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Upscaling of Zeolite Synthesis from Coal Fly Ash Waste: Current Status and Future Outlook

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Abstract

Coal fly ash has been recognised as suitable feedstock for zeolite synthesis, and with this discovery, there has been much literature produced over the years on various synthesis processes with a view to address the disposal problems associated with fly ash wastes. The different synthesis processes can be divided into a pre-synthesis activation with an alkali solution and a hydrothermal synthesis of heating the resulting aluminosilicate gel. However, the challenge lies in up scaling the synthesis to allow production on a commercial scale. The most common pre-synthesis involving high-temperature fusion of fly ash with sodium hydroxide may not be feasible in an economic context, given that a large-scale furnace that would be needed. In this review, the successes recorded in the application of acoustic cavitation by using ultrasonication technique were discussed as a possible alternative to the fusion process on one hand. On the other hand, jet-loop reactor system provides hydrodynamic cavitation, which may be relatively scalable compared to ultrasonication and may offer an economic advantage, if systematically explored, over fusion process for large-scale synthesis of zeolites. It is also recommended that agitation is critical during the crystallisation process and the suitability of an impeller type that offers a minimum shearing to be explored during the hydrothermal process with respect to quality and yield of the zeolite produced. The understanding gleaned from these recommendations may be useful in designing an appropriate scale-up operation for zeolite synthesis from coal fly ash.

Keywords: fly ash, zeolites, up scale, jet loop, hydrothermal agitation

1. Introduction

It has been 30 years since the discovery by Holler and Wirsching that zeolites can be synthesised from coal fly ash [1]. It was found that the coal fly ash contained the necessary elements, namely silicon and aluminium, which are building blocks of the zeolitic structure. This has spawned substantial research into zeolite synthesis from coal fly ash with a view to create outlets for fly ash utilisation, thereby solving the worldwide problem of coal fly ash disposal. Coal fly ash is produced during the coal combustion process, and it is the most predominant coal combustion by-product [2]. The electricity generated from coal combustion accounted for 29.9% of the world's electricity supply in 2011, and this is expected to increase 46% by 2030 [3]. Therefore, there are concerns with the high volumes of coal fly ash waste being produced.

In South Africa alone, approximately 36 million tonnes are produced per annum with 95% of that being dumped in ash dumps [4]. When it is seen that South Africa only accounts for 2.4% of the world coal consumption, it becomes apparent of the scale of coal fly ash produced worldwide. Especially, concerning the large-scale world coal consumers, such as China (50.2%), United States (11.7%), and India (8%) [3], it has been reported that China produced 540 million tonnes of coal fly ash in 2011 with only 68% being reused, while about 61% of the 163.56 million tonnes of fly ash produced in India between 2012 and 2013 was reused [3]. This poses risks to the environment and surrounding populations of these ash dumps. This is due to coal fly ash having the potential to leach toxic heavy elements into the groundwater system [5] and poses a threat to person's health if inhaled [6]. Due to the problem of coal fly ash disposal, many studies investigated its use with regard to different applications, such as in agriculture, in construction, in wastewater treatment, and for the synthesis of geopolymers and zeolites as can be seen in a recent review [3]. The views of these studies were to find outlets for the utilisation of this waste, thereby addressing the disposal problems. However, these applications have not solved the problem of coal fly ash disposal, as they are not at the scale required to deal with the high volumes of coal fly ash being produced.

There is a need to investigate further into the feasibility of scaling up some of these applications. Although recent studies have been focusing on some fundamental investigations regarding scale-up development for the synthesis of zeolite from coal fly ash [7, 8], there remains a significant amount of studies to be conducted in order to realise the end goal of synthesis on a commercial scale. This book chapter aims at giving a review of the work that has been produced regarding the synthesis of zeolites from coal fly ash with a view to recommending outstanding investigations to be carried out regarding the up scale of zeolite synthesis from coal fly ash. It will justify the necessary procedures that need to be studied in the future to realise the end goal of large-scale zeolite synthesis from coal fly ash.

2. Coal fly ash

Coal fly ash is mainly composed of silica (SiO_2), alumina (Al_2O_3), ferrous oxide (Fe_2O_3) and calcium oxide (CaO) with also some unburned carbon detected through loss on ignition tests

(LOI) [9, 10]. The chemical properties depend on the type of coal being burned, along with handling and storage procedures [3, 9, 10]. This gives rise to the high variability in coal fly ash compositions obtained from different batches of coal processed in the same power station [8]. The major and minor elements in coal fly ash are expressed as oxides, with the main ones being already mentioned previously. However, it also consists of trace elements, with some being As, B, Ba, Be, Cd, Co, Cr, Cu, Ge, Hg, Li, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, U, V and Zn [10]. The major phases of coal fly ash are amorphous glass, mullite and quartz with various others in smaller amounts [10, 11]. A recent comprehensive study by Musyoka [12] on the mineral phases of South African coal fly ash reported that the ash yielded percentage amounts ranging from the more amorphous content of 57.54% to less amorphous content of 41.55%. The mullite ranged from 34.55 to 22.27% and the quartz from 21.38 to 11.92%. Another comprehensive study was performed by Vassilev and Vassileva [11] on coal fly ash from Spain, Bulgaria, the Netherlands, Italy, Turkey and Greece. The amorphous content ranged from 85 to 34%, the mullite from 40 to 0.3% and the quartz from 14 to 2%.

Furthermore, the combustion rate and temperature of the coal combustion process affects the morphology of the coal fly ash particles [10, 13]. Coal fly ash mainly consists of spherical particles, such as solid spheres and hollow spheres (cenospheres), with some irregular unburned carbon, as determined by scanning electron microscopy (SEM) analysis [3, 13]. The colour of coal fly ash ranges from water white to yellow, orange to deep red or brown to opaque and is due to the iron and unburned carbon content [3, 14]. Coal fly ash containing more than 70% $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and having a low lime content of 5% is classified as class F fly ash, while if the $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content is between 50 and 70% and a high lime content of between 10 and 35%, it is classified as class C fly ash [9, 10]. It follows from the aforementioned that class C fly ash can be produced from lignite and sub-bituminous coal while class F from bituminous and anthracite coal [10, 11].

There have been numerous studies investigating the leachability of coal fly ash into the groundwater system that surrounds the ash dumpsites [5, 15–26]. In a more recent article by Nyale et al. [5], it was reported that the disposed ash at the dump site was able to release trace elements into the environment over time, and the study revealed that all the trace elements studied (As, Zn, Pb, Ni, Mo, Cr and Cu) were significantly leached from the labile phases (4.42–27.43%). The inhomogeneity of the ash dump was also attributed to the observed differences in the elements leached from varying core samples. Besides this type of environmental problem, the potential threat of coal fly ash to the health of the surrounding population and the mine workers exposed to the ash has been reported [6]. The leachability of genotoxic compounds from fly ash into human lungs if the ash dust is inhaled has been reported [6], and conditions such as lung cancer, asthma and many others are typical diseases attributed to fly ash inhalation [6, 27].

However, there have been several studies that investigated potential application of fly ash with a view to mitigate the disposal of this fly ash; some of the applications investigated include uses in agriculture, construction, extraction of rare earth elements, wastewater treatment and synthesis of geopolymers and zeolites [3]. Furthermore, only 5% of coal fly ash is being re-used as reported by Eskom [4]. A comprehensive and recent review of some of the applications of

coal fly ash is reported by Yao et al. [3]; however, these authors recommended the need to explore commercialisation of the applications. The following section will focus on the various synthesis methods employed in the application of coal fly ash for zeolites synthesis and assess studies aimed towards the up scale of the synthesis process.

3. Zeolites

Zeolites are crystalline aluminosilicates of which possess cavities and pores on a molecular scale [28]. They do occur as natural minerals but are more useful being synthetically produced in laboratories for uses such as sorbents, catalysts and exchange materials [28]. The zeolite consists of SiO_4 and AlO_4 tetrahedra of which gives it an anionic framework with the negative charge of Al being compensated by extra framework cations, some being Na^+ , K^+ , Ca^{2+} and Mg^{2+} [29]. This can be illustrated in **Figure 1**.

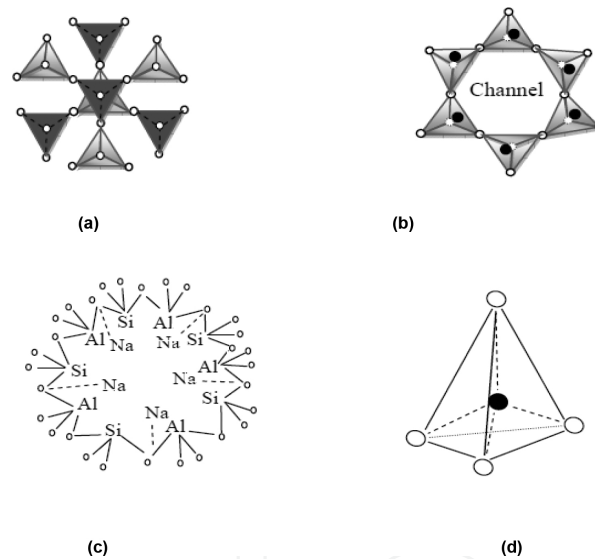


Figure 1. (a) Basic tectosilicate structure of zeolite where dark (i.e. vertex in) and light (i.e. vertex out) shades to add three-dimensional (3D) effect and upside down orientation of the tetrahedra for vertex sharing between two rings of the zeolite structure in its 2D view on a picture plane; (b) single-ring tetrahedron structure and framework of a zeolitic mineral; (c) $\langle i \rangle \text{SiO}_4^- \langle i \rangle$ and $\langle i \rangle \text{AlO}_4^- \langle i \rangle$ in a ring of sodium zeolite; and (d) pictorial representation of a 3D view of a tetrahedra with centrally located Si or Al atoms, exhibited by dotted lines drawn to represent the portion within the body of the mineral [30].

The primary building units of the zeolite structure are shown in **Figure 1(d)**, and they are TO_4 tetrahedra of silicon and aluminium mentioned previously [29]. There is a concept of infinite component units with the zeolite structure regarded as being made of finite component units with infinite component unit-like chains or layers, these are known as the secondary building units, some illustrated in **Figure 2**. The secondary building units can consist of single or double rings with each of those consisting of four-, five-, six- or eight-linked tetrahedral, including the silicon and aluminium atoms [30].

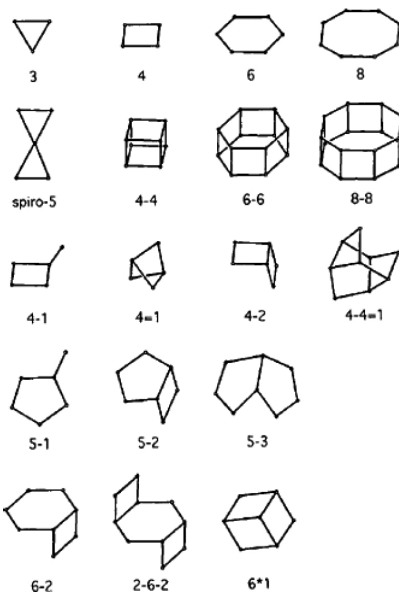


Figure 2. Secondary building units (SBU's) with SBU codes below figures [29].

The varying framework structures seen above give rise to the unique three-letter code system to name each unique zeolite, some of these codes along with the pore sizes of some zeolites are shown in **Figure 3**.

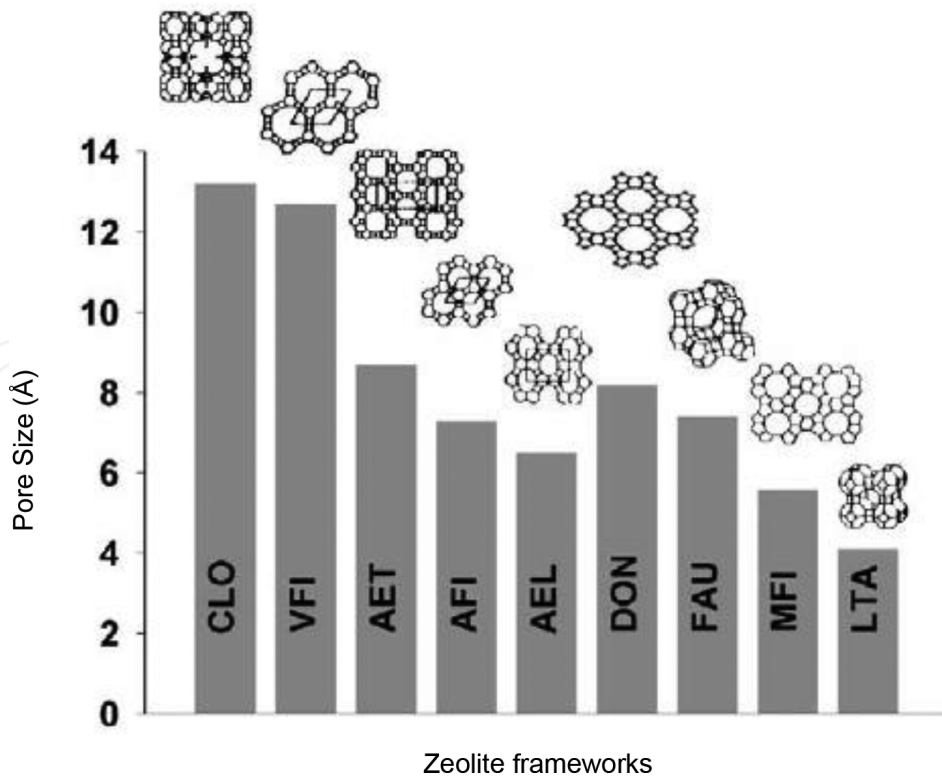


Figure 3. A comparison of the different framework pore sizes [31].

4. Synthesis of zeolites from coal fly ash

As mentioned previously, the synthesis of zeolites from coal fly ash began with the pioneering work of Holler and Wirsching in 1985 [1]. Researchers have found a number of synthesis methods to produce various types of zeolites from the coal fly ash [32–42]. All known synthetic methods can be found on the website of International Zeolite Association (IZA) at URL: <http://www.iza-online.org/synthesis/default.htm> [43]. However some of the prominent methods are reviewed in this section.

All the methods developed mainly involve the dissolution Al-Si bearing fly ash phases with alkaline solutions such as NaOH and KOH with the proceeding precipitation of zeolitic material [2]. The two most well-known routes for fly ash conversion to zeolite are the fusion with sodium hydroxide process developed by Shigemoto et al. [32] and a two-step process developed by Hollman et al. [35]. The two-step process developed by Hollman et al. [35], which followed from the traditional one-step process produced more “pure” zeolites; however, the process was relatively more costly. A comparison of the one-step and two-step process can be seen in **Figures 4** and **5**, respectively. Shigemoto et al. [32] developed the fusion process where coal fly ash is fused with sodium hydroxide using a high temperature, prior to hydrothermal treatment. A ratio of CFA:NaOH of 1:1.2 was optimum with a fusion temperature of 550°C, and this converted the fly ash particles into sodium salts. These salts (silicate and aluminate) after the hydrothermal treatment favoured the formation of zeolite Na-X. The process is illustrated in **Figure 6**.

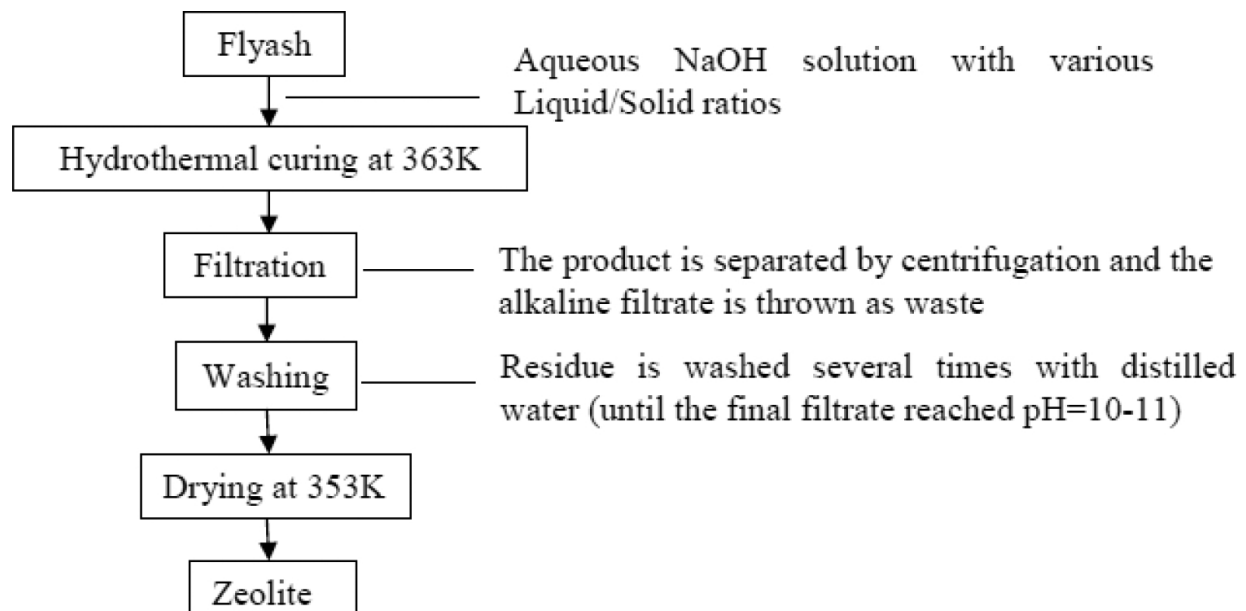


Figure 4. Flow diagram of the traditional one-step process [30].

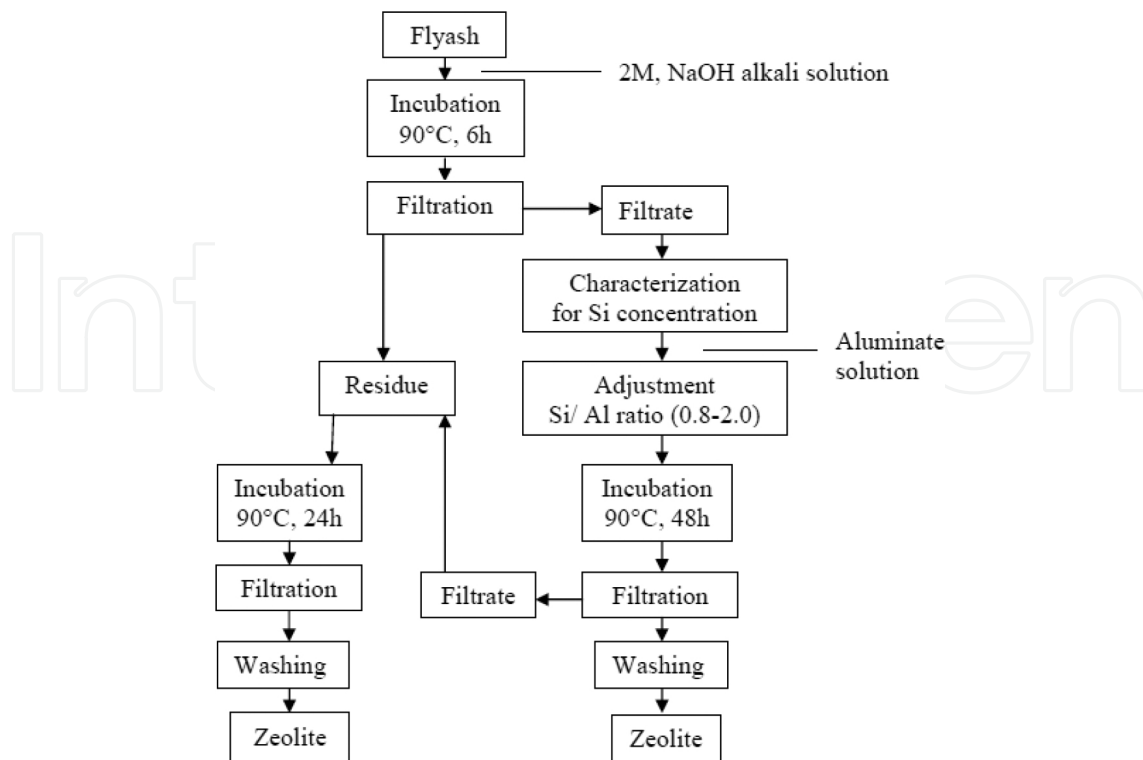


Figure 5. Flow diagram of two-step process [30].

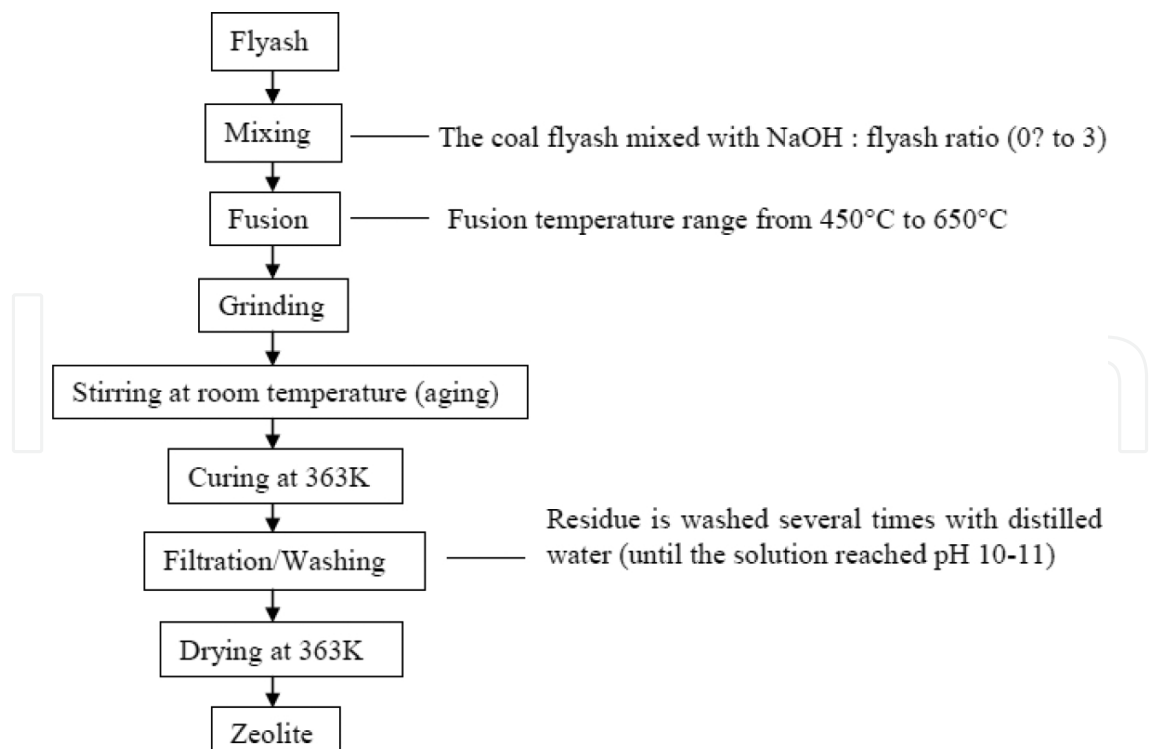


Figure 6. Flow diagram of the fusion-assisted process [30].

Murayama et al. [36] investigated the synthesis of zeolites from coal fly ash using different alkali sources, namely NaOH, Na₂CO₃ and KOH. It was found that regarding the reaction mechanism that three steps exist in an alkali hydrothermal reaction, namely dissolution, condensation and crystallisation. The dissolution step begins at a temperature range of 298–393 K with the amount of OH⁻ in the alkali solution making a great contribution to the reaction. The concentration of Na⁺ in the alkali solution mainly determined the total reaction rate of the zeolite synthesis.

Not only the degree of zeolitisation is affected by the NaOH concentration but also the type of zeolite formed. This is according to Molina and Poole [44] who noted the difference found in the zeolite product was due to the increase in supersaturation achieved from the higher proportion of soluble species from the rise of the NaOH concentration. This phenomenon can be described by the Ostwald's rule of successive transformation with the higher the supersaturation, better the conditions are to nucleate metastable phases [44]. An example being zeolite X which later recrystallises and is replaced by the more stable zeolite hydroxysodalite. Some other factors affecting zeolite formation from coal fly ash are the SiO₂/Al₂O₃ ratio in the feedstock, the NaOH concentration as mentioned previously, the extra framework cations, the water content, the synthesis time and temperature and the agitation used in the zeolite synthesis.

Regarding the SiO₂/Al₂O₃ ratio Inada et al. [38] demonstrated the dependence of this ratio in zeolite synthesis. Two differing zeolites were formed from a silica rich fly ash (zeolite Na-P1) and an alumina-rich fly ash or silica lean fly ash (hydroxysodalite) with the ratio being controlled with SiO₂ and Al₂O₃ aerosil powders. According to Querol et al. [45], this ratio depends on the compositions of these species within the aluminosilicate glass phase of the coal fly ash and not on their bulk composition in the fly since this phase is the first to be activated.

Murayama et al. [36] also showed how the choice of cations could significantly alter the reaction to form one zeolite crystal over another. The Na⁺ ions promoted the formation of zeolite P, while the K⁺ ions promoted the formation of chabazite. Indeed, zeolite synthesis was shown to be favoured by the use of Na⁺ ions over K⁺ ions [46, 47]. This is due to Na⁺ ions stabilising the secondary building units of the zeolite frameworks, while K⁺ ions act as a suppressor due to their promotion of slow crystallisation rates [47].

There is a problem when it comes to zeolite synthesis regarding the water content used. This is due to the increase in water content resulting in an increase in yield when using fly ash as the starting material. This is because the higher water content results in the increase in the crystalline and amorphous phases dissolution rates in the coal fly ash [46, 48]. This led to investigation of using alternate water sources, such as investigating using tap water, distilled water and acid mine drainage (AMD) in the replacement of ultra-pure water. It was reported by Mainganye [8] that tap water and distilled water could produce similar products as the ultra-pure water, while AMD water, however, was not suitable. Musyoka et al. [49] established that AMD could yield hydroxysodalite—a zeolite with less application. However, it was found that circumneutral mine water produced a comparable quality of Na-P1 and X zeolites to ultra-pure synthesis. Zeolite X and ZK-5 were successfully synthesised using seawater at lower temperatures with hydroxysodalite also being formed; however, zeolite A could not be

achieved [42]. Artificial seawater was used at room temperature (25°) to crystallise zeolites A and X in a later study [50].

The thermodynamic stability of zeolite has been reported by Boycheva et al. [51] to follow the sequence in the order of Linderite --> Faujasite --> Chabazite --> Na-P1 --> Hydroxysodalite. It has been observed previously in the transformation of faujasite into more stable phases such as chabazite and Na-P1 at longer synthesis times in the reactant liquor [37, 51]. Due to this metastable behaviour of zeolite X, its formation is always competitive with hydroxysodalite, zeolite X favouring the lower temperatures [42, 51]. It is also known that a higher temperature produces zeolites of a greater particle size [44]. It was found that aluminium dissolution tends to be faster than silicon, of which the two need to be continuously dissolved to promote and feed crystal growth, the silicon dissolution increasing with temperature [44]. Therefore, the Si/Al ratio will favour the formation of zeolite X over A at higher temperatures. When the glassy content is high, the synthesis time drops, while a high content of quartz and mullite requires longer reaction times [2].

Inhomogeneous mixtures can result due to inadequate mixing which in turn has a dramatic effect on zeolite synthesis, this is pertaining to the viscous gel produced before the crystal growth step [52]. These inhomogeneous mixtures produce “pockets” of gel each with differing compositions and each acting like a “mini-reactor”, producing phases based on that “mini-reactor's” composition. The effect of agitation is not well understood and this is due to mixing having to perform the following tasks during crystallisation [52]:

- Reagent dissolution
- Initial gel formation
- Maintaining a homogenous gel
- Aiding in gel structure break-up
- Maintaining a uniform temperature across the reactor
- Transferring “nutrients” to the growing crystals
- Keeping the zeolite crystals in complete suspension on completion of the reaction

The substantial change in viscosity during synthesis is also an important factor to consider. The solution can go from a viscous gel to something resembling water during the course of synthesis [52]. Marrot et al. [53] explained another important factor in agitation, that of shearing, of which can have harmful effects on zeolite synthesis. This can affect the stability of the zeolite and the purity of which can be synthesised. The highest crystallinity was produced by the Archimedes screw impeller due to the low rate of shearing, while higher shearing resulted in lower crystallinities [53]. Agitation during the ageing step of synthesis was investigated by Mainganye et al. [54]. It was shown that agitation during the hydrothermal step of synthesis can have a harmful effect on the stability and purity of the zeolite regarding the shearing produced [53, 54]. It was thought that, during the aging step, shearing may favour the zeolite formation due to it facilitating the dissolution of coal fly ash into the alkaline solution. The four-blade impeller was found to optimum for zeolite synthesis, applied during

the ageing step [54]. It is noted however that regarding the up scale of zeolite synthesis, the hydrothermal reactor used would also need to implement a form of agitation given the need to maintain a homogeneous mixture [55]. From the above analysis, Archimedes screw may be a favourable impeller during the hydrothermal synthesis due to its low rate of shearing; however, further research is required to ascertain this assumption. The synthesis gel that is used in the stage of hydrothermal synthesis varies considerably from the solution during aging. There is a need to understand the effect of agitation during hydrothermal synthesis. Homogenous mixing is critical if large-scale production is envisioned, a large-scale reactor would need to implement some form of agitation.

There have been significant studies on the use of class F fly ash for zeolite synthesis, which is pioneered Musyoka et al. [12, 56, 57]. The more recent studies have focused on using alternate techniques such as ultrasound to either used after fusing to decrease the hydrothermal synthesis time [12, 58], and the temperature needed in hydrothermal synthesis [58, 59] or complete replacement of the fusion process [60]. A reduction in synthesis time was also noted by Musyoka et al. [61] when using ultrasonic synthesis using AMD and circumneutral mine waters in place of ultra-pure water. In addition, studies have also shown that ultrasound techniques can be used to investigate the formation mechanism of zeolites from coal fly ash using in-situ ultrasound techniques, namely of the zeolites A and X (zeolite X with novel hierarchal morphology) [57]. According to Murayama et al. [62], the three main steps involved in the mechanism of zeolite formation from coal fly ash are as follows:

- Dissolution of Si^{4+} and Al^{3+} in coal fly ash
- Condensation of silicate and aluminate ions in the alkali solution making the aluminosilicate gel
- Crystallisation of the aluminosilicate gel-forming zeolites

The above process can be represented pictorially in the following **Figure 7**.

Another technique used is microwave-assisted synthesis as reported by Querol et al. [64]. The activation time need during hydrothermal conversion was radically decreased from 24–48 hours to 30 minutes. It was further explained by Inada et al. [65] that continuous microwave irradiation retards the formation of zeolite in crystalline form, inhibiting the zeolite in the intermediate gel. It was found that early microwave irradiation enhances the zeolite formation. Heating during the middle stage, however, significantly inhibits zeolite formation. Therefore, it was found to be advisable to heat with microwave irradiation early on and then follow with conventional heating.

The feasibility though of scaling-up these alternate processes, such as microwave and ultrasonic-assisted synthesis, would prove challenging regarding the scale needed for large-scale zeolite synthesis. Ultrasound seems promising given its use of cavitation to produce high temperatures and pressures or “hot spots” under nearly ambient conditions [66]. The main form of cavitation being studied is acoustic cavitation generated by sound waves in which ultrasound generates, grows and collapses the cavities in microseconds. These hot spots can

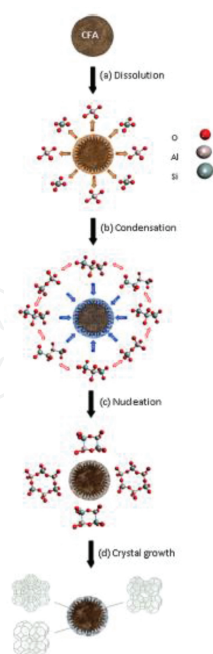


Figure 7. Illustration of the zeolite process of a coal fly ash particle [63].

produce temperatures greater than 5000 K and a cooling rate greater than 10^7 °C/s [60]. In a recent study by Ojumu et al. [60], the 90-min high-temperature fusion was completely replaced by a 10 minutes of high intensity ultrasound irradiation. It was shown that 24% of silicon was extracted from the fly ash, comparable to the 32% from fusion. It also reduced the crystallisation time of zeolite A and would be promising for up-scaling. On industrial scale, there is hardly any process carried out, which allows for up scale of the process. This is due to the lack of expertise in differing fields such as material science, acoustics, chemical engineering, etc. [66]. Hydrodynamic cavitation offers a cheaper alternative. It concerns generating cavitation from the flow of a liquid under controlled conditions through obstructions such as venture tubes and orifice plates. It is generated when the pressure at the throat falls below the vapour pressure of the liquid, the liquid then flashes and generates a number of cavities. When the pressure is recovered downstream of the mechanical constriction, these cavities then collapse [66–68]. The hydrodynamic cavitation is applied on a pilot plant scale within a jet loop reactor. In a study involving the scaling-up of a process to reduce sulphate concentrations within neutral mine drainage, a jet-loop reactor was used [69]. The study showed that the impingement and cavitation mixing techniques applied within the jet-loop reactor played an important role in enhancing the sulphate removal. This was due to the superior mixing in a jet-loop reactor compared to the laboratory-scale experiments that were also performed. The feasibility of scaling up a jet-loop pilot plant to full-scale seems more easily achieved than what would be needed to scale-up the high-intensity ultrasound process. Therefore, it may be necessary to investigate the application of a jet-loop reacting system incorporating fly ash and sodium hydroxide to ascertain the dissolution rates of the silicon and aluminium that can be achieved. A recent study by Nyale et al. [27] showed that the intense mixing within the jet-loop reactor

increased the dissolution of the amorphous content of the fly ash used in the production of geopolymer from a slurry obtained from a jet-loop system. This may prove favourable for zeolite synthesis; however, systematic studies that investigate the potential to use jet-loop reactor as a process to completely replace the high-temperature fusion need to be conducted. This would involve comparison of jet-loop reacting system to the recent studies of involving ultrasound utilisation to determine which process might be more lucrative to up scale.

5. Up-scaling zeolite synthesis from coal fly ash

Querol et al. [48] ran experiments at pilot scale using a 10 m³ R-410-A reactor vessel; the optimum conditions were generated from laboratory-scale experiments using Parr digestion bombs: they were found to be 2 M NaOH solution, solution/fly ash ratio of 21 kg⁻¹, $T = 150^{\circ}\text{C}$, and time of 24 hours. It was concluded that the optimisation of synthesis yields would have to be specific for each type of fly ash from the differing power plants due to their difference in mineralogical and chemical compositions. There were reproducible results, however, in synthesising zeolite NaP1 from a specific power station fly ash. Also, high cation-exchange capacities (CEC) were reported for ammonium and heavy metals for the varying zeolites achieved.

Moriyama et al. [70] compared the CEC values of a conventional method of synthesis to a test unit and a pilot plant. The conventional method conditions were a liquid–solid ratio of 8 dm³/kg, a temperature of 373 K and a holding time of 24 hours. The test unit consisted of a high-pressure kneader with a volume of 5 dm³ fitted with a hot oil jacket around the pressure vessel. It was equipped with two sigma-shaped blades for kneading and a steam exhaust line to remove the water. The pilot plant was also a high-pressure kneader but at the volume of 0.6 m³. This process had benefits of water removal during operation eliminating wastewater treatment. It was concluded that the influence of the pressure on the CEC values obtained depends on the original coal fly ash characteristics and the type of zeolite formed was gismodine (GIS) type.

Mainganye et al. [54] investigated the effect of the impeller design concerning agitation during the ageing step of zeolite NaP1 synthesis. Three impellers were tested (four flat blade, anchor and Archimedes screw) at varying agitation speeds (150, 200 and 300 rpm). The conditions were 48 hours of aging at 47°C and static hydrothermal treatment of 48 hours at 140°C. It was shown that the phase purity of the zeolite was strongly affected by the agitation rate and type of impeller used during the ageing step of synthesis. The optimal impeller was the four-blade impeller at an agitation rate of 200 rpm under the previous conditions mentioned, with a product yield of 0.98 ± 0.05 g zeolite/g fly ash and a space time yield of 15 ± 0.4 kg d⁻¹m⁻³.

Du Plessis et al. [71] developed waste minimisation protocols for zeolite synthesis from coal fly ash. The study effectively constructed two protocols for the minimisation of the waste generated in zeolite synthesis from South African coal fly ash. It was shown that to successfully synthesise zeolites with the waste solution, there needed to be a pH adjustment giving the opportunity to recycle 40% of the supernatant waste back in to the system. With this pH

adjustment, zeolites NaP1 and analcime were successfully synthesised. Due to a high Si/Al ratio in the waste after reusing the supernatant, the more predominant phase was zeolite analcime. It was also shown that it is possible to recycle 100% of the supernatant waste without adjusting the alkalinity but by adjusting the basic synthesis process slightly.

Du Plessis et al. [72] determine the distributional fate of elements during two of the most prominent zeolite synthesis methods from South African coal fly ash, namely the fusion process and the two-step process. An overall elemental material balance was performed around the two process routes. The results indicated that in the two-step method, almost all the elements were concentrated in the solid zeolite product, while in the fusion-assisted process, the elements mainly report to the solid waste. It was shown that toxic elements such as Pb, Hg, Al, As and Nb were found in both the supernatant waste and washing water within both processes.

Wdowin et al. [55] developed a technological line for converting coal fly ash to zeolites on a pilot plant scale. It could be divided into four stages: a reactor loading stage; a reaction stage; separation of the reaction products stage; and a final stage for processing the material obtained. The total volume of the reaction tank was 130 dm³ (with a working volume of 100 dm³). The tank was equipped with three 2-kW heaters, a temperature and tank filling probe and a stirrer. The stirrer was responsible for the homogenisation of the material and prevented aggregation of the material during the reaction process. The zeolite NaP1 was synthesised with a zeolite content of 81% under the conditions of: 20 kg fly ash; 12 kg NaOH; 90 dm³ of H₂O; temperature of 80°C; and duration of 36 hours. The line was fully automated and was able to synthesise zeolites Na-X and Linde-A after changing of the synthesis conditions.

6. Future outlook towards up-scaling zeolite synthesis from coal fly ash

As can be seen from majority of the literature regarding zeolite up-scale synthesis from coal fly ash, the main zeolite being investigated is Na-P1. It is proposed that future investigation should focus on whether the faujasite zeolite (zeolite X) can be synthesised and targeted for large-scale production. Zeolite X is important, being the most widely employed zeolites on industrial scale and used extensively as a fluid catalytic cracking catalyst for refining oil and as materials for adsorbing and removing gaseous emissions [73]. In view of the recent study by Musyoka [12] on the synthesis of zeolite X with novel hierarchical morphology from the clear extract of fused fly ash with NaOH, a significant breakthrough would be to target the zeolite with such novel morphology for up scale. The hierarchical pore structure enables the zeolites to have maximum structural functions in a limited space and volume, thus conferring a high degree of diffusion efficiency [73]. This synthesis route would be much more advantageous over the complicated procedures reported in literature to obtain the hierarchical structured zeolites.

The hydrodynamic cavitation provided in jet-loop reacting system should be explored as suitable alternative to replace the high-temperature fusion process for a large-scale production process. Following from Nyale [27], who showed that the jet loop increased the amorphous

content within the fly ash and reduced the amount of quartz and mullite, which would favour the synthesis of zeolites. It is reasoned that the same method could therefore be used for zeolite synthesis in the replacement of the fusion pre-synthesis. Although in Nyale's study, the goal was to synthesise geopolymers. However, zeolites and geopolymers are very similar regarding their atomic structures of silicon and aluminium atoms. Also, the jet-loop geopolymer produced leached significant amount of silicon which could be used for zeolite synthesis after a curing/leaching process of the slurry produced by the jet loop. This in turn could increase the yield of zeolite by creating a filtrate concentrated in the necessary silicon and aluminium.

Agitation is critical in the up scale of zeolite synthesis from coal fly ash; however, the challenge is to determine the effect of the impeller type and agitation during the hydrothermal treatment stage of the process. Although it has been shown that impeller type and agitation rate have a remarkable effect during the ageing step of zeolite synthesis [54], there is need to investigate these effects during the crystallisation process. It is postulated that impeller type that provide minimum shearing effect would be suitable during the hydrothermal process. At an industrial scale, stirring would need to be required not only to ensure homogeneity but also to ensure uniform heat distribution necessary for the crystallisation step. There have not been in depth studies to show the effect of agitation during the hydrothermal treatment process. Although the recent agitation used by Wdowin et al. [55] to synthesise zeolites from coal fly ash recorded 81% pure phase product, the purity could be due to the shear stress effect of the mechanical stirrer during the hydrothermal treatment process [54]. It is also not clear whether a pure zeolite would have been obtained if the clear filtrate was used instead of the total slurry. The aforementioned highlights the need for an in-depth studies into agitation during the hydrothermal process. The results of such studies might hold the promise for a large-scale synthesis that provides the highest and most pure yield of zeolite.

7. Conclusion

This review highlighted the present status and future outlook with respect to up-scaling of zeolite synthesis from coal fly ash. Although current studies have demonstrated that the seemingly energy-intensive fusion pre-synthesis step can be avoided by using the acoustic cavitation technique provided by ultrasound devices, the scalability of this device for large-scale production remains a subject of debate. The hydrodynamic cavitation provided by a jet-loop reacting system may be a suitable alternative. However, there is a need for systematic studies that would investigate the potential of jet-loop system, in comparison with the fusion and ultrasound pre-synthesis steps, for the dissolution of the silicon and aluminium from the coal fly ash. The critical need for agitation and suitable impeller type, during the hydrothermal synthesis on a large scale, was outlined with an emphasis on the requirement for minimum shearing during crystallisation in large hydrothermal stirred reactors. It is expected that these recommendations would provide understanding towards the design of an appropriate scale up operation for zeolite synthesis from coal fly ash.

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