from XRF results. This is because the concentrations of these substances decrease in the following order: 4M>3M>2.5M>2M. Al^{3+}dissolution showed a pattern of increasing with alkali concentration.

3.5.2 Effect of Hydrothermal Treatment Time

The duration of the interaction between coal fly ash and NaOH under particular pressure and temperature conditions is referred to as the hydrothermal treatment time The XRF data comparing the chemical composition of CFA-based zeolite residues obtained at different crystallisation times of 18hrs, 24hrs, 30hrs, 36hrs and 42hrs revealed a significant reduction in SiO_2 and Al_2O_3 percentages. This indicated that insufficient SiO_2 and Al_2O_3 dissolved for crystallisation on the zeolite residues due to impurities which may have been present in raw CFA and possibly lower hydrothermal treatment times. Furthermore, XRF data from the solid products for the 30hr treatment time revealed a higher concentration of Si and Al compared to the other periods investigated.

3.5.3 Effect of Hydrothermal Treatment Temperature

According to studies, the optimal temperature range for zeolite synthesis is between 90°C and 120°C [11,2]. XRF data from the solid products for the 140°C-treatment temperature, revealed a higher concentration of Si and Al compared to the other periods investigated. It was also observed from XRF data that the higher the synthesis temperature, the higher the nucleation of zeolite nuclei at higher temperature. However, the percentage crystallinity decreases sharply at temperatures greater than 140°C as the composition of SiO_2 and Al_2O_3 decreased.

3.5.4 Effect of CFA: NaOH Ratio

Research has indicated that modifying the CFA: NaOH ratio can affect the produced zeolites' surface area, the and SiO_2/Al_2O_3ratio. As the CFA: NaOH ratio grew from 1:5 to 1:12.5, the carbon capture of synthetic zeolites increased and then began to decline, Wang et al. [5] reported a similar outcome. Figure 4 shows the effect of the synthesis parameters on carbon capture capacity of the zeolites.

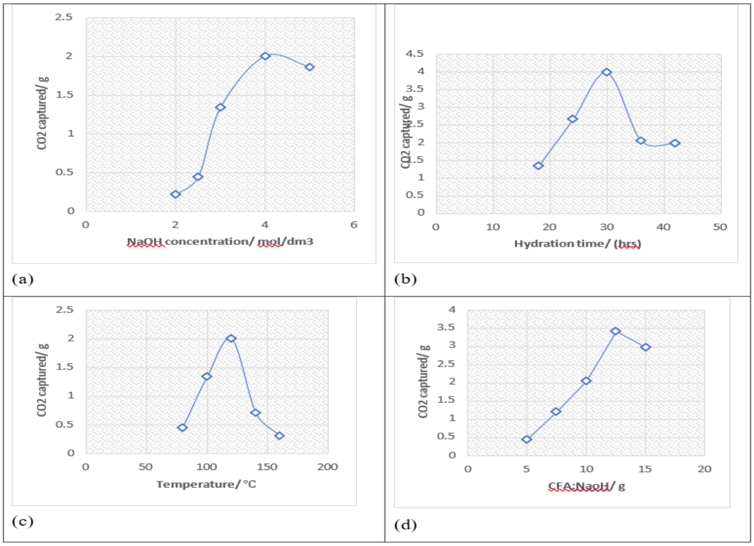

Figure 4: Effect of synthesis parameters on CFA zeolites carbon capture capacity

Figure 4(a) shows that the carbon capture capacity gradually increased from 2M NaOH and reached its peak at 4M, then gradually decreased. The captured CO_2 concentration increased with NaOH concentration due to the increase of Na_2O concentration bonded to the CFA which is crucial for capturing CO_2. Figure 4(b) shows that the carbon capture capacity gradually increased from 18 hours to 30 hours and then drastically decreased. Figure 4(c) shows that the carbon capture capacity gradually increased from 80℃ to 120℃ and then drastically decreased as temperature increased to 160℃. As the fusion temperature increased further, the synthesised zeolite's crystallinity was reduced and non-crystalline sintered glass formed, resulting in a loss in the zeolites' ability to trap carbon. Figure 4(d) shows that the carbon capture capacity gradually increased from CFA: NaOH ratio of 5 to CFA: NaOH ratio of 12.5 and then gradually decreased with the increase in ratio. Throughout the alkali fusion and hydrothermal treatment procedures, hydroxysodalite was formed as a result of more NaOH reacting with soluble silicate and aluminate salts when the CFA: NaOH ratio increased.

Figure 5 shows the effect of contact time on the amount of carbon dioxide captured by the synthesised zeolites.

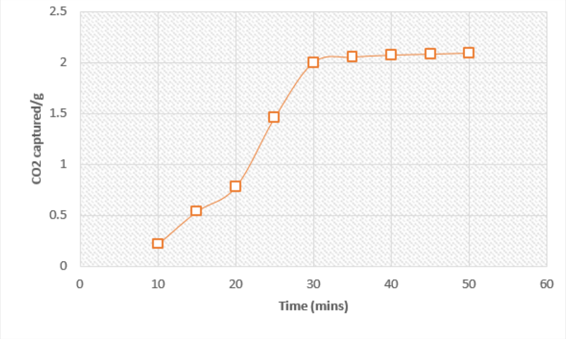

Figure 5: Effect of contact time on the amount of carbon captured

When the contact duration increased, the adsorption capacity of CO_2 increased rapidly from 10 to 30 minutes, then it increased gradually after that. After 30 minutes, the adsorption of CO_2 approximated equilibrium; additional contact time increased just marginally the zeolites' adsorption capacity. There have been reports of a similar tendency [12,13].

Figure 6 shows a comparison between the amounts of carbon dioxide that the commercial and synthetic zeolites are able to extract.

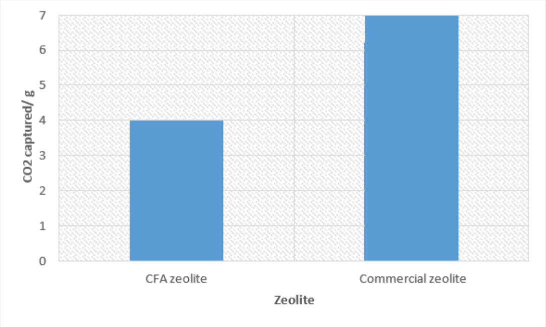

Figure 6:Comparison between carbon dioxide captured by the synthesised zeolites and the commercial zeolites

The carbon capture capacity of commercial zeolites is nearly twice that of zeolites based on CFA. The higher concentration of magnetics discovered in CFA during pre-treatment is the reason for the reduced adsorption capability of the CFA-based zeolites.

Conclusion

Coal fly ash generated from the Hwange power station exhibited the desired characteristics for synthesizing zeolites. The main elements needed for zeolite production, SiO_2 and Al_2O_3 are present in considerable amounts in CFA in the amounts of 42.95% and 31.23% respectively. The framework required for the development of zeolite structures is provided by these components. Moreover, it has sodium (Na) and calcium (Ca). After subjecting the zeolites to a carbon capture test, the highest carbon capture was at 4M NaOH, hydrothermal treatment time of 30 hours, hydrothermal treatment temperature of 120°C and CFA: NaOH ratio of 1:12.5. Due to the higher concentration of magnetics found in CFA during pre-treatment, ineffective CO_2 collection equipment, and ineffective experimental setup, the carbon capture capacity of commercial zeolites was found to be approximately twice that of CFA-based zeolites. This study therefore shows CFA can be utilised to synthesise zeolites for carbon capture and that reaction parameters used in zeolite synthesis and the composition of raw CFA are the major factors affecting the properties of the resulting zeolite and hence the carbon capture capacity of the zeolites.

References

1. Nagarkatti, Kolar. Life Cycle Based Sustainability Index of Coal Power Plants in India | IIETA [Internet]. 2021 [cited 2025 Feb 15]. Available from: https://www.iieta.org/journals/ijsdp/paper/10.18280/ijsdp.160204

2. Zhang Y, Cao B, Yin H, Meng L, Jin W, Wang F, et al. Application of zeolites in permeable reactive barriers (PRBs) for in-situ groundwater remediation: A critical review. Chemosphere. 2022 Dec 1;308:136290.

3. Wilberforce T, Olabi AG, Sayed ET, Elsaid K, Abdelkareem MA. Progress in carbon capture technologies. Sci Total Environ. 2021 Mar 20;761:143203.

4. Mutyavaviri LC, Makepa DC, Chihobo CH. Characteristics and environmental implications of coal fines at Hwange Colliery Company, Zimbabwe: A comprehensive analysis. Results Eng. 2024 Sep 1;23:102743.

5. Wang J, Li D, Ju F, Han L, Chang L, Bao W. Supercritical hydrothermal synthesis of zeolites from coal fly ash for mercury removal from coal derived gas. Fuel Process Technol. 2015 Aug 1;136:96–105.

6. Chai SYW, Ngu LH, How BS. Review of carbon capture absorbents for CO2 utilization - Chai - 2022 - Greenhouse Gases: Science and Technology - Wiley Online Library [Internet]. 2022 [cited 2025 Feb 15]. Available from: https://scijournals.onlinelibrary.wiley.com/doi/10.1002/ghg.2151

7. van der Merwe EM, Prinsloo LC, Mathebula CL, Swart HC, Coetsee E, Doucet FJ. Surface and bulk characterization of an ultrafine South African coal fly ash with reference to polymer applications. Appl Surf Sci. 2014 Oct 30;317:73–83.

8. El Bojaddayni I, Emin Küçük M, El Ouardi Y, Jilal I, El Barkany S, Moradi K, et al. A review on synthesis of zeolites from natural clay resources and waste ash: Recent approaches and progress. Miner Eng. 2023 Jul 1;198:108086.

9. Li X, Hernandez Gaitan JA, Kokuryo S, Sumi T, Kitamura H, Miyake K, et al. Hierarchical zeolites with high hydrothermal stability prepared via desilication of OSDA-occluded zeolites. Microporous Mesoporous Mater. 2022 Oct 1;344:112096.

10. Verrecchia G, Cafiero L, de Caprariis B, Dell’Era A, Pettiti I, Tuffi R, et al. Study of the parameters of zeolites synthesis from coal fly ash in order to optimize their CO2 adsorption. Fuel. 2020 Sep 15;276:118041.

11. Du Plessis P, Ojumu T, Fatoba O, Akinyeye R, Petrik L. Distributional Fate of Elements during the Synthesis of Zeolites from South African Coal Fly Ash. Materials. 2014 Jan 1;7(4):3305–18.

12. Koshlak H. Synthesis of Zeolites from Coal Fly Ash Using Alkaline Fusion and Its Applications in Removing Heavy Metals. Materials. 2023 Jan;16(13):4837.

13. Ren X, Qu R, Liu S, Zhao H, Wu W, Song H, et al. Synthesis of Zeolites from Coal Fly Ash for Removal of Harmful Gaseous Pollutants: A Review. Aerosol Air Qual Res. 2020;20(5):1127–44.

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