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Technology**

**School of Chemical Technology  
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**SYNTHESIS AND CHARACTERIZATION OF ZEOLITE FROM WASTE  
COAL FLYASH FOR TAILORED APPLICATION IN BIOREFINING AND  
PROCESS WATER CLEANING: AN INNOVATIVE APPROACH  
TOWARDS A CLEANER CIRCULAR ECONOMY**

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### Abstract

The purpose of the investigation was to assess if Finnish coal flyash (CFA) waste could be used to synthesize zeolites. The world produces 750 million tonnes of CFA annually which is also the largest quantity waste produced. This figure will only increase as India, China, South America and Africa charges ahead with industrialization. The global recycle rate is 15% annually. Finland produces about 750,000 tonnes of CFA per year. It is also estimated that millions of tonnes of CFA is backfilled globally. Hence there is great potential to use it for high value applications as the raw material security exists. There are also disposal and environmental issues related to CFA which makes it our obligation to find a great solution. The recent trend towards circular economy, waste to value, sustainability, EU and National environmental legislations also provides a great platform to find a solution. Other reasons have been analysed from engineering, policy making, markets, scientific & innovation, national and regional impact, international trade, geographic location and future study perspectives.

The literature section provides insights into CFA, structure, transformation, mechanism, combustion process, applications, environmental issues etc. The Zeolite section gives a deep understanding of origin, history, classification, trends in development, structure, morphology, applications, properties, circular economy context of zeolites, synthesis methods, raw material variations etc. There are 174 zeolite framework types in zeolite families and we put special emphasis on NaX (Faujasite framework) with tailored descriptions. The literature highlights CFA Zeolites, its differences with pure chemical ones, synthesis methods, previous works and global pilot projects.

Conversion of Finnish CFA to Zeolite was a grand success. The overall process involved sieving, batch preparation, ageing, hydrothermal treatment, washing/filtration, drying and grinding. We sieved CFA to collect unburnt carbon (0.2% weight basis) and obtain consistent particle range. Creation of appropriate chemical composition, ageing for 24 hours (650 rpm at 21°C), hydrothermal treatment for 24 hours at 60°C-85°C. Washing is followed by drying the product for 16h and grinding it with mortar and pestle. CFA Zeolites have been made for the first time in Finland and Northern Europe.

Both the CFA and CFA Zeolites were analysed using XRD, EDX, SEM and BET. CFA consisted of amorphous SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> along with crystalline quartz (SiO<sub>2</sub>) and mullite (SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub>). The LOI was 4.57% (weight basis). The BET value for CFA was 366.73 m<sup>2</sup>/g. The CFA Zeolite was pure phase NaX and crystalline without competing GIS, SOD, LTA phases. The BET surface area of CFA Zeolite was approx. 1800-2000 m<sup>2</sup>/g. This is the first time such high values have been reported in the world. The process was scaled up from lab to bench scales. Various repetitive tests were conducted in lab and bench scales to have consistent results. Statistical analysis was conducted to obtain quality control guidelines.

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**Keywords** Coal fly Ash (CFA), Zeolite, NaX, Circular economy, alkaline activation, geopolymers

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# 1 INTRODUCTION

## 1.1 Background

The backbone of modern civilization and industry is based on thermal power, heat and energy in various forms. The energy industry is by far the biggest in the world. In the energy industry, coal powered thermal plants is one of the major players. It is also one of the major polluters in the world. As in any chemical industry there are multiple polluting items and agents hence cannot be generalized. In light of that the key polluting waste generated in thermal power plant is identified as coal flyash (CFA)[1].

The coal powered thermal power industry produces 750 million tonnes of CFA globally on an annually basis[2]. India alone produces 112 million tonnes of CFA/annum as of 2012[3]. This figure will only grow in the next years as India, China, Africa and South America charges ahead in industrialization. Their growing economies will need huge amount of electricity to power their new factories, growing middle class and ambitious infrastructure projects. As coal is available in abundance in those regions[4], it is certain that coal power plants will provide the majority of growing energy needs. Growth and prosperity is the key focus in driving legislation in those regions hence it may or may not have the strictest norms when it comes to coal and CFA related issues. Therefore prohibiting the use of coal powered plants from a global context is not feasible. In such a circumstance the practical solution would be to find multiple applications for CFA. In terms of quantity alone it poses a massive challenge in disposal, recycle, storage, reuse and environmental pollution[5]. The global recycling rate of CFA is 15%[6]. Germany produces 40 million tonnes/annum of CFA [3].

Finland is a highly industrialized country with high emphasis on innovation. The chemical industry in Finland is quite significant and combined with the fact that it is situated in a cold region creates a huge demand for heat, electricity and power. Finland has a lot of coal based power plants all over the country. The annual production of CFA is estimated to be 750,000 tonnes[7]. One of the largest plants to produce CFA is in Kristinakaupunki in the west coast of Finland with annual

production of 119,000 tonnes. The Uusimaa region in southern Finland is a major hotbed of industry, innovation and population. To keep up with the high demand of energy there are multiple energy generation sources but we will focus on coal based power plants. In this context especially Helsinki and Espoo has many coal power plants. The combined production capacity of CFA is anywhere between 75,000-150,000 tonnes/annum. The Salmisaari and Suomenoja power plants in Helsinki region alone have a combined capacity of 65,000-75,000 tonnes/annum[7]. It is evident that all of the CFA is not used and part of it remains. Moreover, we need to factor that there is already couple of million tonnes of CFA stored in silos and landfills. The sheer quantity makes CFA a challenge and an opportunity. From our perspective it is viewed as secure raw material source for any large scale application for couple of decades to come. Hence given the national, EU legislative and environmental obligations at hand we have to find an appropriate solution. Conversion of CFA to zeolite is an answer to that and an opportunity in disguise.

Zeolite is an extremely versatile material. They are microporous aluminosilicates used especially as absorbents and catalysts. It has a wide range of applications in all sectors of the chemical industry in various forms. It can be used in powder, pellet, membrane, thin film and other forms. More about the uses is discussed in the applications sections later. The prices of zeolite vary from 1,000 Euros/tonne-20,000 Euros/tonne based on purity and application[8]. Hence it is evident that producing zeolites could bring higher economic benefits compared to other uses of CFA. Moreover zeolites have high regeneration rates which makes it even more versatile.

The conversion of CFA to zeolite is among the most viable routes when dealing with waste as raw materials. This idea is in our vision and motivation of “clean wastes by waste”. This is further in support of the recent trend towards development of a circular economy. In this trend wastes are considered as valuable materials towards development of products vital for other operations in the same or different industry.

Development of new innovative technology strategy to address industrial wastes problem in Finland to meet national and EU Horizon 2020 environmental mandates



and directives. As of now Finnish industries have not developed adsorbents, ion-exchangers from waste materials such as CFA to be used in other equally valuable operations. This is in line with present trend of an innovative circular economy.

The real challenge is to meet the stringent zeolite type specifications especially when waste raw material such as coal fly ash is used, but that is where the innovative nature of the thesis lies.

## **1.2 Objectives**

The objective of this thesis is:

- To determine the suitability of Finnish CFA for synthesis of any zeolite.
- Conversion of waste coal flyash ash into appropriate zeolite. In our case we would develop FAU type framework zeolite namely NaX. Hence it is development of a product.
- Development of a cost effective synthesis method to develop zeolites tailor made to be used as adsorbents for waste water treatment, ion-exchangers. Hence it is development of a process.
- Characterization and analysis of Coal flyash and final product i.e. zeolites using XRD, SEM, EDX, BET.
- The technology so developed would be based on the idea that they are simple, easy to implement, cost effective, industrially scalable and replicable elsewhere.
- To reinforce the theme of circular economy, ideas will be generated and implemented along the lines of thesis so that there is maximum resource valorisation.

## **1.3 Thesis outline**

The core focus of the thesis is on zeolites, circular economy and sustainability.

The initial part of the thesis describes about the background. It mainly emphasises about CFA production and disposal problems at a global and national level. The

need and economic benefits for the approach is also justified. The literature review greatly emphasizes CFA, Zeolites, CFA Zeolites, Zeolite applications, Circular economy, Context of circular economy in CFA Zeolite concept, legislation, policy making, current and future industrial trends, markets etc. The later part of the thesis emphasizes on CFA assessment, CFA Zeolite synthesis process, excellent results and its global implications. It greatly emphasises the prospect of industrial scalability by means of pilot plant as the technical, logistical and business concerns have been addressed. Hence the thesis addresses the topic from various perspectives.

#### **1.4 Significance of study**

This kind of R&D work solidifies Finland's high ranking in cleantech sector in Scandinavia, Europe and globally. CFA Zeolite is being invented for the first time in Finland and Northern Europe. Hence there is distinctiveness of work.

Industrially relevant project involving the vast power generation industry, waste management industry, mining and metallurgy industry and bioeconomy sectors. It draws synergy between all of these (but not limited to) sectors. It tries to point out how each industry's/regional weakness can be used as food and strength for another industry and sector. The broad ideas of using a specific type of raw materials to make certain category of products which are applied in multiple industries to enhance circular economy is quite significant. Hence the idea that develops synergy between various different industries is significant. The work is based on circular economy which is very topical at the moment.

#### **1.5 Highlights and achievements**

Coal flyash was successfully converted to FAU class NaX zeolite (new product). A simple, cheap, scalable, easy implementation oriented process was developed (new process). The process produced high quality NaX zeolites and in addition was engineered to obtain heat and unburnt carbon. So instead of getting only zeolite, the process was tuned to obtain unburnt carbon and heat as well. It is a low temperature

process having range of 60-90°C. The process is also quick with crystallization period of 24h. Hence there is maximum utilization of chemistry.

The NaX zeolite is of very high quality with BET surface area of 1800-2000 m<sup>2</sup>/g. Such high surface areas are reported for the first time in the world under the current circumstances, processes and systems. It is a highly crystalline structure. Hence there are creative contributions and new results.

Lab scale studies were followed by bench scale studies to give identical products and properties. The product properties were consistent and replicable with less margin of error during lab and bench scale respectively. Hence there is already commitment for further development.

The work has been carried out in Helsinki and Espoo regions and to be applied in Helsinki and Espoo regions. It highlights Helsinki and Espoo has a hub of Nordic and global innovation. It also shows real commitments from Helsinki and Espoo entities such as Aalto University, power generation industry and waste management industry. It also highlights the enthusiasm of researchers who would undertake such project which makes a better environment with good sustainability and economic implications. The project has environmental, legislative and economic implications relevant to Finland in EU and globally.

The zeolite has been specifically designed for adsorption in waste water treatment, bio-refining catalysis and as controlled substance delivery agent in agriculture. They have been tested by third party and proved promising and consistent. Hence there is immediate practical application of research.

Results are of high importance to academia, industry, society and professionals with commercial implications.

## **2 LITERATURE REVIEW**

### **2.1 Coal Fly Ash**

#### **2.1.1 Introduction**

Coal flyash (CFA) is produced when combustion of coal takes place for primarily energy production. It has received attention over the last decades to find more sustainable use. To save and optimize natural resource utilization it is essential to use by-products generated in one industrial process into another. This approach helps in reduction of energy and material consumption.

There are various methods of coal combustion. Depending on kind of process, layout and type of coal, we get various kinds of coal flyashes namely fluidized bed ash, pulverized bed ash among others. In our case we will discuss about pulverized bed ash and utilization. CFA is produced when combustion typically takes place in a pulverized bed at 1000-1700°C. The presence of a variety of components makes CFA one of the most complex anthropogenic materials. As such 316 individual minerals and 188 mineral groups have been identified in various CFAs[9].

The annual global production of CFA is 750 million tonnes. The utilization figures are 39% in USA, 47% in Europe and global average is 15%. Moreover CFA is the world's largest waste produced in terms of quantity[2]. Hence a considerable amount of CFA have to be disposed.

#### **2.1.2 Mineralogy and Chemistry**

Coal is one of the most complex natural materials consisting of organic and inorganic constituents with various origins formed in sedimentary environment. Inorganic components constitute a small part of coal but most of the problems associated with coal is due to this fraction. The mineral matter of coal provide information about possible toxic trace elements. Ultimate analysis of coal by various researchers reveals it contains 60-80% carbon, 10-15% sulphur dry weight basis. The inorganic minerals present are quartz (majority), muscovite, calcite, dolomite, ankerite, hematite, gypsum, cerussite, illite, kaolinite and pyrite. There is

infinite variation based on coal origin, deposition and geology involved[10]. The complex mixture undergo milling and processing before being sent for various applications[11]. In our case they are sent to pulverized combustion boilers. The combustion boiler designs and energy efficiencies are completely separate topics. The phenomenon of heat, mass, momentum transfers are very complex and have been researched and modified for more than a century. We will not go deep as it is not our focal area. So we would limit our discussion by providing chemical equation for simple understanding.



Coal combustion takes place between 1200-1600°C in boilers to produce mainly heat, unburnt coal, carbon monoxide, carbon dioxide, oxides of nitrogen and sulphur[12]. A large amount of inorganic residue is produced known as CFA and bottom ash. How the CFA residues are formed is a complex topic with no clear explanations until now[13]. There are some hypotheses but absence of concrete answers is mainly due to difficulty in executing and monitoring structural changes at 1500°C. But most of the hypotheses revolve around the fact that it requires very high temperatures for formation of molten materials. The high temperatures facilitate the particles being molten. The molten particles mix, intertwine and form into a spherical shape so as to reduce surface tension[12]. During combustion there is sudden cooling of the flue gas which passes from the boiler to chimney. This sudden heating, cooling and pressure variation in a very short period of time leads to amorphization of particles[13]. The sudden loss of pressure also facilitates the expansion of particles. It is also thought that high melting point materials like iron oxide retain part of their original earth shapes hence they may not be spherical in the SEM pictures. This a very logical explanation verified by various researchers from SEM images and other instrumental approaches[14].

The main components of CFA are glass, silica, alumina, ferrous oxide, calcium oxides with unburnt carbon (LOI). The silica and alumina components forms the majority of constituents. CFA chemistry is largely determined by the type of coal burned. In general CFA from sub-bituminous and lignite coals are characteristic of higher calcium oxide with lower silica and alumina. Bituminous and lignite CFA

that possess less than 10% CaO in total often have aluminosilicate glass without any crystalline components. Such a CFA could be suited for zeolite precursors [2]. In terms of mineralogy the CFA consists of glass, mullite, quartz, hematite-magnetite, feldspars etc in a case by case basis. CFA also contain trace amounts of As, Cr, Pb and Se among others. It is also to be noted that the CFA mineralogy and chemistry varies depending on where it has been stored and collected in the power plant, e.g., coal bottom ash is different from coal flyash, ash collected from hopper is different from ash collected from elsewhere which again varies from plant to plant having different coal and processes in place[15][16].

Quartz present in the coal is mostly unreactive but part of it undergo phase transformation to form cristobalite (polymorph) in the combustion chamber. The clay minerals in coal transforms to mullite and amorphous substances. The proportion of mullite in CFA is broadly related to proportion of clay (sometime also mica when present) in coal feedstock. Ca related to organic matter, carbonates, gypsum and basanite present in coal reacts with aluminosilicate materials present in clay to form anorthite. Small quantities of Ca-aluminosilicates such as gehlenite, diopside etc are also formed. The Ca not taken up by aluminosilicates forms anhydrite and portlandite and rest integrated in an amorphous mix. Anhydrite forms by interaction of Ca and SO<sub>2</sub> variations. Lime and periclase gets formed from low ash coal. Pyrite (FeS<sub>2</sub>) reacts with mainly oxygen to form hematite and other iron phases. Hence the proportion of iron phases are related to amount of pyrite present[17]. Thus the paragraph provides an interesting view of mineral transformation and materials chemistry perspective of CFA.

One of the most common standards for CFA are the ASTM standards. As per that method CFA is primarily grouped into C and F class. Class F has combined SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> greater than 70%. Class C CFA has the same composition greater than 50%. Moreover it often generalized that class F CFA is derived from anthracite coal[18]. Class F CFA is considered as pozzolanic material. The chemical composition of CFA has traditionally been the foundation for examining its suitability in various applications.

The morphology of CFA is dependent on combustion temperatures and cooling rates. SEM analysis revealed that CFA consists of solid spheres, cenospheres (hollow spheres) and uneven shaped unburnt carbon. As the focus is on inorganic minerals and residues hence we would try to describe its origin and processing. The inorganic materials which come along with coal are broadly derived from two sources. Some of it comes along with the organic particle and the rest are discrete mineral gains during mining process and additions during coal processing and combustion processes. The formation of CFA is explained hereafter. The first step is conversion of coal to char. The char completely burns out at much higher temperatures. The inorganic minerals inside the char are released as fragments. At this stage the minerals convert to gases and eventually condense back to solid form as ash particles. The condensation results in ash particles with size ranging from 0.02-10 $\mu$ m. The extraneous minerals undergoing complex transformations until now have been converted to spheres with a size range between 10-90  $\mu$ m. Moreover the latter particle sizes is a rough generalization and various deviations occur due to multiple reasons in case to case basis. Some of the newly found reasons are particle grouping during solid and liquid phases, mutual aggregation of spheres, spheroids, debris etc which may or may not be from primary intrinsic origin. One major aspect of coal combustion is the unburnt coal may have the sizes exceeding 90 $\mu$ m. The temperature ranges cannot be generalized as it depends on a myriad of factors such as coal origin, legislation, plant type, mineral admix, emission controls etc[2].

After the combustion of pulverized coal in the furnace the majority of non-combustible materials remain among the furnace gases. The combustion gases from boiler are transferred to the electrostatic precipitator. This gas is now renamed as 'flue gas' which is captured at the boiler outlet. About 20% of the solid collected is bottom ash which was taken from the furnace bottom [1]. But bottom ash is not the focal topic at the moment

### **2.1.3 Environmental problems and disposal**

CFA poses a challenge and depending on the geographic location on earth it can be dire to regular. As 750 million tonnes of CFA is produced every year and it will

only increase in years to come depending on the geographic location hence disposal and storage is a massive issue. Most of it is landfilled and dumped in pits or just stored behind the factory premises with water. In less regulated nations they are often dumped in rivers, streams and ponds. Disposal of CFA has been a significant environmental problem due to its impact on terrestrial and aquatic ecosystem. CFA contains toxic elements such as selenium, chromium, barium, mercury, chromium, boron etc[2]. These among others could leach out from CFA into ponds, rivers, streams and landfills. CFA contains minor quantity of these but millions of tonnes at a site will make this trace quantity into a major problem. To make it more vivid if only 1% of CFA is trace toxic element(s) then 100 kg will have atleast 1 kg of toxic elements then 1 tonne will have 10 kg of toxins and 100 tonnes will have one tonne of toxins. So 750 million tonnes will have atleast 7.5 million tonnes of toxins each year. The simple calculation provides a good insight into the extent of the problem facing the society. Even if we don't consider the individual effects of the toxins, the very sheer quantity poses a great challenge in itself.

There are several impacts of CFA on terrestrial eco-system. Leaching of toxic elements into soils and ground water. The toxic elements may enter plants through ground water and contaminate the whole food cycle of plants, animals, humans and fishes. This also increases the adverse mobility of toxins throughout the food chain. Reduction in plant growth due to adverse chemical reactions posed by the CFA[16].

The dumping of CFA in ash dams and ponds has a direct effect in aquatic ecosystems by water and ground water contaminations. The primary changes associated with water chemistry include pH variation and increase in concentration levels of toxins in water. It often results in excess soluble salt concentrations, elemental imbalances due to pH, as well as concentration and compaction of soil in bottom of lake.

CFA often brings excess salinity to soil but cannot be generalized as it depends on the kind of ash[2].

There are more adverse effects but as the thesis focuses on zeolites hence only a few aspects have been provided.



#### **2.1.4 Application**

The complex nature of the CFA and its variation at various parts of the world has posed to be a barrier in its uniform bulk application. Each component may be useful or neutral in a specific application but could be detrimental in another applications. Most applications have been in low cost end and finding high value application could be beneficial with respect to environment and economy. Some of the key applications have been discussed hereafter.

CFA possess pozzolanic properties and are widely used in partial replacement of clinker in Ordinary Portland Cement. CFA application in blended cements is a well-established technology[6].

CFA is composed of oxides of silicon, aluminium, calcium, iron etc. Due to this composition it is used as a low cost material for manufacture of ceramics, glass-ceramics and glassy materials[19].

It is an interesting fact that concrete is the second highest used material by humanity after water. The production of concrete produces a lot of CO<sub>2</sub> emissions and hence even a minor reduction in production could lead to great drop in CO<sub>2</sub> levels[20]. High volume fly ash concrete (HVFA) is a solution and is used widely. The final composition produced is at par to building codes and required strength properties[21].

CFA is used in geotechnical operations. Some of them are embankments, mine reclamation, grout, aggregate in bricks etc. These are high volume usage with low end margins[2].

CFA is used to make geopolymers which is a broad new group of materials first termed in 1970s. It involves a chemical reaction between alumino-silicates and alkali metal precursors to yield activated alkali alumino silicates. These class of materials have excellent physical, chemical and mechanical properties. Some of them are low density, micro-nano porosity, low shrinkage, high thermal stability, chemical resistance etc. They are seen as potential renewable and sustainable alternatives to construction, aerospace, mining, transport and metallurgy sectors[22].

CFA is used in synthesis of zeolites and mesoporous materials. Zeolites are an important group of crystalline aluminosilicate minerals. Zeolites have a large variety of families with unique structure, framework and properties. It is widely used in various applications which have been discussed in other sections.

Mesoporous materials are extremely valuable materials with applications in separations and catalytic processes. There is a great demand for new mesoporous materials because their current manufacture requires high cost and toxicity of reagents involved[23]. The synthesis methods of zeolites and mesoporous materials are quite similar.

## **2.2 Zeolite**

### **2.2.1 Introduction**

Zeolites are crystalline aluminosilicates with general formula  $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2$  where M is the cation, n is the valence of cation and y varies from 2 to infinity. Structure wise zeolites are crystalline polymers based on 3-D arrangement of  $TO_4$  tetrahedra ( $SiO_4$  or  $AlO_4^-$ ) connected through their oxygen atoms to form subunits. These subunits (unit cells) join together in repeating blocks to form large lattices. The structural formula of zeolite (chemical composition) is  $M_{x/n}(AlO_2)_x(SiO_2)_y$  where M is the cation, n is the valence of cation M, x+y is the total number of tetrahedral per unit cell, y/x is the atomic Si/Al ratio varying from 1(Lowenstein rule) to infinity[24].

The word zeolite comes from Greek words “zeo” and “lithos” meaning “to boiling” and “stone” respectively. Zeolites were first discovered 250 years ago by Swedish mineralogist Cronsted. For 200 years these were mostly museum attractions[24].

It was not until experts realized that zeolites existed in large quantities in deposits that they gained real importance for various applications. Their success in applications and unique properties led experts to seek for ways to produce them in laboratories. The laboratory experiments were successful and that led to synthesis of tailor made zeolites for possible myriad range of properties and applications.

Until now zeolites have been synthesized from pure chemicals but lately attempts have been made to produce zeolites from industrial wastes and other side streams.

In nature about 40 different kinds of zeolite exists. Synthetic zeolite chemists continue to make new zeolites and until now about 130 different zeolites have been conceived. The first synthetic zeolites were zeolite (A, X, Y) and found wide spread applications[24].

Table 1 provides a timeline for various zeolite synthesis with unique frameworks.

**Table 1:** Milestones in zeolite synthesis[24]

<b>Year</b>	<b>Event</b>
1930-1940	Pioneering work by Barrer et al in synthetic zeolite synthesis
1949-1954	Discovery and synthesis of zeolite (A, X, Y)
1954	Commercialization of zeolite (A, X, Y)
1967-1969	Synthesis of high silica zeolites MFI and BEA
1980s	Specialized zeolites by secondary synthesis routes (dealumination, iso-morphous substitution etc)
1982-1986	Synthesis of alumino-phosphates (SAPO)
1983	Synthesis of titanium silicalites TS1
1992	Mesoporous molecular sieves MCM41
1994-1998	Nano crystalline zeolites made from pure chemicals
1995-2015	Synthesis of zeolites from various industrial wastes and side streams
2007-2008	Emergence of tailor made theoretical zeolites predicted by computational methods
2009-2015	Emergence of zeolites made from industrial wastes and side streams. Development of waste to zeolite pilot and production facilities(Zeolite X, Y, P1 etc along with their variations)

### 2.2.2 Classification of zeolites

There are various ways to classify zeolites. One of the most common ways is based

on occurrence. Hence we have natural and synthetic zeolites. Some examples of natural zeolites are Clinoptilolite, Mordenite and Phillipsite.

Another method is based on structure. In such a classification zeolites are grouped based on specific frameworks and other parameters. They are written as Group 1, Group 2, Group 3, Group 4, Group 5, Group 6, Group 7[25]. Exact Group and subgroup can be pinpointed by finding the Si/Al ratio or  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio combined with XRD data.

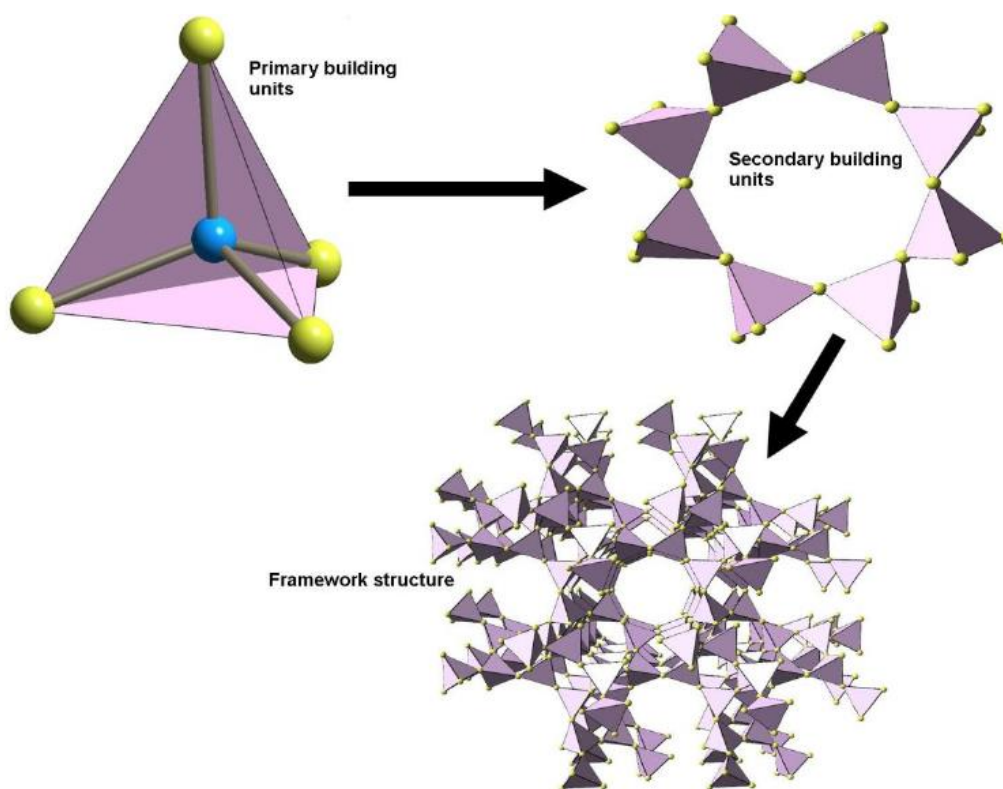
Another way of classification is based on framework structure types only. Here the framework is central and chemical composition or  $\text{SiO}_2/\text{Al}_2\text{O}_3$  consideration is secondary. In such a classification all of the zeolites are categorized in families and then sub divided into specific types. Some of them are FAU (Faujasite), MOD (Mordenite) etc. Naturally FAU type framework are found in X and Y zeolite types. XRD data are central to such classification.[26]. In practice the classification based on just families are used more often.

### **2.2.3 Zeolite Framework**

Zeolite framework structures are key to understanding zeolite chemistry. A framework type in zeolite describes the connection of tetrahedral coordinated atoms (T-atoms) in the highest possible symmetry. The framework composition, observed symmetry and actual unit cell dimensions are not considered. Hence multiple materials can be put under one designation, e.g., garronite, Na-P1, Na-P2, SAPO-43 etc are all grouped under GIS framework. A three letter code is assigned (eg GIS, FAU etc) which is governed by structure commission of IZA (International Zeolite Association). The codes are derived from name of zeolite, mineral or type material, e.g., FAU is derived from mineral faujasite, MFI as Zeolite Socony Mobil etc. Until now about 176 zeolite framework types have been confirmed by the IZA[27].

The feature that is common to zeolite or zeolite like material is that they all have a 3-D, 4-Connected framework structure constructed from corner sharing  $\text{TO}_4$  (T is the metal such as Al, Ti, Fe etc) tetrahedra. The framework structures are open, consisting of channels and cavities.

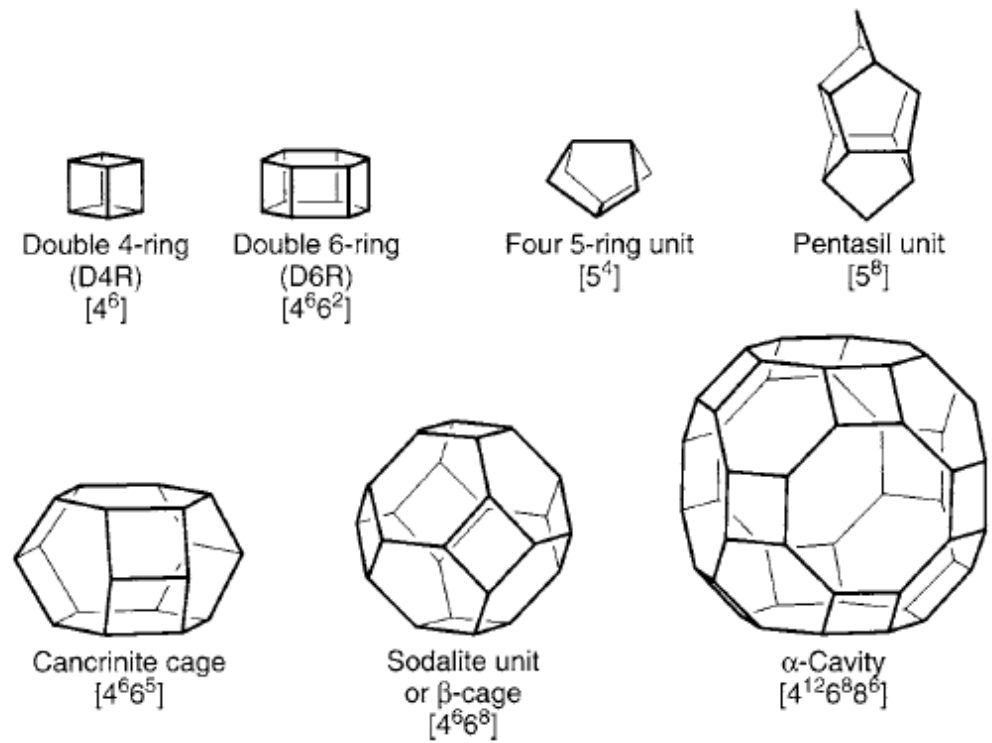
It is believed that zeolite is formed by two kinds of structural building units which are primary and secondary structural units. The Primary Building Unit (PBU) consists of  $\text{SiO}_4$  and  $\text{AlO}_4$  which are arranged in such a manner that four corners of tetrahedron are occupied by oxygen atoms surrounding a central ion ( $\text{Si}^{4+}$  or  $\text{Al}^{3+}$ ). The PBU join together in intricate patterns to form secondary building units (SBU). The so formed SBUs connect to form different zeolite frameworks[28]. In another perspective it can be seen that SBUs combine to form unique pores and channels. These pores and channels are also called oxygen windows. The numerous combination of similar SBUs gives rise to 176 different framework zeolites. Figure 1[29] illustrates the above idea.



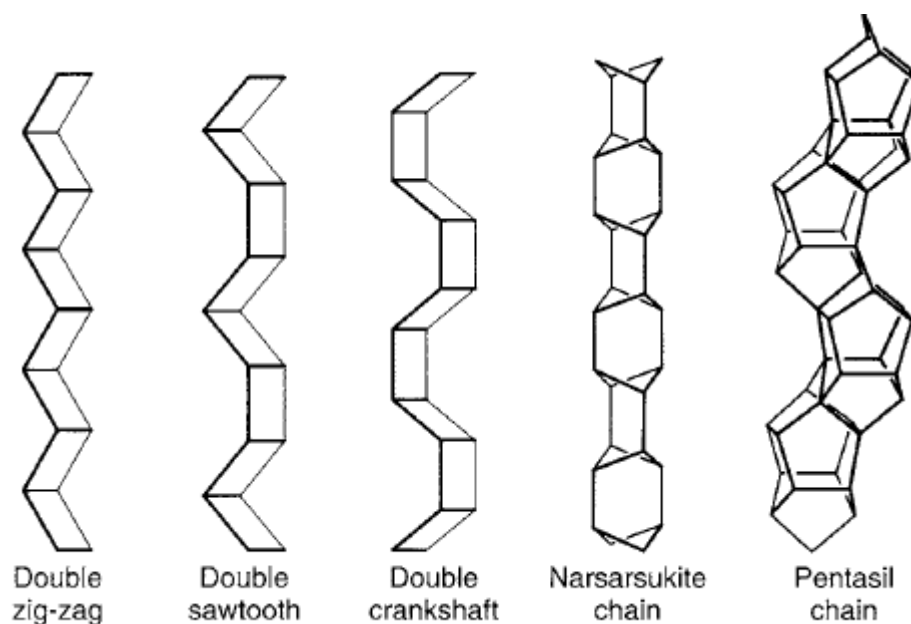
**Figure 1:** PBU, SBU and their combination to form framework structures[29]

A detailed theoretical description of zeolite always begins with framework type, size of pore opening and dimensionality of pore channel system. Pore openings are described by the size of ring that opens the pore i.e n-ring where n is the number of T atoms (usually also the number of O atoms). An 8-ring is considered as small

pore opening, 10-ring a medium one, 12-ring a large one with the effective pore widths calculated by using effective oxygen radius of 1.35Å. This is just a rough estimate as the rings can be distorted. A number of structural features such as cages, channels, chains and sheets are found in various zeolite framework types. A Truncated octahedron in sodalite cage of zeolite is expressed as a surface with 4-rings and eight 6-rings. This would be designed as  $[4^6 8^6]$  cage. Figures 2 and 3 below illustrates some cages, subunits and chains[30].



**Figure 2:** Zeolite cages and subunits[30]



**Figure 3:** Recurring chains found in zeolite frameworks[30]

Although there are 176 accepted framework types of zeolites, only a few of them have found wide scale industrial applications. Approximately 17 framework types find wide scale applications but this is a rough estimate. They are SOD, LTA, FAU, EMT, CHA, GIS, MFI, MEL, MOR, MWW, BEA, TUN, AFI, VFI, CLO, ETR, UTL[30].

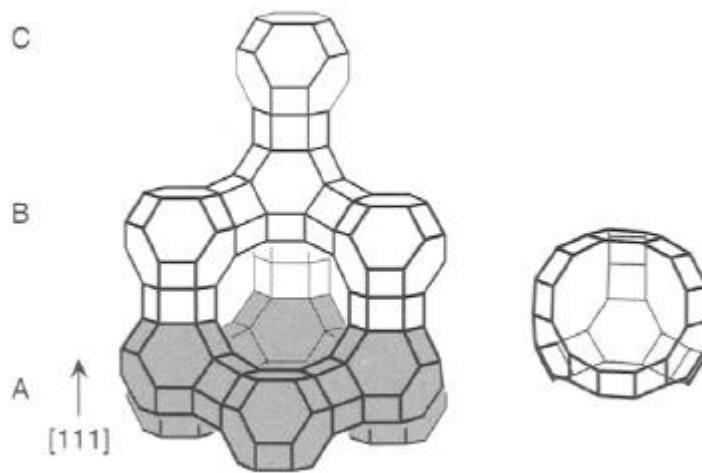
As there are 176 framework type zeolites with possible variations using different cations and T-atoms, it is impossible to provide a generalization of physical and chemical properties. Each type of zeolite (NaX, NaA etc) needs to be treated separately in terms of physical and chemical properties. In some way it is like organic chemistry with each zeolite framework analogous to each organic functional group. Furthermore, the orientation of inorganic secondary building units determines each type of zeolite which is analogous to organic chain length and bond variations.

### 2.2.3 Framework type FAU

This thesis involves synthesis of zeolite NaX which is in the family of FAU framework. Hence in this section we try to describe a bit more about FAU framework type zeolite.

FAU (Type material: Faujasite,  $[(Ca, Mg, Na)_{29}(Al_{58}Si_{134}O_{384})(H_2O)_{240}]$ )

FAU framework is primarily made of sodalite cages or SOD. They are joined to each other by double 6-rings. This formation creates a super-cage with four tetrahedrally oriented, 12-ring pore openings and 3-D channel system along  $\langle 110 \rangle$ . It has a low framework density of 12.7 T-atoms per  $1000 \text{ \AA}^3$ . The presence of inversion in each of double 6-rings creates puckered layers of sodalite cages related to each other by inversion. Figure 4 [30] illustrates the structure. The framework type can be visualized as ABCABC type stacking of layers.



**Figure 4:** NaX Zeolite with FAU framework type and supercage[30]

The IZA has a public database of zeolite frameworks and Figure 5 [31] shows the information card for typical FAU framework.

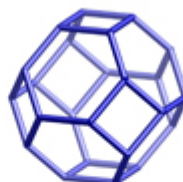


## Framework

Space Group:	Fd-3m (origin choice 2)		
Cell Parameters:			
$a = 24.345 \text{ \AA}$	$b = 24.345 \text{ \AA}$	$c = 24.345 \text{ \AA}$	
$\alpha = 90.000^\circ$	$\beta = 90.000^\circ$	$\gamma = 90.000^\circ$	
Volume =	14428.77 $\text{\AA}^3$		
$R_{\text{DLS}} =$	0.0009		
Framework density (FD <sub>Si</sub> ):	13.3 T/1000 $\text{\AA}^3$		
Topological density:	TD <sub>10</sub> = 579	TD = 0.476190	
Ring sizes (# T-atoms):	12 6 4		
Channel system:	3-dimensional		
Maximum diameter of a sphere:			
that can be included	11.24 $\text{\AA}$		
that can diffuse along	a: 7.35 $\text{\AA}$	b: 7.35 $\text{\AA}$	c: 7.35 $\text{\AA}$
Accessible volume:	27.42 % (additional data)		
Secondary Building Units:	6-6 or 6-2 or 6 or 4-2 or 1-4-1 or 4		
Composite Building Units:			



*d6r (t-hpr)*



*sod (t-toc)*

Natural Tiling

*t-hpr* *t-toc* *t-fau*

Tiling arrangement      3d Tilings display

Coordinates:

List (T-atoms), CIF (T and O atoms)

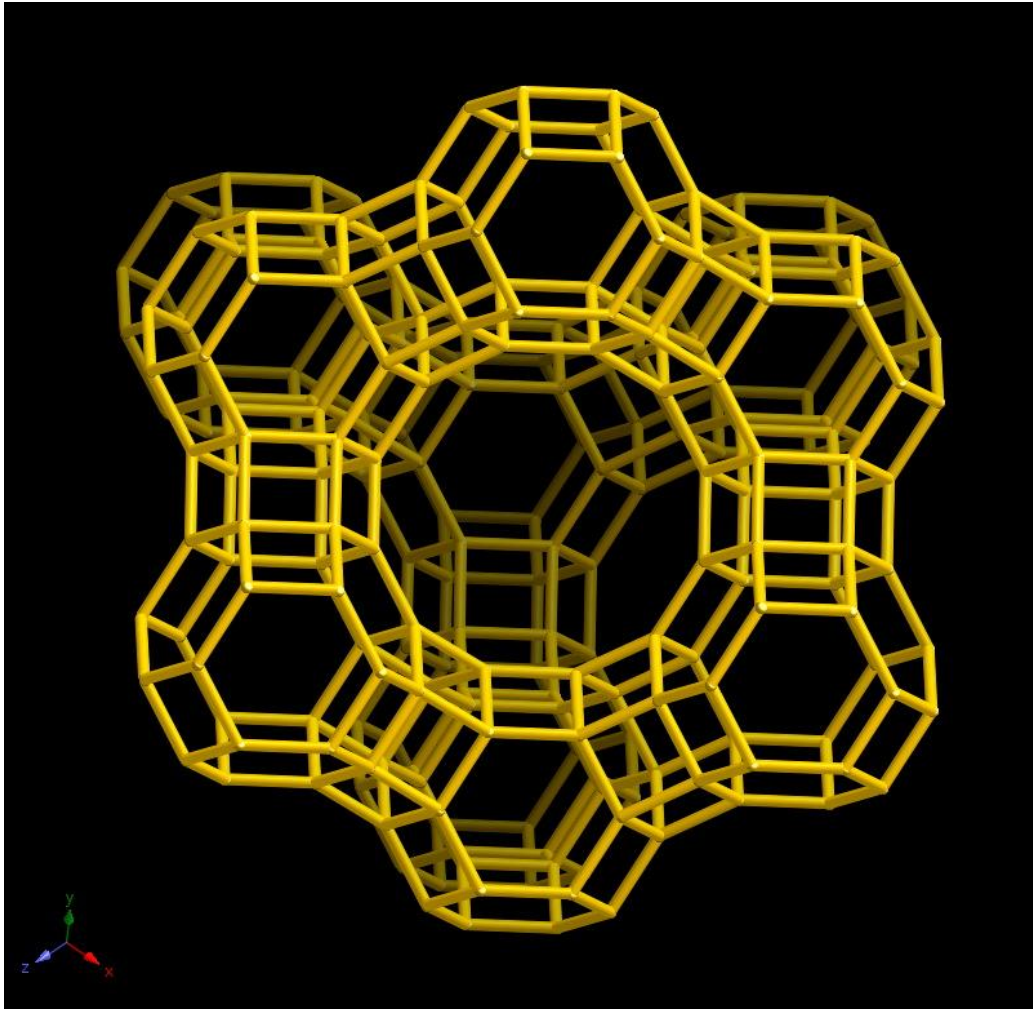
Coordination sequences:

List

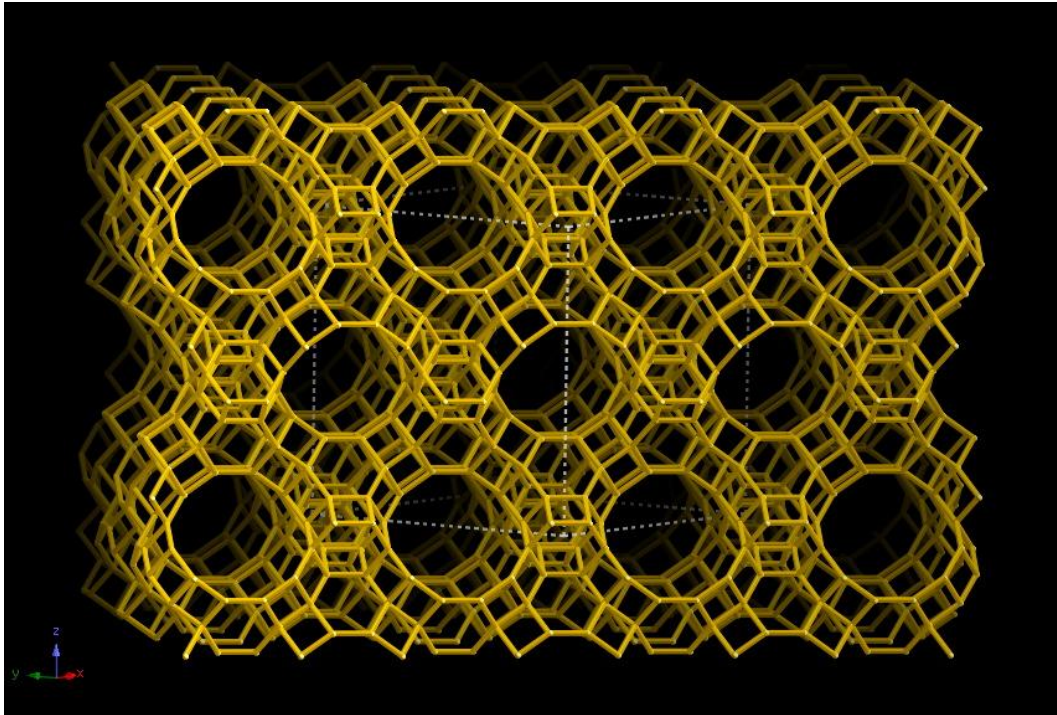
+ Vertex symbols

+ Loop configurations

**Figure 5:** Information card for NaX Zeolite with FAU framework[31]



**Figure 6:** NaX Zeolite with FAU Crystal[31]



**Figure 7:** FAU framework matrix[31]

The combination of large void volume (50%), 12-ring pore opening, 3-D channel system makes the thermally stable FAU framework type ideal for many industrial applications.

#### **2.2.4 Zeolite precursors**

Various kinds of raw materials with varied percentages can be used for zeolite synthesis. The raw material sources can be grouped into silica source, alumina source, silica-alumina source, alkali source. Silica sources are sodium water glass, colloidal silica, fumed silica, tetramethylaluminosilicate, tetraethylorthosilicate. Aluminium sources are sodium aluminate, pseudo-boehmite, aluminium hydroxide, aluminium-isopropoxide, aluminium nitrate, aluminium sulphate, aluminium metal. The alkali sources could be sodium based alkali, potassium based alkali or both. The use of alkali carbonate or hydroxide also forms a factor. Certain kinds of zeolites could be synthesised using specific sodium, aluminium, alkali, alkali-anion source and solvent. Hence it is quite complicated and hard to generalize. But for specific zeolites we have specific proven precursors which give desired results[25]. As the framework structures have greatly increased to include phosphorous, gallium

etc hence there is a whole other range of such precursors which can be used. In our case we are dealing with silica-aluminium zeolites hence our discussions will be limited to relevant precursors only.

### **2.2.5 Synthesis techniques**

Zeolite synthesis strategies are an active field of research in academia and industry. From Table 1 it can be clearly seen that zeolites were pioneered and commercialized mostly by industries during the early phases. Hence many of the synthesis routes were subject to industrial patents and in-house secrets. The advent of new framework structures are attributed to the greater understanding of the very complex formation and crystallization mechanisms. The use of complex industrial waste makes the understanding of the process even more difficult.

This section provides a glimpse of various synthesis routes.

#### **2.2.5.1 Hydrothermal Synthesis**

Barrer and Milton were the pioneers in hydrothermal synthesis of synthetic zeolites[25]. Hydrothermal synthesis is considered as a primary method for synthesis of zeolites. Hydrothermal synthesis usually refers to reactions occurring at conditions of high temperature and pressure (>100 °C, >1 bar) in aqueous solutions with closed system. Many researchers also consider conditions below 100 °C and above 1 bar pressure as hydrothermal range[30] [32]. This is hence loosely defined and partly depends on researcher. In general hydrothermal method has been used in various fields such as complex ceramics, superionic conductors, condensed materials, chemical sensors etc[33].

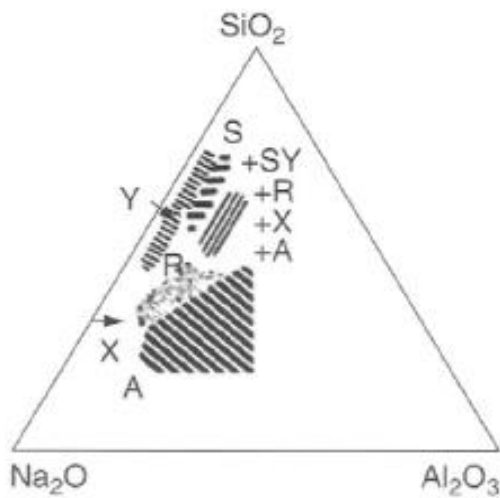
The appealing aspects of hydrothermal synthesis are high reactivity of reactants, easy control of solutions, formation of metastable phases, reduced air pollution, low energy consumption etc[19].

Hydrothermal synthesis can be classified into subcritical and super critical routes. In sub critical synthesis the temperature is in range 100-240°C. In super critical route we have upto 1000°C and pressures of 3000 bar. Water acts as a mineralizer or catalyst at elevated pressure-temperatures. The thermodynamics and mass

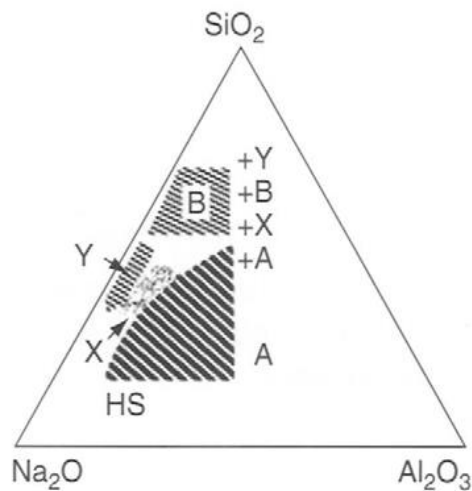
transfer properties of high temperature water are very different than ambient water. The solubility of non-polar species increases and that of ionic and polar compounds decreases. Moreover under hydrothermal conditions the physical and chemical properties of reactants change considerably. High temperature and pressure hydrothermal conditions accelerate rate of reaction in complex ions, intensify hydrolyzation reaction and change the redox potential of reactants. Low temperature hydrothermal synthesis with saturated vapour pressure is much simpler. If reactions are carried out below boiling point of water then the phenomena involved are not very complex. The viscosity of water decreases with an increase in temperature Hence the mobility of ions in water is also enhanced. The pressure and temperature diagram of water is essential especially for reactions above the boiling point of water. In case of hydrothermal conditions below boiling point of water the pressure-temperature diagram may not be very significant. But if the pressure needed is not significant and there is a large reaction vessel then the saturation pressure is less and hence safe. In general the degree of filling is 50-80% by volume for hydrothermal synthesis. In case of low temperature synthesis of  $<100\text{ }^{\circ}\text{C}$  the saturation vapour pressure generated is not very significant[30]. In our case we will be dealing with low temperature hydrothermal synthesis.

There are various factors affecting the synthesis of zeolites[32]. Most zeolites are formed in metastable phases. Zeolite crystallization represents one of the most complex chemical problems in crystal nucleation and growth[30]. It involves complex reactions such as solution precipitation, polymerization-depolymerisation and nucleation-crystallization[30]. The use of complex industrial waste as raw materials which contain more interfering chemicals than pure chemicals makes the explanation even more difficult. The large number of variables which affect formation of specific zeolite phases are batch composition, reactant sources, Si/Al ratio, alkalinity, water content/dilution, inorganic cations, organic templates, and solvents, structure directing agents/seeding, temperature, aging and stirring[34]. Hence the use of industrial waste such as CFA often results in formation of mixed phases of variety of zeolites[34]. It has been recognized that of the above parameters the most crucial parameter which govern synthesis are batch composition, aging, alkalinity, water content, temperature and reactivity of precursors[35]. Based on

chemical mix and other parameters mentioned above, there are various phase diagrams. These phase diagrams provide a good approach to design specific pure zeolite systems theoretically. An example of such a phase diagram is provided in figure 8 [30]. The system is  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  at  $100^\circ\text{C}$  with water content of 90-98 mol%, colloidal silica is being used. Another system is  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  at  $100^\circ\text{C}$  with water content of 90-98 mol%, sodium silicate is being used (Figure 9 [30]).



**Figure 8:** Phase diagram[30]



**Figure 9:** Phase diagram[30]

It is interesting to observe that the use of different precursor gives rise to different phase diagrams even though all other parameters are same. This is due to level of reactivity and solubility of the different pre-cursors.

#### **2.2.5.2 Solvothermal Synthesis**

Solvothermal synthesis is similar to hydrothermal synthesis but instead of water as the solvent, a wide variety of organic solvents are used in case to case basis. Naturally the corresponding reaction parameters and reactivity of species and other crucial elements are modified. In general, slow reaction rates are found with variation in viscosity[25]. High viscosity solvents reduce mass transfer by convection and hence favour large crystals. This fact can be used vice-versa based on desirability. BASF was the first company to patent non-aqueous solvothermal synthesis of zeolites in 1982. They manufactured ZSM-5 in ether-water media. In a specific case CAN type zeolite was synthesised in butane 1,3-diol solvent[36]. The resultant zeolite was free from any barrier, defects compared to one synthesised in water. It has to be noted that each solvent system will have variety of evaporation temperature hence pressure-temperature diagrams for specific solvent system being used needs to be addressed for safety and other reasons. Until now a variety of alcohols have been used as solvent[37]. The solvent provides the medium for reaction. It also dissolves or partially dissolves the reactants to form solvent-reactant complexes which affects the chemical reaction rates. The polarity of the solvent is the primary factor determining solvating property. The solvent polarity empirical parameter  $E_T^N$  indicates precursor nutrients as function of crystallization.  $E_T^N$  is different for solvents with different polarity[36].

#### **2.2.5.3 Fusion and hydrothermal route**

This method involves using highly unreactive and crystalline precursors such as waste materials. This is a very useful method and involves making a batch composition and then heating it in open vessel in ambient air at 400-600°C for 1-2 hours. This results in melting of crystalline chemical mix into an amorphous mix and gradual conversion into aluminosilicates. This product is fused and very hard. This needs to be powdered and mixed with requisite amounts of solvent and used in hydrothermal treatment for zeolite production. Fusion temperature, time are

crucial factors determining final product. One of the key raw materials for this kind of approach is CFA, coal bottom ash, waste ceramics etc. Fusion helps to get rid of volatile unwanted materials present in reaction mix[35] [38] .

#### **2.2.5.4 Microwave assisted synthesis**

Microwave is an electromagnetic radiation in the range of 0.3-300 GHz. It has been recently used in various applications such as chemical reactions, organic-inorganic synthesis, selective sorption etc. In case of zeolites it has also been put to test. There have been many reports of the use of microwave assisted methods for zeolite synthesis. Many variation exists for the microwave assisted synthesis. Some varieties of zeolites have been made completely using only microwave and some had a mix of microwave with hydrothermal in various order. The use of microwave synthesis is also thought to be a great alternate for fusion method/step[39]. Microwave synthesis is fast, cheap and clean. Zeolite synthesis by microwave method was first patented by Mobil Corp in 1988. Microwave influence include uniform heating of reaction mixture, increased reaction rate, changing the association between species in synthetic mixture. The reactions may be enhanced due to microwave field, absorption of microwave energy by reactants, intermediate species etc. The distribution of microwave energy can be altered by various factors such as reactor geometry, temperature, frequency, dielectric permittivity. The resultant energy distribution can have effects in product quality and quantity[40].

#### **2.2.5.5 Combinatorial synthesis method**

Combinatorial chemistry involves making libraries of compounds which are permutations of a set of physical or chemical parameters[41]. This has attracted a lot of attention in material science because of immense possibilities. This is widely being used in drug discovery, new materials discovery for organic, inorganic and complex compounds. In recent years this approach has also started to find application in zeolite synthesis[41]. In 1998 the first zeolites were synthesised by combinatorial method[42]. This generally involves multi autoclave system arranged so that rapid experimentation takes place to reach the optimum results in the shortest possible time. Lately Combinatorial method has been exclusively used in hydrothermal synthesis. In various systems the work is automated with automatic



sample mixing, dispensing machines and insitu product washing mechanisms. This also involves greater accuracy with low sample preparation quantity resulting in greater savings and higher gains[43]. Even if the sampling is not automated with machines it does not mean that it is not combinatorial approach. The core idea is based on carrying out rapid permutations of parameters at a time, e.g., a permutation set for 10 different chemical compositions are made and put in an oven with certain temperature[44]. This process can be carried out with a different temperature set or other variations in parameters. Hence a large family of compounds could be made in a short time following a logical path.

In 2005 a new strategy involving combinatorial and computational method was developed for zeolites. The combined approach is a very powerful strategy for new zeolite discovery. The molecular simulations interaction energies of host-guest systems, templating ability SDA combined with a possibility to carry out rapid rational experiments would be the future of new zeolite/materials discovery[45]. It is believed that extensive mapping of multi component systems could be carried out using combinatorial approach coupled with rational design of SDAs using computational method is the way forward.

#### **2.2.5.6 Other methods**

Apart from these popular methods there are also other routes under investigation. Some of them are ionothermal method[46], F<sup>-</sup> synthesis method[47], microemulsion based hydrothermal synthesis[48], dry gel conversion method[49] etc.

#### **2.2.6 CFA Zeolite**

Various types of zeolite (NaP1, NaX, NaY, LTA etc) could be derived from CFA[35] [32]. CFA Zeolites have been researched since 1990s and various reports from all over the world has verified that it is indeed possible to make and work with it sustainably. There are reports from USA[32], India[35], China[32], South Africa[50], Spain[32], Brazil[51], Japan[52], South Korea[53], Australia[54], UK etc. However it remains an unexplored area in Finland and Northern Europe.

CFA precursors contain other components such as Ca, Fe, Ga etc. and hence they get trapped or encapsulated in the zeolite matrix. CFA Zeolites are often formed in mixed phases[32]. The formation of pure phase zeolites are quite complicated and generally not achieved by low cost hydrothermal methods. Hence the zeolite could be a mix of NaX-A or even more exotic depending on the composition following the phase diagram[32]. It is worth to note that when using a specific CFA a combinatorial approach could yield a useful phase diagram. This phase diagram could be used to predict families of new zeolites from the same CFA. The use of fusion provides a good chance to obtain pure zeolites[35]. But fusion is often expensive to maintain and technically hard to handle because of high temperature, special vessels, stiff products etc. The presence of interfering elements in the gel mix such as C, Ga, Co, Ti, Ca, Fe etc causes unknown effects. This is one part which has not been actively researched yet. Its effect in synthesis mechanism is unknown. But if the primary mechanism is made good enough (assuming presence of only reacting species such as silica and alumina) then the interferences can be balanced away. Naturally the smaller the quantity of these elements, the better the chances to get a high quality product. It can also be thought that unwanted elements are trapped in the zeolite cages and channels. Moreover these interfering elements are quite minute so there is no concern of leaching. CFA Zeolites are often brown or light brown in colour. This is due to presence of transition elements which impart such colour. The presence of unburnt carbon also gives it a dark look which gradually fades with multiple washing steps[28]. The size range of the zeolite varies a lot depending on the process followed. It also depends on the quality of original CFA used. So does the morphology and purity. Depending on the above parameters we can get CFA Zeolite which could be inferior or even superior to standard commercial zeolites. The presence of high amorphous phase in CFA is crucial to have equivalent amount of zeolite as end product. The quartz, mullite and other crystalline phases remain inert.

In case of waste materials such as CFA which is a very complex chemical mix in terms of composition, size range, reactivity of each component, crystallinity and amorphous content, interfering species in the CFA mix makes the design of experiments very tricky. Due to its heterogeneous mix and range the use of CFA as

precursor requires extensive research in a case to case basis for consistent results[35] [23]. More specific information has been provided in results and discussions.

CFA Zeolites have been researched since 1990s and various reports from all over the world have verified that it is indeed possible to make and work with it sustainably.

The advent of circular economy and large volumes of CFA has prompted experts to find practical scale-up routes for CFA Zeolites. There are confirmed reports for CFA Zeolite pilot plants in Spain[55], India[56] etc. Detailed discussion about pilot plants are out of scope for this literature.

## **2.3 Zeolite properties and applications**

### **2.3.1 Cation Exchange**

Zeolites are highly porous substances with lots of channels inside. The cations such as sodium, potassium, calcium etc are bonded to the framework. However, they can be displaced by cations of greater charge.

Cation exchange capacity of CEC is determined by, strength of adsorption[57] such as:



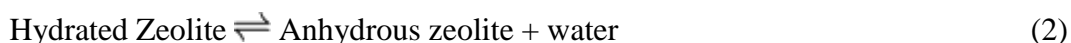
And the relative concentration of cations in solutions.

The most common applications involve radioactive decontamination such as removal of strontium and cesium from waters originating from nuclear power stations[57]. Industrial water softners to stop lime-scale blocking in cooling pipes[25]. Environmental remediation by removal of heavy metals such as lead, zinc, copper, mercury, cadmium etc[35]. The most commonly used zeolites in this case are zeolite X, zeolite Y, silicalite etc.

### **2.3.2 Dessication**

Zeolite are excellent drying agents[58]. They remove water/moisture from atmosphere around them. Moreover zeolite holds water of crystallization, the exact

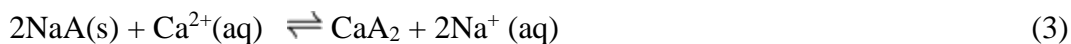
number varies from zeolite group and subcategories hence hard to generalize. But the reaction below summarizes the process:



Moreover, the loss of water by zeolite will result in the zeolite taking back the water in order to establish equilibrium in the system as per Le Chateliers principle[59]. The most common variety of zeolite used in this case are zeolite X and zeolite Y.

### 2.3.3 Water softening

Hard water contains  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and is a major issue. Water softening is often obtained by passing hard water over a column packed with zeolites. Moreover it is also used in detergents as water softeners. The zeolites encapsulate the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Infact zeolite is a prime choice instead of polyphosphates because it prevents algal bloom effect of pollution by phosphates [58]. Hence latest detergent formulations use zeolites instead of polyphosphates. The most commonly used zeolites in this case is Zeolite A. The equation below describes:



$\text{Na}^+$  does not precipitate with soap as  $\text{Ca}^{2+}$  does hence the water has been softened. Since it is an ion-exchange reaction hence the sodium zeolite can be regenerated by passing concentrated sodium chloride which shift the equilibrium as per Le Chatelier's principle[60].

### 2.3.4 Anion absorption

Toxic anions could be removed by reaction of heavy metal cations previously ion-exchanged into zeolites[61].



The above equation 4 is an excellent example of silver ion-exchanged zeolites used for removing radioactive iodine (iodide) in the form of insoluble  $\text{AgI}$ [62]. The unique thing about the process is that the insoluble  $\text{AgI}$  is both formed and caged inside the zeolite pores. Zeolites are often tailored to cage radioactive substances or allow it to form separate precipitate. The saturated zeolites can be removed for disposal. Similar approach can be applied to cyanide, arsenic, chromate, molybdate etc[63].

### **2.3.5 Molecular sieves**

Categories of zeolites with small pores selectively adsorb small polar molecules such as water and so these zeolites are outstanding drying agents[25]. Moreover these molecular sieves are also used in separation of large and small molecules in separation technologies[64].

### **2.3.6 Hydrocarbon separation**

Zeolites are used extensively in petroleum, petrochemical, biorefining and fine chemical sectors for hydrocarbon separation[25]. An example to that can be separation of linear n-alkanes (needed in various utilities including detergent manufacture) from branched alkanes[65]. It is obtained by passing them through a column of packed zeolite 5A. The n-alkanes pass more slowly into the zeolite channels as they are absorbed more selectively than the branched alkanes. Hence the property of selectivity is of prime importance here. Millions of tonnes of n-alkane is produced annually by this method[64].

### **2.3.7 Medical applications**

Zeolites are applied to wounds in accidents and surgeries. They cause rapid inhibition of bleeding[66]. Zeolites are commonly used in kidney dialysis[67] instruments to absorb ammonia from blood and preventing it from building up in the body. Some commercial products are Hemosorb and QuikClot[68].

### **2.3.8 Agriculture**

Agriculture finds great use of zeolites[67]. Zeolites are used to reduce loss of nitrogenous nutrients in three ways. Urea is caged within the zeolite matrix which prevents it from leaching into root zones. Urea trapped inside zeolite matrix slows down the conversion of urea into ammonium ions by soil bacteria. Adsorption of ammonium ions into zeolite matrix protects them from nitrifying bacteria which could convert them to leachable nitrate ions. The ammonium ions could be released slowly into the soil over time.

Ammonium zeolites are often mixed with phosphate minerals to slow release ammonium phosphate fertilizers. As more of the fertilizer is absorbed by plants more of the phosphate is released from the zeolite adhering, according to Le Chatelier's principle[67].

### **2.3.9 Desulphurization operations**

Zeolites are used widely in various desulphurization operations[65]. One such example is nickel exchanged zeolites that can absorb sulphur compounds from diesel in an aim to reduce emissions from transportation[24]. As this is directly related to acid rain, it is a hot topic.

### **2.3.10 NO<sub>x</sub> Removal**

Vehicle and industries have high NO<sub>x</sub> emissions. One of the key substances used to decrease NO<sub>x</sub> is using zeolites[65]. An example is use of catalytic convertors in vehicles where a very high quality, high endurance catalytic zeolite is used. In many cars the most costly item is the catalytic convertor containing the high grade zeolite[69]. EU and North American legislations demands the use of very powerful catalytic convertors in vehicles to be permitted in streets.

### **2.3.11 Construction industry**

Zeolite is a light weight building material as it can be easily cut with hand saw and very durable in dry climates. It is also fabricated into light weight cements. China consumes 2.5 million tonnes of construction zeolites per year[70].

### **2.3.12 Heating systems**

When water is adsorbed in zeolite it releases heat[58]. This principle can be used in a heat pump system which uses the available energy for real heating rather than let it be wasted[25].

### **2.3.13. Separation of gases**

This application is one of the largest users of zeolites[65]. One critical application involve separation of oxygen from air[71]. The oxygen purity attained is 95% and is often used for patients with breathing and lung disorders. Nitrogen is selectively absorbed into the zeolite instead of oxygen because of higher electric quadrupole moment. This leads to separation of nitrogen (80%) of air and hence giving only pure oxygen[24].

Other examples where NaX zeolite is exclusively used include industrial drying of gas[65]. Solvent vapour recovery[72], air pollution control[73] and removal of trace ammonia[74]. Industrial production of oxygen and nitrogen from air[75]. Hydrogen production from steam-methane reforming gas and refinery off-gas[76]. CO<sub>2</sub>-CH<sub>4</sub> separation from landfill gases, alcohol dehydration and gas chromatography[24].

### **2.3.14 Liquid separation and purification**

In bulk liquid separation zeolites are widely used. Separation of paraffins/isoparaffins, aromatics[58]. Separation of p-xylene[77], o-xylene and m-xylene[77]. Separation of glucose/fructose[78]. Separation of p-diethyl benzene/isomer mixture[79]. Chromatographic analytical separations[75].

### **2.3.15 Biomass upgrading and derivatives**

The key properties of zeolites used in this category of applications are acidity (presence of acidic sites) and shape selectivity making zeolites a catalyst of choice for C-C bond rearrangements[80]. The key applications are catalytic cracking and hydrocracking which allows reduction of molecular weight of heavy biomass constituents. The key biomass components are vegetable oils (disaccharides), polymers such as cellulose, hemicellulose, lignin etc[81]. In addition, isomerization reactions are also catalyzed by zeolites. It involves valorization of n-alkane rich fractions from triglyceride deoxygenation[82]. Moreover, sugar transformation reactions yielding simple sugars from more complicated ones are also an important class of applications[83]. A new set of biomass upgradation reaction also includes alkylation of aromatics[83]. As such this approach is used in transformation of

aromatics and phenols obtained from lignin conversion. Various families of zeolites including FAU class NaX ones are used in various applications mentioned above in this section[80]. In the present context we can also say that NaX zeolite is used in biodiesel production[84]. Acetone a common industrial chemical is produced from bioethanol, biomass, biomass wastes (sewage sludge, fermentation residue, livestock manure) using various zeolites including NaX[80]. Lactic Acid, an important intermediate is often produced by transformation of trioses or other sugars using FAU catalysts such as NaX[85]. Dehydration of sugars to esters are conducted using FAU catalysts[86]. FAU class of zeolites are used in aldol condensation of furfural with acetone (from biomass) to obtain aldehyde-ketone category of products[87]. The examples provided are just some highlights and in practice there are much more cases.

### **2.3.16 Geotechnical Applications**

Zeolites are often used in grouting[88], asphalt filler[89], sub-grade stabilization[90], pavement base course[91], general engineering fill[22], structural fill[22], soil amendment and infill[90]. In case of soils and fills zeolite adsorbs and absorb water which leads to control of water in release and absorption. This is a key aspect because it prevents swelling of soil. If soil or filler swells too much then they could expand when wet and shrink when dry. This creates pressure which can crack pavements, basement floors, driveways, pipelines and foundations. Zeolite addition in geomaterials brings positive benefits without upsetting the basic chemical composition as most components are silica and alumina in various forms[92].

## **2.4 Circular economy**

### **2.4.1 Introduction**

Circular economy is the next generation concept for transformation of traditional patterns of economic growth. Until now the industrial production has followed a linear path but as natural resources become scarcer and legislation stronger a new concept has been developed. This concept of circular economy is considered a



possible solution. This is still a general term and a precise definition has not been framed yet as this combined concept is new.

The origins of circular economy can be traced back in 1983 when Gro Harlem Brundtland[93] former director general of WHO (World Health Organization) lead an initiative to explore a global agenda for change with the sole purpose of creating a bedrock for development of long term sustainable strategies and its implication by 2000 and beyond[94].

#### **2.4.2 The current situation**

The current industrial system at a global scale is a linear one, where the concept of holistic synergy between industries is lacking which leads to high yield of wastes and outgoing streams. In the current linear style environmental degradation takes place by depletion of natural resources by mining and indiscriminate exploitation. This leads to a decrease in value of natural resources available due to overexploitation and pollution originating from waste [95].

From an ecosystem point of view an industrial symbiosis is where one industry uses the other's waste as raw material. From the service sector perspective efforts are being made to make high quality materials which ensures a longer life cycle of the product and hence lesser production, lesser wastes and delaying waste generation. This is a logical extension of Rs i.e Reduce, Reuse, Recycle policy of Sustainable development framework programs[96].

#### **2.4.3 Basic concepts and perspectives**

One of the ideas of the circular economy concept is that there is ultimately no net effect on nature and it infact restores damages done during natural resource acquisition. One key aspect is that during the entire product life cycle there is no net generation of waste. Circular economy concept compels us to investigate an “approach to redesign approach”. This is a radical approach which will be critical to next generation industry and policy making and it is a pity that these have not arrived in school text books yet. The uniqueness in this approach lies in the fact that

we focus on redesigning systems for manufacturing, service supply ecosystem and not merely the individual components or resource utilization[97].

Another inherent meaning which can be formulated in the very term “circular economy” is the idea of cycle relating to biogeochemical cycles and recycling. Hence from those we know a cycle can adapt to change but the key aspect is the rate of change and its management.

#### **2.4.4 Key trends and new perspectives**

The key trend for circular economy is that the initiatives arose because of legislations rather than push by the academic and scientific community. Resource crunch and environmental disasters were the key drivers in the evolution of this concept and they still are. From a business and legislative perspective circular economy can be seen as natural balance between economic development and resource, environmental protection.

Most of the sustainable framework plans have a triad approach with benefits in economic, social and environmental regimes. The drawback on framework plans in case of circular economy is that no foreseen benefit could be predicted in the social front. It is understood that efficient resource utilizations bring immense benefits to not only our generation but secures the next generation but an explicit recognition of the social aspect is still missing and needs to be rethought[98]. It still needs to be thought how circular economy framework can lead to greater equality in society but perhaps between all beings on earth. Hence it will be a debatable issue when framing policies and redesigning the new approach[99].

Circular economy for companies makes great business sense to keep rare materials in their loop and use less raw materials especially when their prices are volatile and forecasted to rise. It further enhances the independence of companies and whole nations. This kind of approach could create new jobs and preserve old ones. Moreover instead of creating new mining jobs there will be a lot of recycle related vacancies [100]. Hence jobs from mining would be diverted to new eco-friendly and sustainable sectors. The trend with various waste service companies are shifting from a centralized processing facility to scattered modular system of processing

units. These are often known as modular service systems with onsite processing and purification with real time monitoring[101].

#### **2.4.5 Policy making initiatives for circular economy in various countries**

The European Commission adopted a policy of “Towards circular economy: a zero waste programme for Europe” in December 2014. Initially this was greeted with great resistance by industrial lobbies. But later it was thought to be inevitable for the security and self-sufficiency of Europe. It is widely believed that this will be a great step to make Europe self-sufficient in natural or rare earth resources[102]. It would play a direct role in reducing conflict in commercial markets and to stop wars over natural resources. One EU report concluded that aluminium cans can have infinite recycling possibility and hence this can be used to greatly replace constant demand for some other product that utilizes aluminium. Increasing recovery rates and putting a levy fee/refund policy on each can go a long way to encourage recycling and engaging in less mining[95]. Redesigning what we consume, how we consume, incentives will go a long way to stage a conducive platform for constant development of circular economy. The EU believes that 2 million new jobs will be created in Europe itself and 600 million euros will be saved annually with self-sufficiency among other benefits[103].

In the UK a prominent think tank Ellen Macarthur Foundation commissioned a number of reports in 2012-2014. The topics of these were drawbacks of linear economy, resource loss, service ecosystem erosion and the eventual threat to global prosperity. In another report new business models were developed to address benefits of circular economy in cost of production, life span aspects of products, waste as raw material and essence of circles which culminates into source material remaining uncontaminated leading to greater distribution and material productivity and lesser costs. In November 2014 the UK government encouraged the principle and went forward to endorse it. We can be quite optimistic about new laws coming in favour of circular economy soon[104].

In France the concept has been greeted with enthusiasm and as recently as in June 2014 during the “Green Week” The French Executive Commissioner for

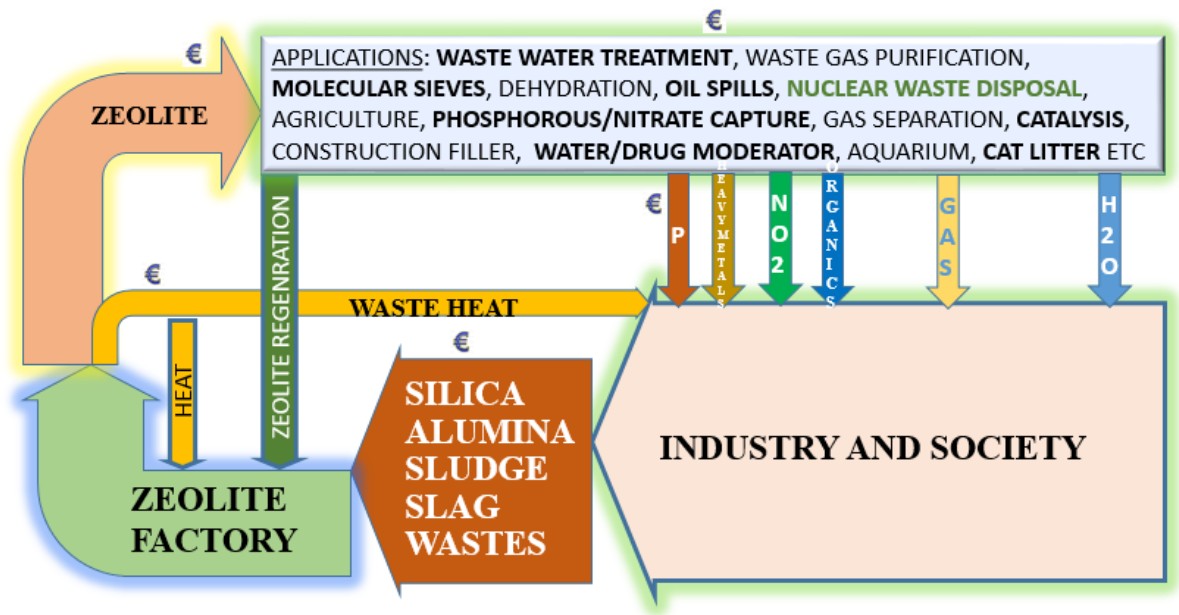
sustainable development confirmed France's commitment to convert the nation into a leading player into circular economy sector. Various French firms such as SNCF, La Poste, Capenergies etc have partnered with various institutions to develop business models in this field[105]

In Finland, clean technologies sector is a growing and is thought to be the game changer to bring greater economic prosperity. Motivated by EU Environmental mandates the government of Finland has also passed policies encouraging circular economy from 2014 onwards. For instance using landfills for various types of ashes will be prohibited completely from 2016 onwards. Lot of investments are being made by companies to upgrade their production to suite to a circular economy ecosystem. The waste management companies are in the forefront of these pioneering initiatives as this means greater business and adherence to legislations. In Finland more of the policy support came from SITRA through its social experiments and other initiatives which showed that circular economy is worth 2.5 billion euros in Finland alone[106]. Hence a lot of funding is being provided by TEKES, government and various institutions to make innovative firms which can exploit this growth opportunity in Finland and globally[107].

The first of the initiatives for circular economy in China took place in 1990s and concrete visible policy adjustment in the 5-year plans started taking place since 2005. The drive behind circular economy has been to stop conflicts between economic growth, resource shortage and pollution. In China it has been implemented in three levels i.e., cleaner production in companies, environment friendly special economic zones, overall provinces, cities and towns[108].

It is clear that in the future there would be whole departments or ministries looking into circular economy. In terms of legislations one major drawback is issue of permit allocation. The side streams and by-products of industries termed as special category waste materials/ hazardous waste can be handled by limited entities which greatly prohibits innovation. One unique example is exclusive rights to handle hazardous waste and its incineration.

## 2.4.6 Circular economy aspect in CFA Zeolite production and application



**Figure 10:** Circular economy concept for zeolites

A circular economy model has been created for waste to zeolite production and application. Figure 8 illustrates a mechanism which is truly eco-friendly, holistic and sustainable. The industry and society produces the raw materials termed as waste/by-products/side streams. In our context these waste materials are silica, alumina, alkali rich substances in the form of ash, sludge and slags. It is worth noting that the industries under consideration are truly huge and quantity of waste produced is immense. The sectors from which these wastes are derived forms the very foundation of modern industry and society. Power plants, silicon, aluminium, steel, caustic soda etc to name a few. The appropriate disposal is a great issue among other problems associated with these wastes. As the quantities involved are quite large there is economic value attached to it. Hence collection of these wastes leads to a certain fee (€). The waste materials are converted to zeolite in the zeolite factory. The zeolite factory utilizes the unique process developed by us. The factory produces zeolite and extractable heat. The zeolite could be sold for revenue. The heat energy could be sold to society and industry. The heat energy can also be circulated back to the zeolite factory for internal needs leading to lesser operating costs. Zeolites are very versatile materials with large scale applications. Some of

the applications have been shown in Figure 10 and section 2.3. Considering the example of waste water treatment for heavy metal removal, we can use zeolite for removing heavy metal, which generates revenue followed by selling of those heavy metals generating additional revenue. The used zeolite is regenerated multiple times and finally used in low value applications such as geotechnical projects (road construction, fillers etc) at the end of its life cycle. It could also be melted and powdered to extract remaining valuable metals at the end of its life cycle. The powder is mostly amorphous silica, alumina or clay and can be easily reused for zeolite precursor or other purposes. Both the heavy metal and treated water is circulated back to society and industry.

In case of water laden with ammonia or phosphorous the zeolite would be used to remove organics. The ammonia/phosphorous laden zeolite would be used as fertilizer. As zeolite is silica, alumina or clay material, it integrates with the soil without any hindrance. The water is circulated in society and industry. Hence multiple revenue streams are generated from water purification service, fertilizer revenue and treated water reuse revenue/savings.

From both the examples above we can understand that the model illustrated is truly circular, holistic and sustainable. It does not involve use of net virgin natural resources. This approach benefits the social, economic and environmental regimes. Hence we can conclude that our current approach of circular economy is truly eco-friendly, sustainable and economically advantageous for industries to embrace it quickly.

## **3 EXPERIMENTAL**

### **3.1 Coal Flyash**

The CFA under consideration has been sourced from a major Finnish energy generation company. Various analytical methods were used to analyse the CFA. Analysis techniques such as EDX, SEM, XRD, BET were used. These variety of techniques were employed to determine if the CFA was the appropriate sample/raw material eg: pulverized bed ash has a completely different morphology than fluidized bed. Hence with conjunction of various analysis techniques the decision about suitability of raw material could be achieved.

#### **3.1.1 Pre-treatment**

The raw CFA was sieved using Sieve shaker SV005 (Contact Impact Test Equipment Ltd, Milton Keynes, England) to get rid of excess unburnt carbon. The sieve gratings (in microns) used were 600, 400, 200, 150, collector at the bottom. The process of sieving was conducted for 30 minutes non-stop. The sieved CFA was termed as “refined CFA”.

The refined CFA was weighed before and after (being heated at 130°C) to find amount of adsorbed moisture.

The refined CFA was thermal treated at 1050°C for 2h hours to find out LOI (loss of ignition).

The raw CFA and refined CFA was subjected to temperature of 1050°C for 2 hours each to find the effect of sieving on unburnt carbon removal.

The machine used for heating and drying was HTC 03/14-HTC 08/16 (Nabertherm, New Castle, Germany). The machine had a temperature accuracy of  $\pm 3$ .

## 3.2 Zeolite

### 3.2.1 Synthesis process

The process starts with mixing of requisite amounts of CFA with NaOH and water. The solution was then aged for 24 hours (fixed time). The solution was continuously stirred at 650 rpm for the whole duration of ageing. Ageing and stirring were conducted at ambient room temperature of 21°C. The solution chamber was made airtight to avoid loss of water and hence keep the chemical composition constant. The stirred and aged solution was transferred to teflon autoclaves. The teflon autoclaves were put in a preheated oven at various temperatures between 60-85°C for crystallization. The temperatures used were 60°C, 65°C, 70°C, 75°C, 80°C, 85°C. It was a single step hydrothermal process. The zeolite was retrieved and washed with distilled water. The washed zeolite was put in an oven for drying. The drying temperature was 105°C and time was 16 hours. The zeolite was retrieved and grinded using mortar and pestle to make it a fine powder. The powdered zeolite was stored in a sealed container. The synthesis process was optimized to produce unburnt coal and waste heat. The unburnt coal was retrieved during sieving and waste heat was produced during batch composition preparation.

The primary challenge was quantification of amorphous SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> from CFA. The part of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> from CFA should be amorphous for reaction. The amorphous and crystalline content of silica and alumina could not be distinguished quantitatively due to the mixed phase and complex nature of CFA hence a technique was devised to overcome that technical challenge.

A specific SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was assumed each time. This ratio was considered the reactive amorphous part. This would be typically lower than EDX values because of the presence of inert quartz and mullite. Hence the overall amorphous SiO<sub>2</sub> is lower because it is distributed in quartz and mullite components. Hence the real reactive SiO<sub>2</sub> would always be much lower. The corrected Al<sub>2</sub>O<sub>3</sub> (only present in mullite) would also be less compared to original EDX values, but the amount of total decrease would be less compared to SiO<sub>2</sub>. The optimum SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed with calculated parts of other chemicals will only give NaX if the reactivity among



amorphous phases is not too stark. With the specific  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio a fixed calculated ratio of NaOH and water (based on stoichiometry) was reacted to get NaX zeolite. The idea is based on the fact that only the correct amorphous and reactive  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio will react with complete NaOH stoichiometrically to give a pure form NaX zeolite. If the incorrect  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is used with NaOH and water then there will be different products/ multiple products/ mixed zeolite phases due to unused or over used active phase. Specific molar ratios of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , NaOH and water (with homogeneous reactivity) at specific temperature range gives specific zeolites only. Explicitly  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was considered because it is the core  $\text{TO}_4$  building structure.

This is a very new approach to find a real solution to amorphous quantification of CFA in a very short time. Such an approach has been engineered and implemented for the first time in the world in case of CFA Zeolites.

To implement the above idea, rational planning of experiments were conducted with combinatorial approach. CFA Zeolite Phase diagrams from literature were used but due to the variation of different CFA all over the world it did not prove very helpful. Among all the chemical synthesis methods available, hydrothermal treatment was chosen for its simplicity in implementing and scale up. The oven used for hydrothermal synthesis was “VT 6025, Heraeus” manufactured by Thermo Scientific.

### **3.3 Chemical composition and EDX analysis**

EDX analysis of CFA and zeolites were carried out in Åbo Akademi University Process Chemistry Centre in Turku. The instrument used was Thermo Scientific UltraDry SDD EDS-system (Thermo Scientific, Waltham, USA). The EDX analysis was used to determine chemical/elemental composition of CFA.

The CFA used for experiments related to zeolite synthesis were all refined CFA.

### 3.1.3 SEM Analysis

The refined CFA and zeolites were subjected to SEM analysis carried out at Åbo Akademi University Process Chemistry Centre, Turku. The instrument used was Leo 1530 Gemini (Zeiss, Jena, Germany). The samples were carbon coated. Sample preparation and instrument handling was conducted by a third party expert.

### 3.1.4 XRD Analysis

The refined CFA and zeolites were subjected to XRD analysis carried out at Aalto University Department of Inorganic Chemistry. The instrument used was PAN Analytical XpertPRO MPD $\alpha$ 1 (PANalytical, EA Almelo, The Netherlands). The radiation source was Cu-K $\alpha$ 1. Standard sample preparation procedure was followed[109]. Each sample was scanned for 30 minutes. The data matching software used was Xpert HighScore. The database used for matching was ICDD (International Centre for Diffraction Database). The graph has been plotted by processing XRD raw data in Origin PRO.

### 3.1.5 BET Analysis

The refined CFA and zeolites were subjected to BET analysis carried out at Aalto University Department of Forest Products Technology. The instrument used was TriStar II 3020 (Micromeritics, Norcross, USA). Standard sample preparation procedure with degassing was followed[110]. The adsorption-desorption experiments were carried out at 77K.

### 3.2.6 Statistical Analysis

Various BET data for zeolites at 75°C were collected and statistical analysis carried out. Some of the parameters and formulas used are provided below[111] [112]:

$$\bar{X} = \frac{\sum X}{N} \quad (5)$$

$$\sigma = \sqrt{\frac{\sum d^2}{N}} \quad (6)$$

$$s^2 = \frac{\sum(X-\bar{x})^2}{N-1} \quad (7)$$

$$S. E = \frac{\sigma}{\sqrt{N}} \quad (8)$$

$$\text{Skewness} = \frac{\sum(X-\bar{x})^3}{(N-1)s^3} \quad (9)$$

$$\text{Kurt} = \frac{n \sum_{i=1}^n (X_i - \bar{x})^4}{(\sum_{i=1}^n (X_i - \bar{x})^2)^2} \quad (10)$$

$$\text{Range} = X_{\max} - X_{\min} \quad (11)$$

Where:

$\bar{x}$  (sometimes call the X-bar) is the symbol for the mean.

$\sum$  (the Greek letter sigma) is the symbol for summation.

$X$  is the symbol for the scores.

$N$  is the symbol for the number of scores.

$\sigma$  (little sigma) is the standard deviation.

$d^2$  is a score's deviation from the mean squared.

$s^2$  is sample variance

S.E Standard error

Kurt is Kurtosis

n score number

The results have been calculated in MS Excel 2013 using the Data Analysis tool.

## 4 RESULTS AND DISCUSSION

### 4.1 Coal Flyash

#### 4.1.1 Pre-treatment

**Table 2:** Drying data

Serial Number	Weight before drying (g)	Weight after drying (g)	Moisture loss (Wet basis %)	Moisture loss (Dry basis %)
1	10.01	9.99	0.19	0.20
2	20.06	20.04	0.10	0.09
3	30.00	29.97	0.10	0.10
Average	-	-	0.12±0.05	0.13±0.06

$$MD_n\% = \frac{(WB-WA)*100}{WA} \quad (12)$$

$$MW\% = \frac{(WB-WA)*100}{WB} \quad (13)$$

$$AD = \frac{MD_1 + MD_2 + MD_3}{3} \quad (14)$$

$$AW = \frac{MW_1 + MW_2 + MW_3}{3} \quad (15)$$

Where  $MD_n\%$  is moisture loss percentage (dry basis)  
 $MW_n\%$  is moisture loss percentage (wet basis)  
 WB is weight before drying (g)  
 WA is weight after drying (g)  
 n is integer (1,2,3) corresponding to serial number  
 AD is average of moisture loss percentage (dry basis)

AW is average of moisture loss percentage (wet basis)

Table 2 provides moisture content data. We can observe that average of moisture loss percentage (dry basis) and average of moisture loss percentage (wet basis) are  $0.13\pm 0.06$  and  $0.12\pm 0.05$  percentage each. This shows that CFA does not adsorb high quantity of moisture. This also shows that this specific CFA is hydrophobic. This is in agreement with literature which have values of approx. 0.2% [113]. The practical implication would be it could be stored without complicated desiccation system. It can also be stored in a humid environment without grave implications. Hence there is less initial investment and maintenance cost.

**Table 3:** LOI of refined CFA

Serial Number	Weight before combustion (g)	Weight after combustion (g)	Loss of ignition %
1	10.02	9.59	4.29
2	20.70	19.78	4.44
3	30.78	29.43	4.38
Average of refined CFA (AR)	-	-	$4.37\pm 0.05$

**Table 4:** LOI of raw CFA

Serial Number	Weight before combustion (g)	Weight after combustion (g)	Loss of ignition %
1	10.02	9.55	4.69
2	20.46	19.50	4.69
3	31.11	29.76	4.33
Average of raw CFA (AC)	-	-	$4.57\pm 0.2$

Where WB is weight before combustion (g)  
 WA is weight after combustion (g)  
 LOI is loss of ignition  
 AR is average of refined CFA LOI  
 AC is average of raw CFA LOI  
 n is serial number

$$AR = \frac{LOI_1 + LOI_2 + LOI_3}{3} \quad (16)$$

$$AC = \frac{LOI_1 + LOI_2 + LOI_3}{3} \quad (17)$$

Tables 3 and 4 shows LOI of refined and raw CFA. The average of refined CFA LOI and average of raw CFA LOI are  $4.37 \pm 0.05$  and  $4.57 \pm 0.2$  percentages (weight basis). This shows that raw and refined CFA contains 4.57% and 4.37% carbon (weight basis) respectively. Thus it can be said that CFA contain high quantity of unburnt carbon. This is in agreement with literature where CFA contain 1.7-3 % unburnt carbon[113]. The effect of sieving can also be inferred from the data. Basic sieving removes 0.2% (weight basis) of carbon. The economic and logistical implication of the data is quite immense. A real production plant with 20,000 tonnes of CFA/annum will produce 4000 tonnes of unburnt carbon. This carbon can be sold for revenue. Moreover the unburnt carbon present in CFA after sieving has size range lesser than 150 microns. Thus, 0.2% of unburnt carbon is in the size range of >600 to 150 microns or generally more than 150 microns.

#### 4.1.2 Chemical composition and EDX analysis

**Table 5:** EDX Elemental Analysis of CFA

Oxide	Percentage
Na <sub>2</sub> O	1.66±0.61
MgO	1.36±0.10
Al <sub>2</sub> O <sub>3</sub>	23.50±0.14
SiO <sub>2</sub>	56.93±0.15
P <sub>x</sub> O <sub>y</sub>	0.97±0.04
S <sub>x</sub> O <sub>y</sub>	1.42±0.07
K <sub>2</sub> O	2.67±0.05
CaO	4.21±0.12
TiO <sub>2</sub>	1.58±0.12
Fe <sub>2</sub> O <sub>3</sub>	5.70±0.27

EDX Analysis involves carbon coating of samples. Due to this the carbon content of CFA cannot be detected accurately by this method. So the EDX analysis gives accurate information of all elements present (except carbon). The elemental quantification for CFA is accurate if the carbon content is neglected. But overall (100% composition basis) EDX provides rough estimates of elements and its calculated stoichiometric oxides. Thus when we attempt to find the overall chemical quantification of CFA we can at best obtain rough estimates. In this case we are mostly interested about SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and alkali components.



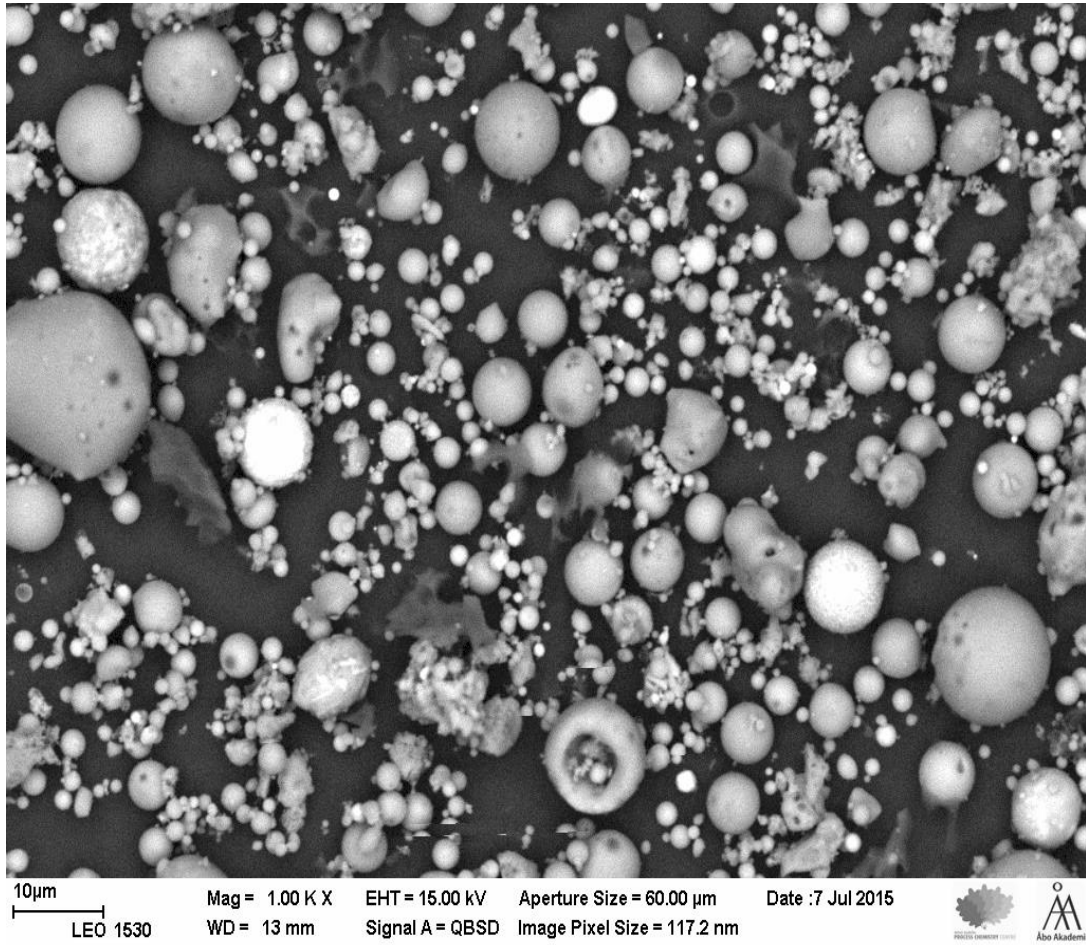
The majority of CFA consists of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . It also contains high amounts of iron oxide and calcium oxide. There is very minor quantity of  $\text{TiO}_2$ . One of the positive aspects of this CFA is that it lacks toxic leachable elements such as Co, Cr, V, Cd, Ar, Pd etc. Hence there should be less negative interference from those elements. It also contains some Na and K which should provide some charge stabilization to zeolite framework. Some drawbacks include high percentage of unburnt carbon, iron oxide, sulphur and calcium oxide. The effects of these are explained in later sections of zeolite synthesis. The CFA sample can be classified as F-class[114], medium grade. A standard called ASTM C618 is used for the classification. Table 6 below shows the comparison:

**Table 6:** CFA comparison and standardization[114]

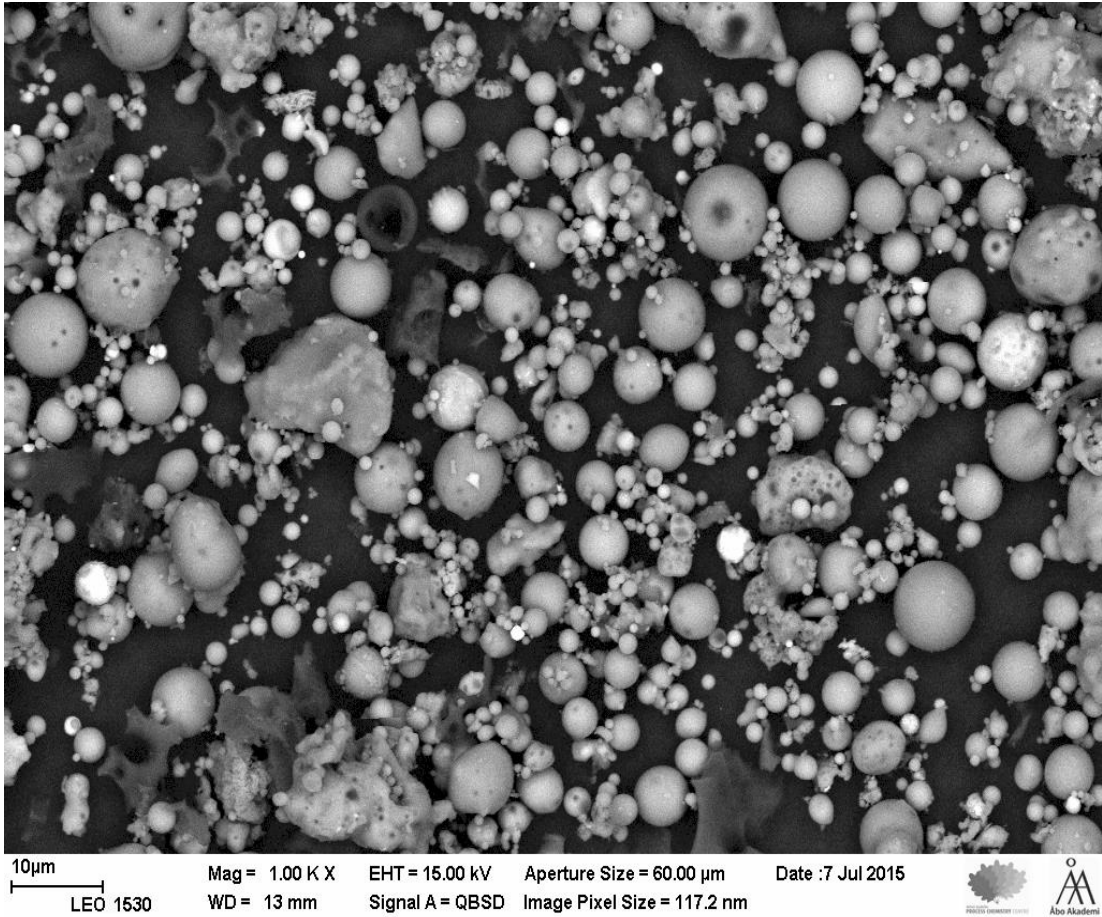
Property	CFA (%)	ASTM C618 Requirements, (%)
$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	85.43	70 (minimum)
$\text{SO}_3$	1.42	5 (maximum)
Moisture content	0.13	3 (maximum)
Loss on Ignition	4.57	6 (maximum)

The combined thermal and EDX analyses provide rough estimates of oxide quantities. It provides no information about crystal or amorphous phase identification/quantification in CFA.

### 4.1.3 SEM Analysis

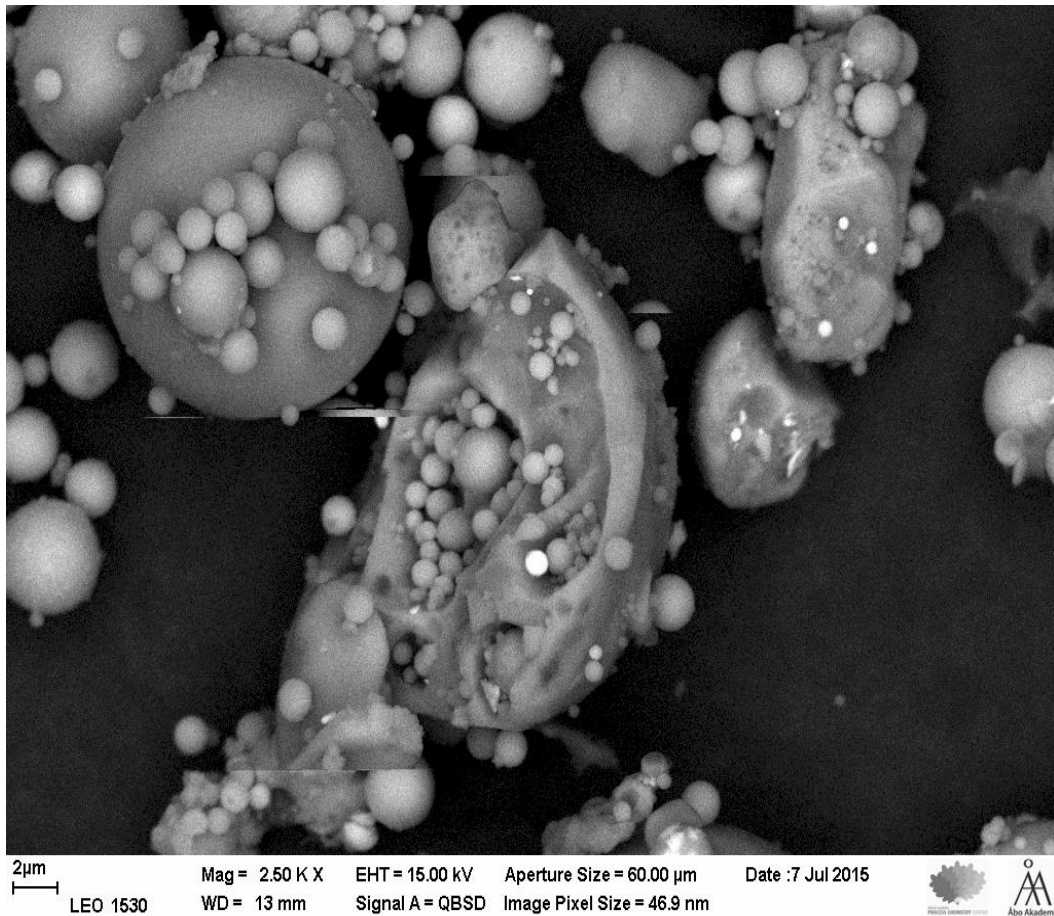


**Figure 11:** Pulverized CFA



**Figure 12:** Pulverized CFA





**Figure 14:** Fractured CFA particles

The spherical balls are amorphous materials consisting of glass. Some spherical balls also represent crystalline non-reactive quartz ( $\text{SiO}_2$ ) and mullite ( $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ )[34]. The dark agglomerations are unburnt carbon. Presence of residue iron oxide phases are indicated along with lots of CaO. Oxides of iron and calcium are also present as spheres often intermixed with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ [13].

The CFA particles get their spherical shape because of cooling and solidification of molten droplets of inorganic coal residue[12]. The surfaces are smooth and “glassy” but in some samples they tend to be rough and pebbly on micro scale, some are partly covered with powder deposits condensed from vapour phase after the spheres have solidified. The powder is often alkali sulphate and easily soluble[15].

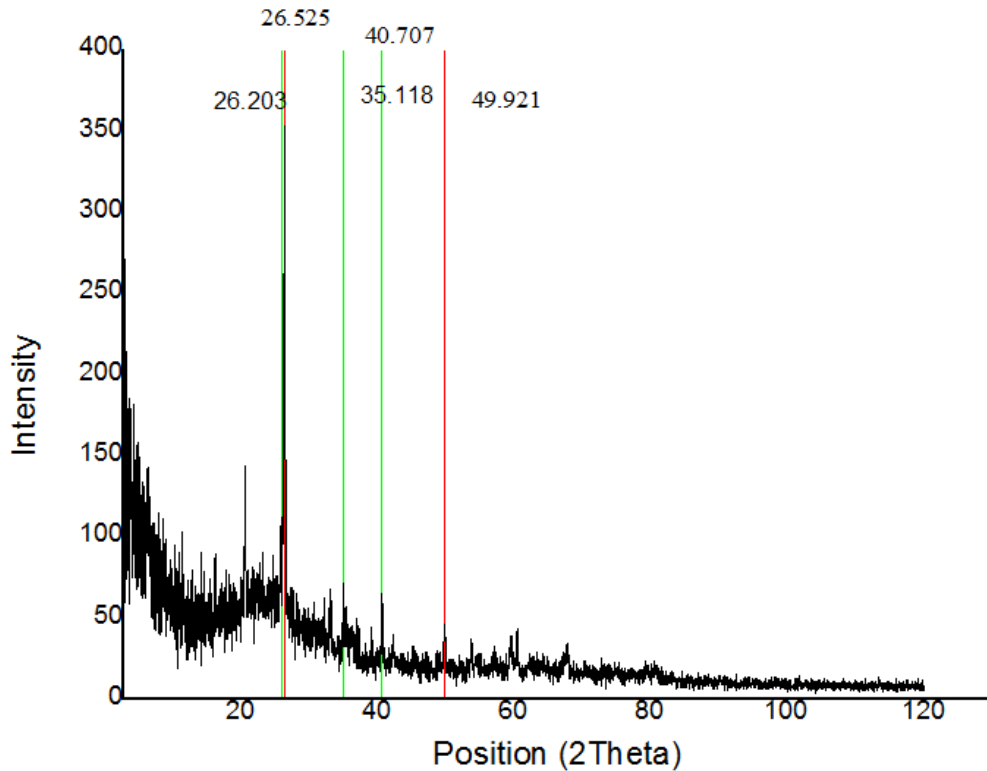
Some particles solidify around a trapped gas bubble and become thin-walled hollow spheres[9] as evident from above images. In addition we also find hollow spheres with a solid sphere inside or sometimes hollow as well. Empty hollow spheres are

called cenospheres and hollow sphere with another sphere inside is called plerospheres[12]. The exact factors in their formation is not known but cenospheres can be segregated from CFA by flotation methods[15]. The hollow spheres are completely glassy. Solid spheres can be glassy as well but they tend to have some crystalline segments in the interior. The reason is there is rapid cooling/heat transfer on the surface but in case of interior there is slower cooling which creates more time to crystallize[2].

SEM has revealed some aspects of morphology in our raw material particles. Its complex chemistry is attributed to its complex structure. A closer look at various spots in CFA reveals an interesting phenomenon. Most CFA particles are not solid. They are semi solid with hollow spherical structures inside. The smaller spheres inside may have multiple hollow structures inside. As evident from figure 14 above, a large sphere is partially solid inside with its own hollow spaces filled with multiple hollow spheres of various size ranges. Thus we can also generalize to an extent that the primary large sphere is the thickest and the ones inside are less thick.

It is evident that CFA particle size is not homogeneous and instead spread over a range. Some of the reasons are particle grouping in liquid and plastic states. Intermixing of spheres, spheroids, debris and other particles has also played a role in currently seen morphology and particle range. One reason for particle range is also the char/unburnt coal. The function of particle size range for char could be due to the coal itself and its processing aspects. The char particles are represented by particles which are slightly charged, semi-coked or coked[12]. The coked and semi-coked particles are produced by complete and partial melting of organics. The slightly charged particles are ones which were exposed to temperatures above 550°C. Slightly charged particles are common in coarse grained fractions over 100 microns in size[15]. The coked and semi-coked ones undergo melting[12]. They condense into spheres, spheroids. The faction that underwent incomplete oxidation became coarser faction. They tend to have irregularity of shape from the coal raw material. This is a very logical explanation derived from analysing coal combustion process in a boiler and observing the SEM images.

#### 4.1.4 XRD Analysis



**Figure 15:** CFA diffractogram

From the XRD peaks we have identified quartz ( $\text{SiO}_2$ ) and mullite ( $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ). They tend to be the only abundant crystalline structures. The red vertical lines at angles 26.5 and 49.9 are used to highlight quartz peaks[35]. The green lines at angles 26.2, 35.1 and 40.7 are used to highlight mullite peaks[35]. One of the reasons for the peaks of quartz and mullite around  $26^\circ$  to almost overlap is due to presence of  $\text{SiO}_2$  components in both quartz and mullite crystals. Moreover the placement of peaks also indicates the combustion temperature they went through. In this case it was around  $800\text{-}900^\circ\text{C}$  [115]. The broad diffraction peak between  $25\text{-}35^\circ$  indicates presence of amorphous phase[34]. The literature data on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  have peaks at 35 degrees [116].

#### 4.1.5 BET Analysis

BET analysis indicate that CFA has a BET surface area of  $366.73 \pm 6.67 \text{ m}^2/\text{g}$ . This surface area is attributed to presence of a large range of particles. It also suggests

that CFA has a lot of small particles. Moreover it proves that CFA is not agglomerated which exposes a lot of surface area for reaction. Hence CFA is present as fine powder and not as granules. It reinforces previous results that CFA contains very low moisture. Moisture tend to make CFA and zeolite like materials stick and swell reducing overall exposed surface area. Some of the surface area is also attributed to char and may act as semi activated carbon. This also indicates that there is a lot of small particles below 160 microns in the CFA attributing to the surface area. This further reinforces our findings in sieving. This also tells us why sieving was not effective to remove more carbon.

## **4.2 Zeolite**

### **4.2.1 Zeolite Synthesis process**

The initial batch composition plays a very crucial role to determine the kind of framework we attempt to get hence that was taken care by use of combinatorial approach with our assumption technique described in the experimental section. Ageing is a tool to control product phase purity and crystal size. Batch ageing is a suitable approach to generate nuclei by itself for the upcoming crystallization and growth process. Long ageing periods leads to formation of greater number of nuclei. This results in smaller crystal size leading to higher surface areas. This also leads to greater acceleration of crystallization in later steps. In our case we opted for room temperature ageing of 24 hours at 21°C. This is best suited for FAU type frameworks and NaX zeolite as concluded from literature[30].

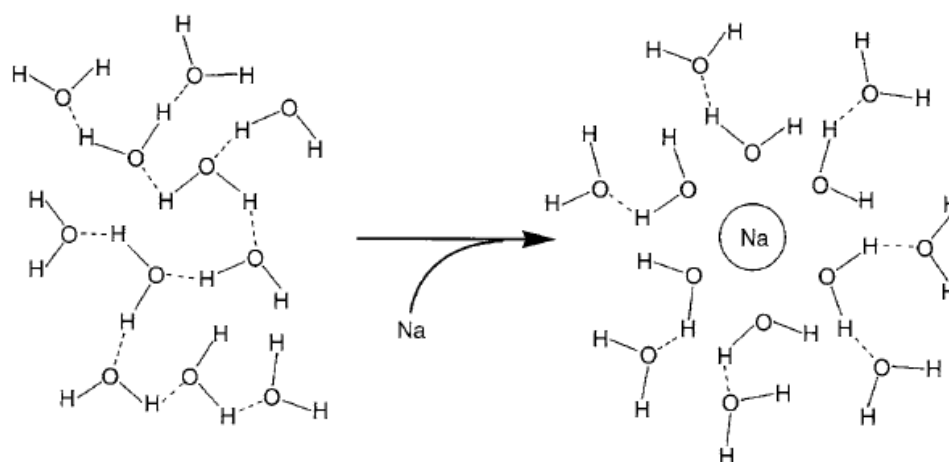
Implementing a batch ageing has a distinct advantage of not using expensive structure directing agents or templates[30]. Hence there are cost and disposal advantages.

The use of water in hydrothermal method is of paramount importance. The amount of water determines the specific type of zeolite. Thus the concentrations of reactants are varied with water quantity. Typically dilution of the gel mixture causes lower supersaturation[30]. Crystal growth is favoured instead of nucleation resulting in large crystals with low surface area[30]. Hence to avoid this, requisite quantities of



water were added to maximize the size effects. This goes in parallel with our mechanism which shows how presence of a large amount of water (not too large) favours formation of large pore, high surface area NaX zeolites. This is another perspective of claims made in literature that the amount of water influences zeolite formation regions in a phase diagram[25]. Hence it can be said that water acts as a structure directing agent. Crystallization at lower water contents suffers from high initial viscosities[30]. There would be different results if a different solvent was used. Due to advantages of water the choice of solvent for solvothermal treatment was made and renamed as hydrothermal.

Alkalinity is very crucial aspect in our system. Higher alkalinity increases the solubility of Si and Al species[38]. It decreases degree of polymerization of silicate anions and accelerates degree of polymerization of polysilicate and aluminate anions. Higher alkalinity favours smaller particle size and narrow size distribution[25]. This agrees with our trials that had a low alkalinity. This also affects aspect ratio (length/width). Other competing phases are GIS, SOD, ANA, LTA[34].



**Figure 16:** Interaction of alkali in framework directing activity [30]

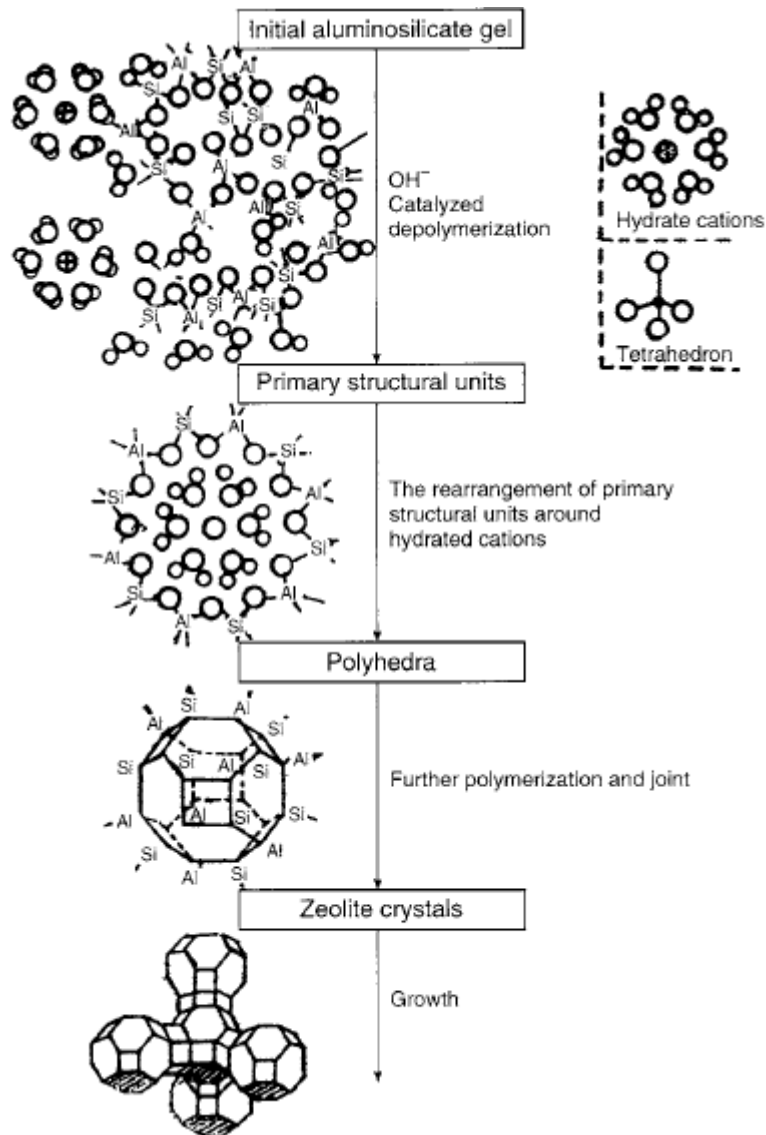
Presence of other cations such as calcium and potassium originating from CFA must had some effect. CaO has a detrimental effect in zeolite formation as it directs the reaction towards a cementitious system[39]. Calcium silicate inhibits zeolite synthesis. Potassium and sodium gets integrated in the zeolite matrix. Potassium

takes free spots of cations for charge balance. The charges of potassium and sodium are different thus it may upset the overall charge stability. But the quantity of excess potassium is so small that there is minimal effect (if any).

The presence of iron brings down the strength of framework and decreases stability. Hence high iron content zeolite is not ideal for high temperature applications such as steam reforming etc[32]. The last paragraphs provide vital highlights about undesirable elements in CFA mix and their possible effects during synthesis. The last paragraphs can be considered part of descriptive error analysis.

The overall reaction kinetics would be hard to generalize because of the complex chemistry and morphology of CFA. The rates of dissolution would be slower when alkali attacks the outer sphere compared to inner spheres. As there is partial vacuum inside the spheres thus rate of reaction accelerates and there is rapid dissolution of inner sphere(s). Thus the only way to fine tune the above competing factors is to optimize the experiments as done by us.

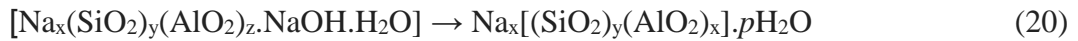
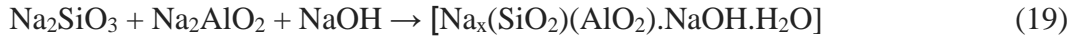
We also conclude that reactivity of amorphous CFA is uniform as it gives pure zeolite. If the reactivity level was stark then we would surely get a mix of different zeolites.



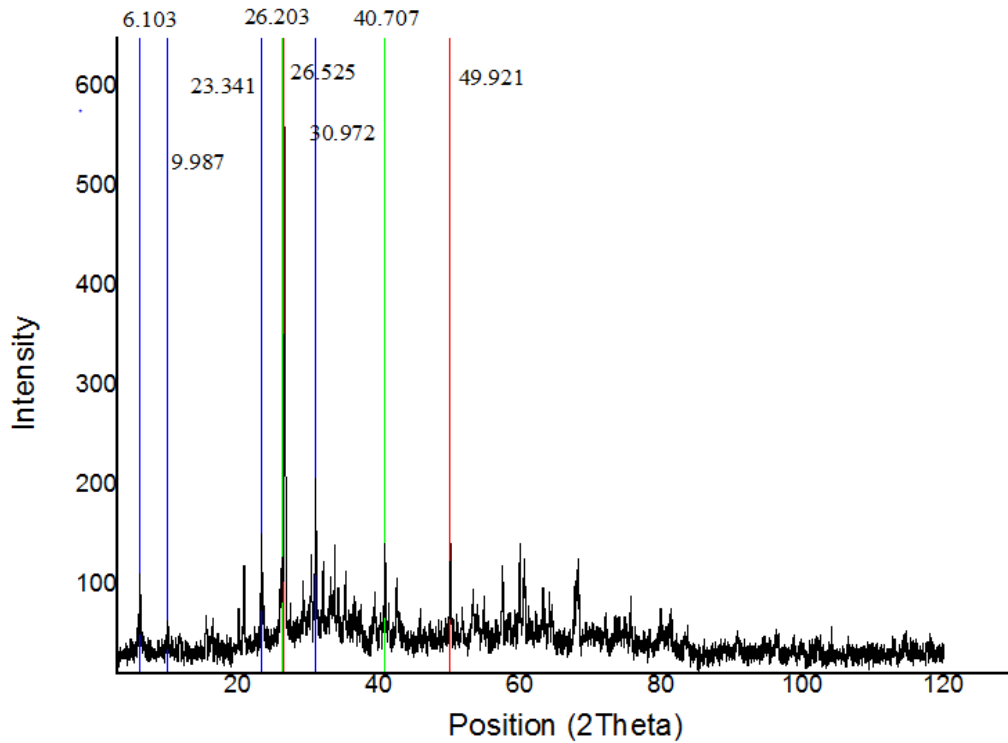
**Figure 17:** Zeolite transformation mechanism[30]

Figure 17 illustrates the mechanism. The initial amorphous silica, alumina and aluminosilicates combine with alkali sodium to gradually form sodium aluminate, sodium silicate. This also involves conversion of the basic silica, alumina to specialized D4R, D6R rings. All of these occur during batch preparation and ageing steps. These sodium aluminate and sodium silicates mature during ageing step to form active nucleation sites. These active nuclei derive their nutrients and energy from the broth during crystallization to conclude maturity. With the passage of time and crystallization temperature the nuclei undergo growth and propagation. This involves formation of sodium aluminosilicates and correct ring orientations. Next step involves joining of sodalite blocks with D4R and D6R rings in correct

orientations to form appropriate zeolite crystals (NaX). Once all the blocks and rings are aligned to each other they join and propagate rapidly to form long range ordered crystal series and stacks. Figure 17 illustrates the entire process. Having multiple nuclei centres avoids growth of large crystals. We have provided some general reactions to throw more light on the proposed mechanism[117].



#### 4.2.2 XRD Analysis

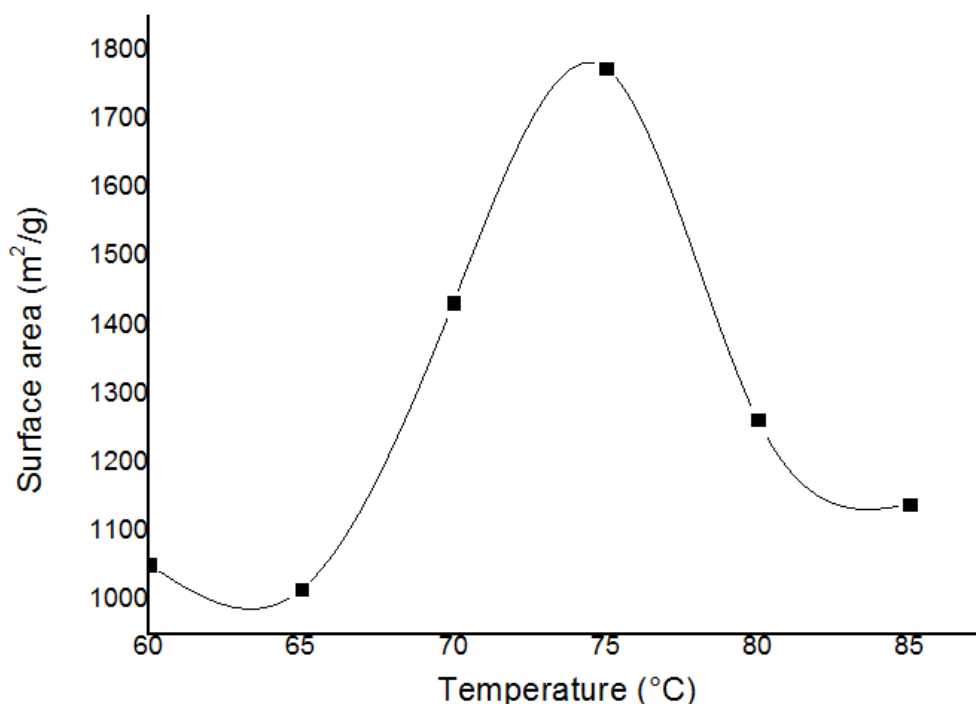


**Figure 18:** CFA Zeolite diffractogram

The blue lines mark NaX peaks at 6.103, 9.987, 23.341, 30.972 as per literature [25] [30]. The quartz peaks at 26.525, 49.921 are still prominent[35]. The mullite peaks at 26.203, 40.707 are also present[35]. The presence of quartz and mullite shows that hydrothermal reaction had no effect on these inert entities. This is parallel with our prediction as quartz and mullite have melting points anywhere between 500-

1600°C[118]. The zeolite peaks tend to be a bit broad indicating small particle sizes. This is in agreement with our pictures and conclusion in zeolite SEM section. It is also worth noting that the broad diffraction present between 20-30° have been replaced by zeolite peaks. This is also in agreement with our conclusions from various sections that the amorphous part gets converted to zeolite NaX.

#### 4.2.3 BET Analysis



**Figure 19:** BET Surface area distribution over a temperature range

Figure 19 depicts the surface area distribution of zeolite over a temperature range of 60-85°C. We can see that the surface area is minimal at 60-65°C range, then gradually increases upto 75°C (maxima) and then starts decreasing. The surface area flattens at 80-85°C range whose values are similar to the ones at 65-70°C. This trend is in agreement with previous literature[34].

The logical explanation of such a behaviour is that the nuclei start forming at room temperature during ageing and starts to crystallize during elevated temperatures. But the nuclei formation continues even at elevated temperatures until crystallization can start[25]. That nuclei completion requires a certain temperature

which is 60-65°C for a certain period of time. After 60-65°C the onset of crystallization takes place which involves the growth of these nuclei into full-fledged crystalline structures (growth and propagation). The optimum growth and propagation requires elevated temperatures, which is 75°C in our case. As the temperature reading depends on where the sensor is kept inside the oven hence we can safely say that the optimum temperature is 75°C  $\pm$ 3 (the oven was calibrated as such).

Growth and propagation also occur at 60-65°C range but their rate is less which translates to less energy supply in that specific time interval of 24h[30]. It is theoretically possible that better crystallization may occur at longer intervals[44]. But it would also lead to development of mixed phase zeolites of similar nature [119]. The more matures nuclei will transform faster to zeolite phase NaX and with time they will transform to next phase[44]. Hence this approach was not taken.

For the crystallizations taking place at higher than optimum temperature there is another phenomenon. In such scenarios the crystal growth is accelerated from the beginning leading to joining of nearby small crystals to form large size crystals[62]. Higher temperature leads to supply of higher energy for the nutrients in the media. This phenomenon continues throughout the mix leading to larger crystal size. Applying lesser time would lead to immature termination of crystallization leading to many unused active spots[62]. Larger crystal size leads to smaller surface area. In another perspective it can also be said that there is less number of crystals for the same mass. The BET surface areas correlate to adsorption capacities which has been verified by third party tests.

**Table 7:** Zeolite comparison

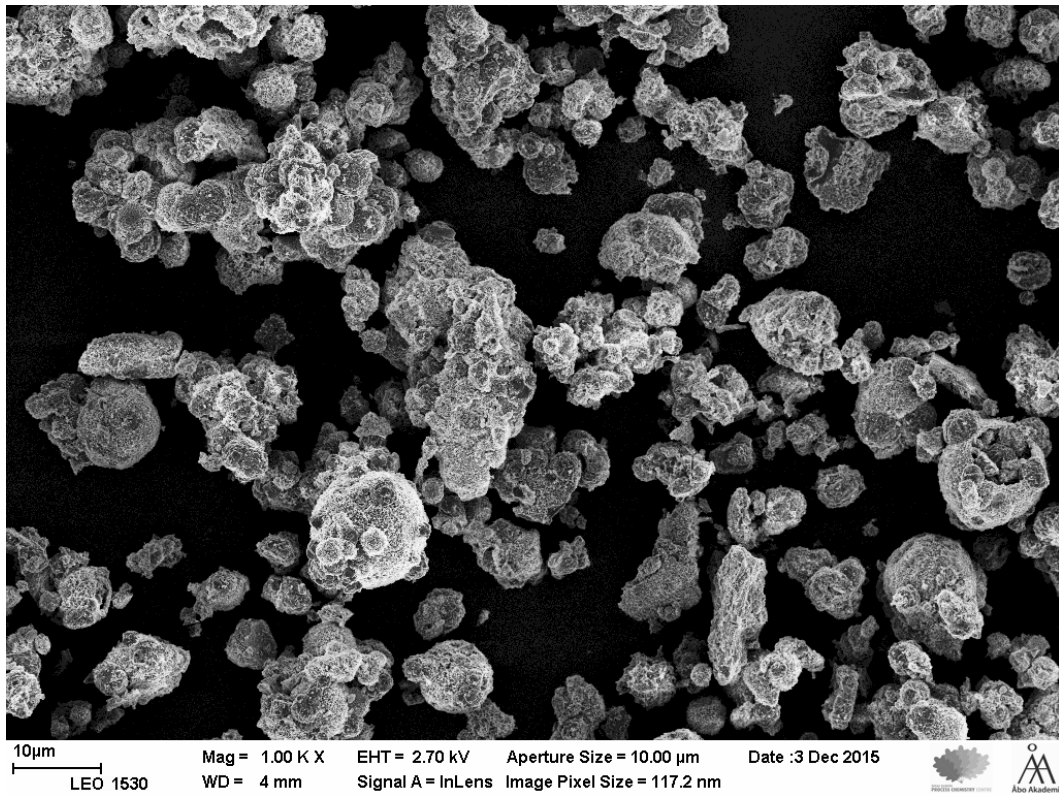
<b>Pure Chemical lab Zeolites (m<sup>2</sup>/g)</b>	<b>Commercial Zeolites (m<sup>2</sup>/g)</b>	<b>CFA NaX Zeolites (m<sup>2</sup>/g) Global</b>	<b>CFA NaX Zeolites (m<sup>2</sup>/g) Finland</b>
464[120]	695[121]	383[34]	1773.3
604[120]	800[122]	445[122]	1850.71
585.88[123]	950[122]	320[84]	1967.61
567[124] [125]	478[34]	272[122]	1955.34

From table 7 we can observe that Finnish CFA Zeolite (75°C variant) clearly possess superior quality in terms of surface area. Column 1 shows values obtained by various labs using pure chemicals as precursors. Hence there are less technical hurdles compared to waste materials as precursors. Column 2 shows values of commercial zeolites made by various companies such as UOP, Zeolyst etc. Column 3 shows values of zeolites made of CFA and column 4 shows our zeolites. The commercial zeolites ranges from 478 to 950 m<sup>2</sup>/g. Global CFA Zeolite ranges from 272 to 445 m<sup>2</sup>/g. We can clearly see that Finnish CFA Zeolite is 5-6 times (5-600%) better than other CFA Zeolites made globally. Finnish CFA Zeolites, even though made from waste has much higher surface area than some of the best commercial zeolites available in the market today in its category. Finnish CFA NaX zeolite has 2-3 times (2-300%) higher surface area than its commercial counterparts made from pure chemicals.

This clearly proves that our understanding and approach about zeolite synthesis is truly world class. This also reinforces the fact the possible new ideas explained earlier have made real effects to obtain these results hence there is new creative contributions.

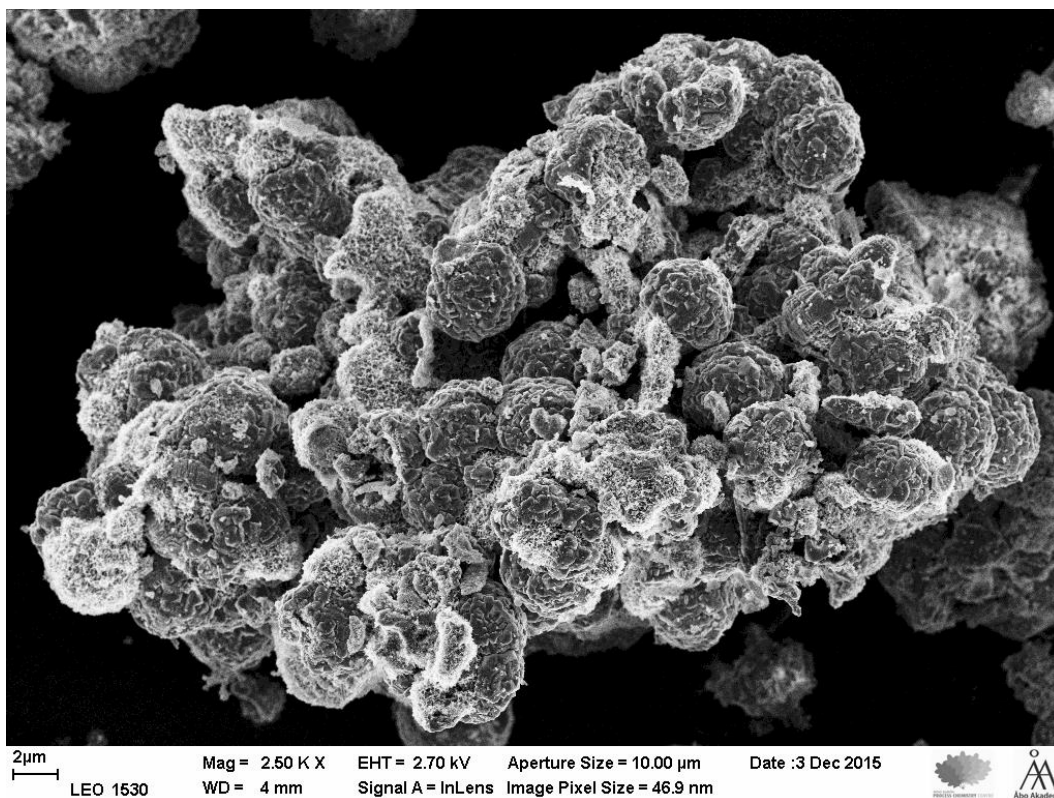
The occurrence of success led to repetitive studies. Consistent repetitive results led to bench scale production and studies. Consistent results in lab and bench scales made the project a grand success.

#### 4.2.4 SEM Analysis

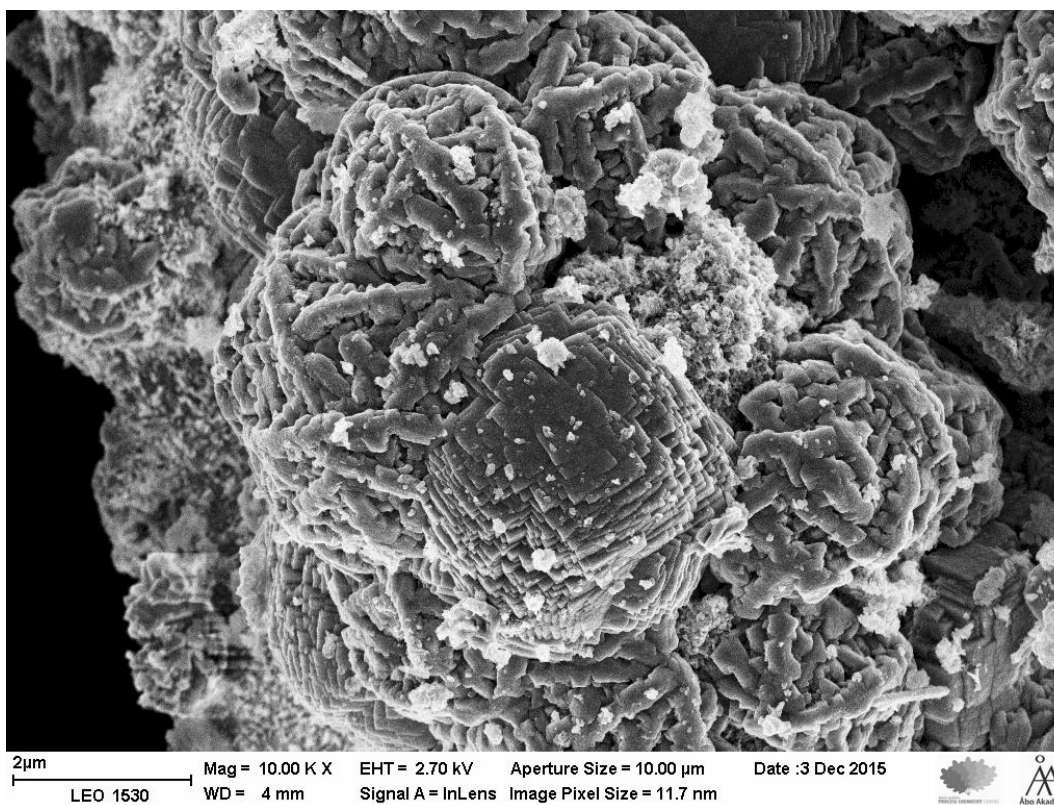


**Figure 20:** Overview of CFA Zeolite conversion

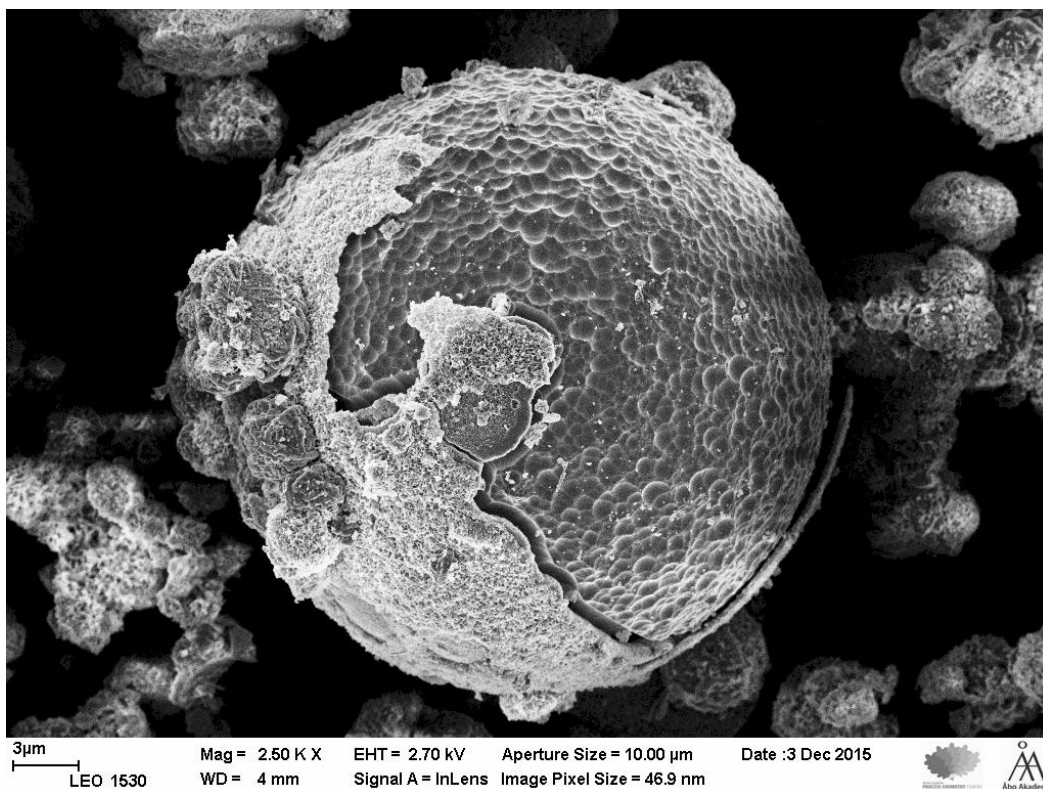




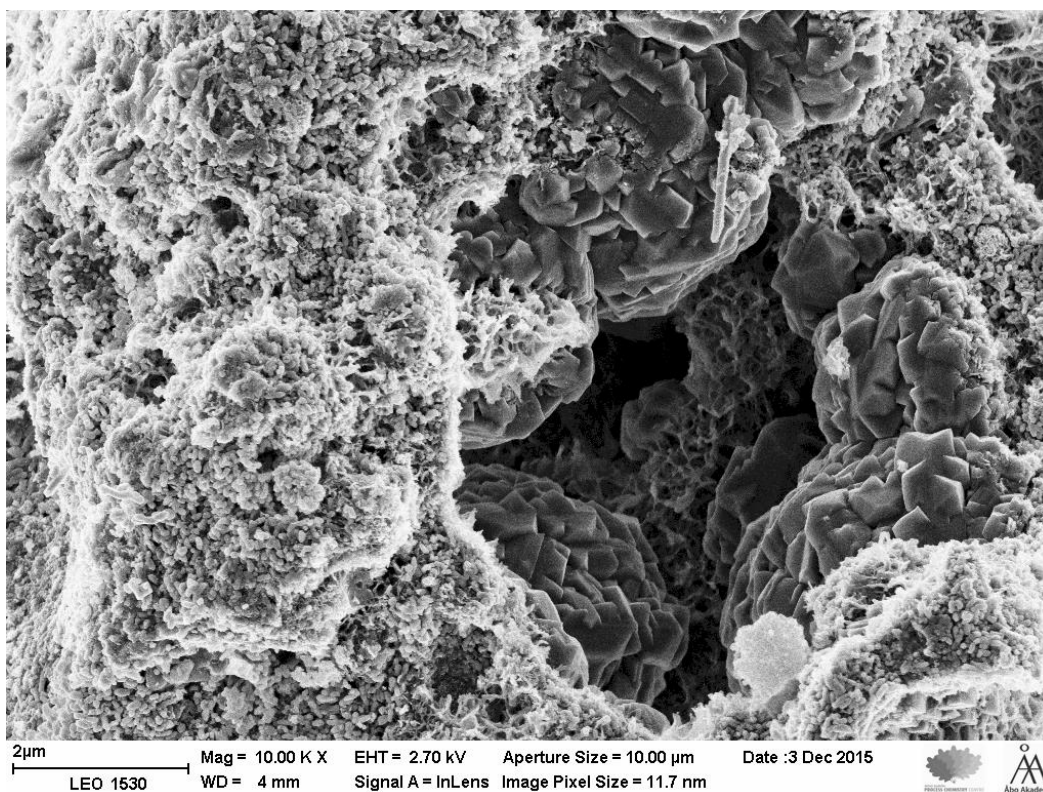
**Figure 21:** CFA Zeolite (presence of long range order)



**Figure 22:** CFA Zeolite (presence of long range order)

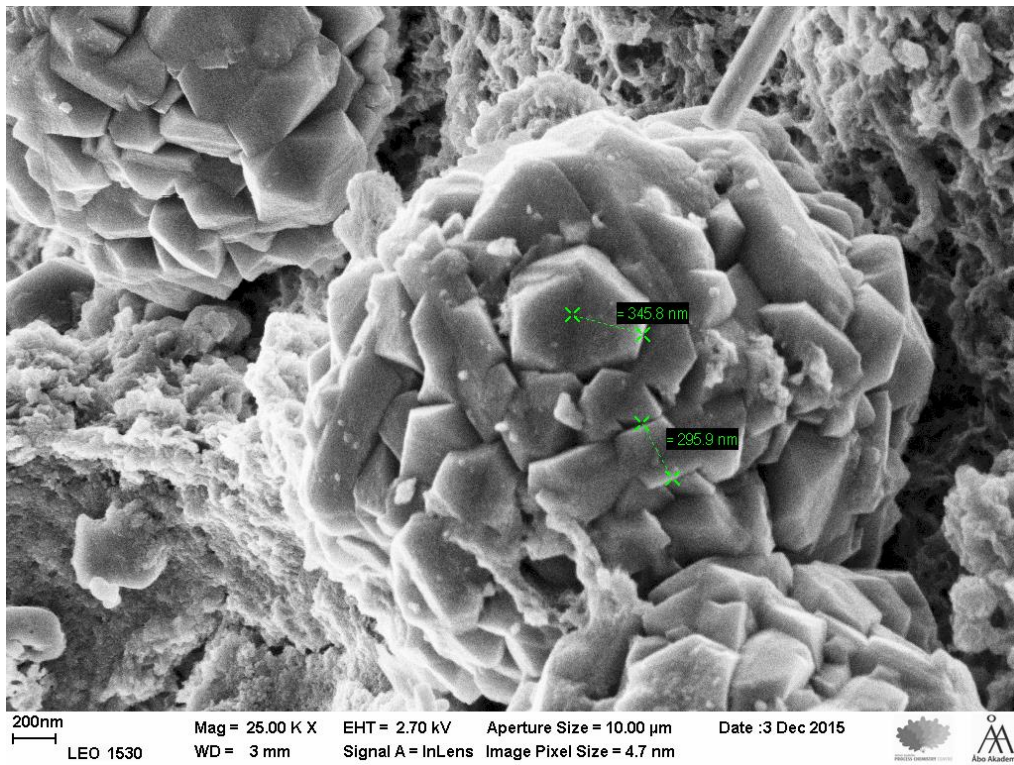


**Figure 23:** Zeolite inside a hollow sphere with quartz outer shell

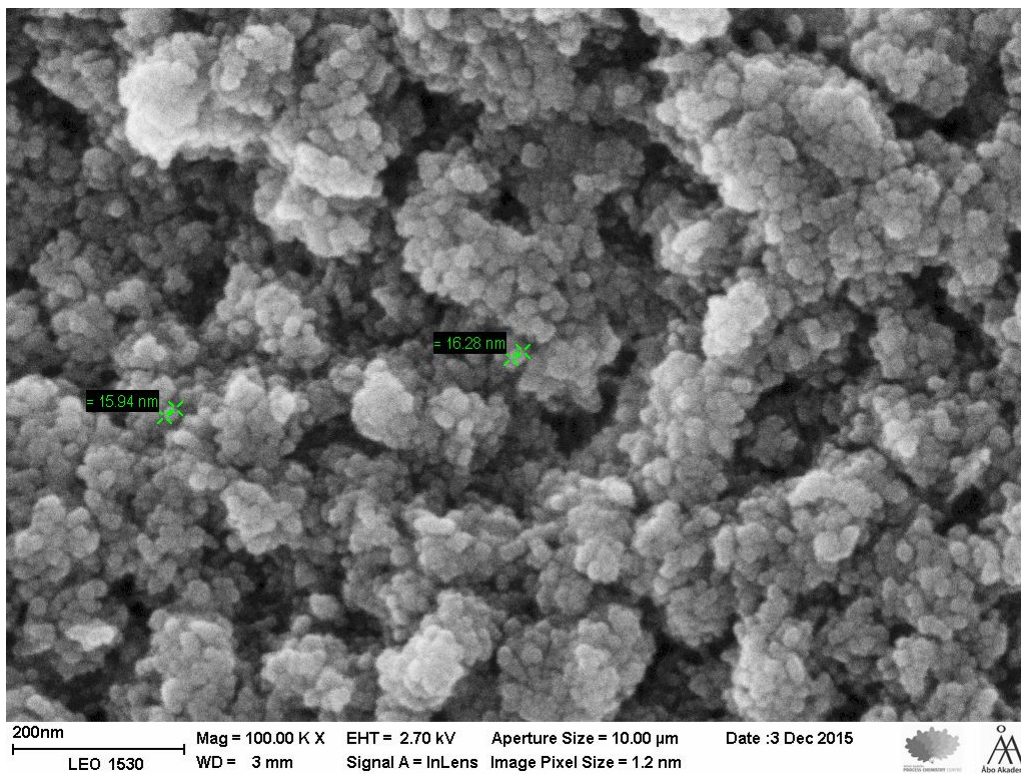


**Figure 24:** CFA Zeolite (proof of semi vacuum approach)





**Figure 25:** CFA Zeolite with big crystal size



**Figure 26:** CFA Zeolite with small crystal size

The images show that the particles are distinctly different from CFA. This provides visual confirmation that there has been a reaction on CFA particles to yield zeolite products. It is clear that zeolites formed are porous, crystalline with a layered structure. Images illustrate that conversion and surface coverage is totally homogeneous, indicating that all of the glass has been converted to zeolite. The extent of conversion is also visible into the inner structure of CFA as many spheres have exploded and their inner materials converted to zeolites (figures 23, 24). The zeolite appears to be an ordered and crystalline structure (figures 20, 21, 22, 25, 26). The presence of long range order is clearly visible from the stacks/apartment floor like structures of zeolite clusters (figure 22). This is reinforced by XRD data as well. Figure 22 indicates that crystallization and propagation has occurred in a linear trajectory which reinforces our claim of layered structures in the bulk solid. Figures 22, 24 clearly illustrate that CFA skeletal collapse of amorphous part. The outer glassy part converted to zeolite indicated by the semi-linear trajectory. Moreover, the presence of semi-vacuum inside the CFA spheres has accelerated the rate of reaction by luring alkali deep inside hollow spheres and allowing rapid reaction. The partial vacuum plays a role in sucking the alkali once the outer structure collapsed completely or partially (figure 23). This is support of our semi-vacuum theory can be found in figure 23 where the outer hollow sphere is quartz with some reaction spots indicating zeolite centres. Those zeolite centres were amorphous glass. The dissolution of the spots led to exposure of vacuum where the alkali rushed in to fill the void and reacted with inner glass to synthesize zeolites. The effects of small sizes would be clearly reflected in very high BET surface area values and high application/adsorption capacity in field tests. As the particle size varies hence certain part of the sample will have higher surface area/application capacity than other part of the same powder mix. The size distribution is also quite varied (figures 25, 26). The various images clearly indicate that size distribution ranges from 345 nm to 16 nm.

It is quite evident that majority of CFA was amorphous material which led to zeolite synthesis. This in turn supports our previous claim of CFA XRD analysis which ascertains amorphous content as majority stake in CFA.

#### 4.2.5 Chemical composition and EDX analysis

**Table 8:** EDX analysis of zeolite prepared at 75°C

Oxide	Percentage
Na <sub>2</sub> O	14.91±0.23
MgO	0.86±0.10
Al <sub>2</sub> O <sub>3</sub>	31.21±0.27
SiO <sub>2</sub>	43.89±0.29
CaO	3.38±0.19
TiO <sub>2</sub>	2.99±0.14
Fe <sub>2</sub> O <sub>3</sub>	2.76±0.23

The EDX analysis provides a rough estimate of the elemental composition. It does not include carbon because the samples are carbon coated. The sample consists of Na<sub>2</sub>O, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in majority. They make up 90% of the final product. This is a typical sign that alkali added during zeolite synthesis has been integrated into the final product. This is an indication that reaction has gone forward with zeolitization. The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> values include unreacted inert quartz and mullite. It is in agreement with literature where Na<sub>2</sub>O, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> form 75-90% of CFA Zeolite[32][34][35]. Direct comparison is difficult because of the heterogeneity of CFA source. It has been observed during experimentation that some of the unburnt carbon floats over the reaction mixture and that is often disposed during washing. Hence it can be said that the amount of remnant carbon in the final product is considerably low. The low quantity oxides of calcium and iron suggests that their detrimental effects in the NaX structure will be nominal. The absence of leaching elements is also a promising sign as it makes it easier to implement it in

geotechnical applications after its final use. The absence of K, S, P has been noted and believed to have washed out.

#### 4.2.6 Statistical Analysis

The grand success of synthesizing CFA Zeolites at lab scale led to scale up at bench scales to obtain more products and check consistency. Table 9 describes various BET values obtained at 75°C over a number of repetitive tests.

**Table 9:** List of BET values

BET Values (m <sup>2</sup> /g)
1773.3
1850.71
1967.61
1955.34
1577.99

A statistical analysis is being made based on values of table 9. The statistical analysis results are provided in table 10.

**Table 10:** Error analysis table

Mean	1824.99 (m <sup>2</sup> /g)
Standard Error	71.30(m <sup>2</sup> /g)
Median	1850.71 (m <sup>2</sup> /g)
Standard Deviation	159.43(m <sup>2</sup> /g)
Sample Variance	25418.49(m <sup>4</sup> /g <sup>2</sup> )
Kurtosis	0.57
Skewness	-1.03
Range	389.62 (m <sup>2</sup> /g)
Minimum	1577.99 (m <sup>2</sup> /g)
Maximum	1967.61 (m <sup>2</sup> /g)
Count	5

We are concerned with product manufacture and quality control hence the standard deviation value could be a goal as it allows restrictions in results. Point to be noted is that in our case we are making standard deviation of a quantity which is not volume based. Instead it is product property based hence a large standard deviation away from provided above should be avoided. Sample variance value is needed to calculate standard deviation. In our case standard deviation provides a better idea due to nature of context. The median value is the 50th percentile i.e half the values are higher than this value and other half lower than this value i.e 1850.71 m<sup>2</sup>/g. Standard error is a quantity which gives a good idea how close our observations to the fitted value/mean. In our case a small value shows that our data points fit well to the mean. The skewness factor is just in range to claim that results are symmetrical[126]. The positive kurtosis value shows the distribution is more peaked than the Gaussian distribution. The remaining statistical values are not descriptive towards final application in terms of present context. Please note that these are not exhaustive analyses and more raw data could be used to create longer analyses.

The error analysis/statistical approach gives some figures which would be essential when doing and analysing next level of experiments and scale up. The benchmarks obtained could be followed as guideline values when obtaining BET values of CFA NaX Zeolites in pilot and factory scales. The BET values correspond to surface areas which in turn corresponds to application potential. Hence obtaining those values ensures quality control. A good quality product could command favourable prices thus directly affecting the whole supply chain.

## 5 CONCLUSIONS

CFA has been analysed and classified as F-Class, medium grade. The complexity of CFA makes its accurate quantification very difficult. CFA primarily consists of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  combined to give 85.43% weight basis. Part of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is amorphous and rest is crystalline quartz and mullite. Crystalline phases are being detected by XRD analysis. LOI is 4.57% with sieving retrieval of 0.2% weight basis. The presence of CaO and  $\text{Fe}_2\text{O}_3$  is a cause for concern whereas the lack of toxic leachable elements is a cause of rejoice. CFA has spherical morphology consisting of cenospheres and plerospheres which have a wide particle range. Majority mass of the particles are less than 160 microns and they are reflected through sieving experiments and BET value of  $366.73 \text{ m}^2/\text{g}$  which is an above average number for CFA. Overall CFA has very low moisture content of 0.13% weight basis with great practical implications. The amorphous and crystalline phase dwell among each other and the presence of exclusive spots are not found. However a hollow sphere can be crystalline on the outside but amorphous in the inside has been reported through zeolite growth studies and observance through SEM for the first time. Careful analysis of CFA has led to other new insights especially in relation to CFA combustion and final morphology which would be beneficial for other researchers.

CFA Zeolite has been synthesized by hydrothermal method with combinatorial approach. The process involves batch composition design, ageing for 24h at  $21^\circ\text{C}$  with 650 rpm. This is followed by hydrothermal treatment for 24h between  $60\text{-}85^\circ\text{C}$ . The optimum results were obtained at  $75^\circ\text{C}$ . We did not use any expensive structure directing agents or templating agents. Thus saving costs and disposal issues. To achieve the correct batch composition, rational mass experiment design with combinatorial approach as taken. The logical design involved use of various phase diagrams. A new experimental approach to find appropriate CFA Zeolitization reactive parts due to lack of instrumental quantification was developed. A new idea was proposed where CFA particles are semi-vacuum and alkaline activated thereafter. The new concept also highlights how and why alkali would penetrate inside spheres and synthesize zeolites. An overall mechanism was also proposed



with reaction equations which make the process clear to the next researcher. This was supported by explanations of the structure and chemistry involved. Focus was made on creating zeolites with high surface area and that was achieved by appropriate theoretical approach and experimental fine tuning. Detailed explanations were provided for the effect of temperature on morphology development. Instrumental analysis by SEM, EDX, XRD and BET confirms the product as CFA Zeolite with pure NaX phase only. It is a key achievement that only pure phase NaX zeolite has been created instead of mixed phase zeolites. Literature indicates using waste as raw materials and hydrothermal approach often yields mix of NaX with competing phases of LTA, SOD, GIS etc. Instrumental analysis also prove that NaX zeolite is highly crystalline with long range order. Various techniques reinforce each other in claims. CFA Zeolites have a particle range of 345 nm to 16 nm which has been reflected in very high BET surface area values. The approximate values range from 1800-2000 m<sup>2</sup>/g. Such values have been reported for the first time in the world.

Thus a very indept understanding of zeolites and synthesis process led to a simple, green, eco-friendly, cheap and scalable process. Excellent understanding of materials chemistry played a key role in designing the whole concept which emphasized on self-activation rather than SDA oriented development. The core of our idea was circular economy and green synthesis and use of SDAs such a TMA which are hazardous flammable chemicals with disposal issues were avoided.

Once a new material is developed it is essential to ascertain repeatability, maintain standards and quality control. Hence multiple repetition studies were done in lab scale and bench scale. In lab scale we were producing 2.0g sample and we scaled to bench level to produce 100g samples. BET analysis at both levels were made to obtain a lot of data, that data was made subject to statistical and error analysis. Certain benchmarks and small guidelines were developed which could be followed in the future for manufacture and quality control.

## 6 FUTURE WORK

Future work involves:

- Scaling up the process to pilot scale.
- Identification and use of grinding equipment for powdering of large scale zeolites during the post drying phase.
- Quantification and utilization of waste heat produced during pilot studies.
- Try other CFA obtained from other operational power plants in Finland.
- Use of older silo stockpiled CFA and check if that could be an added source of raw material.
- Diversify by utilizing other raw materials such as silica, aluminium and caustic soda industry side streams.
- Develop more quality control guidelines for the above mentioned ideas.
- Utilize the broad range of data from above initiatives to create an interactive real time database/app which provides instant process parameters for zeolite production using ashes or other side streams.
- The above vision takes into account circular economy, digitalization and internet of things for a truly sustainable future.
- Creation of a network of ash modification and waste to value plants which produce zeolite among their commercial products.

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