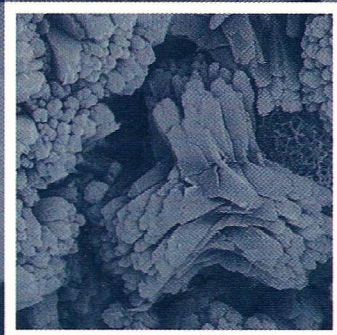




GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen
Universiteit Utrecht

No. 183



Synthesis of zeolites from
coal fly ash

Guido Hollman

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Synthesis of Zeolites from Coal Fly Ash

Synthese van zeolieten uit kolenvliegash

(MET EEN SAMENVATTING IN HET NEDERLANDS)

PROEFSCHRIFT TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
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PROMOTOR: PROF. DR. R.D. SCHUILING

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To my father (†) and mother

Cottleston, Cottleston, Cottleston Pie
A fly can't bird, but a bird can fly
Ask me a riddle and I reply:
"Cottleston, Cottleston, Cottleston Pie"

A.A. Milne
Winnie-the-Pooh, 1926

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Summary

The combustion of coal in power stations produces large quantities of coal fly ash (CFA). At present, in the Netherlands, this combustion residue is almost completely used for the production of building materials. Expectations that the present use of CFA would be affected in the near future by legal and technical developments and by competition with other residual materials, started an interest in new possible applications. One of these is the synthesis of zeolites, the subject of this thesis.

Chapter 1 is an introduction to the research carried out and presents background information on the reasons for this research and on the characteristics of zeolite and CFA.

Chapter 2 focuses on that part of the research that was carried out to establish the optimal conditions for the synthesis of zeolites from Dutch CFA. A large number of zeolitization experiments was carried out to examine the influence of the different reaction parameters such as reaction time, temperature, molarity and type of alkaline solution. Depending on the combination of parameters applied, different types of zeolites were synthesized, such as zeolite Na-P1, zeolite K-G, and zeolite ZK19. It was shown that the conversion results in a sharp increase of the cation exchange capacity from 1.9 to 190-240 meq/100 gram. Contents up to 40 wt. % of zeolite were measured after conversion.

The presence of non-zeolite phases in the conversion products, limits the cation exchange capacity of the zeolitized fly ash and reduces their value for application in the field of ad- and absorption. Therefore, it was examined, as described in **Chapter 3**, if it is possible to synthesize pure zeolites from CFA by modification of the 'traditional' zeolitization process described in Chapter 2. This appeared to be possible by submitting the CFA to a silica extraction prior to the zeolitization process and subsequent synthesis of pure zeolite from this extract. In this study up to 70 gram of pure zeolite was synthesized per kg of CFA treated.

For its applicability, the zeolitized fly ash has to comply to the environmental regulations. This is discussed in **Chapter 4**. The behavior of heavy metals during the zeolitization process was examined, and the leaching behavior of the zeolitized fly ash was tested by standard column experiments. It is shown that the leaching of potentially hazardous elements from CFA is reduced by its zeolitization, and that this reduction is even greater when the CFA is treated prior to zeolitization with organic extractants. In the latter case, the leaching of elements didn't exceed the Dutch norms.

One of the analytical techniques that is of special interest to geochemical engineering is quantitative X-ray powder diffraction (QXRD). The reason for this is that it offers the possibility to assess the degree of success of a conversion process involving crystalline phases, i.e. in this research how much of the glass phase in CFA has been converted in to zeolite. In **Chapter 5**, the applicability of a conventional QXRD method, i.e. standard

addition, was compared to that of a newer technique, the Rietveld method. This latter method comprises the calculation of the diffraction pattern from the instrumental and crystallographic structural parameters and fits this pattern to the observed diffraction pattern. Both methods tested gave similar results when analyzing CFA and CFA converted to zeolite Na-P1, except for quartz concentrations that were much higher in the results of the Rietveld method. It is concluded that the Rietveld method indeed lacks much of the problems for the standard addition method if appropriate structure data are available for the starting model.

Samenvatting

Bij de verbranding van steenkool in elektriciteitscentrales komen grote hoeveelheden vliegashoudend stof vrij. De in Nederland geproduceerde kolenvliegashoudend stof wordt nu nog vrijwel volledig toegepast in bouwmaterialen. Echter, door strenger wordende milieuregels, veranderende verbrandingsprocessen en competitie met andere restproducten is deze afzetmarkt voor kolenvliegashoudend stof in de toekomst niet gegarandeerd. Om een nieuw afvalprobleem te voorkomen, is het van belang dat andere toepassingsmogelijkheden worden ontwikkeld. Eén van deze mogelijkheden is de synthese van zeolieten uit vliegashoudend stof, het onderwerp van dit proefschrift.

Hoofdstuk 1, de introductie, beschrijft de achtergrond en de doelstellingen van het project waarbinnen dit onderzoek is uitgevoerd. Daarnaast wordt ingegaan op het ontstaan, voorkomen en de eigenschappen van vliegashoudend stof en zeoliet.

Hoofdstuk 2 richt zich op het gedeelte van het onderzoek dat is uitgevoerd om de optimale condities voor de synthese van zeolieten uit Nederlands kolenvliegashoudend stof te bepalen. Een groot aantal zeolitatie experimenten is uitgevoerd om de invloed van reactieparameters (zoals reactieduur, temperatuur, molariteit van de loogoplossing en de soort loogoplossing) vast te stellen. Afhankelijk van de combinatie van toegepaste parameters zijn verschillende soorten zeolieten gesynthetiseerd, waaronder zeoliet Na-P1, zeoliet K-G en zeoliet ZK19. Resultaten laten zien dat door de zeolitatie de kationuitwisselingscapaciteit (CEC) scherp toeneemt van 1.9 naar 190-240 meq/100 gram. Het gezeolitiseerde product bevat tot ongeveer 40% zeoliet.

Doordat het gezeolitiseerde product behalve zeoliet ook andere mineralogische fasen bevat, wordt de kationuitwisselingscapaciteit gelimiteerd en daarmee de waarde voor de toepassing van dit product als adsorptiemedium. Om deze reden is, zoals omschreven in **hoofdstuk 3**, onderzocht of het mogelijk is zuivere zeolieten te synthetiseren, door het traditionele, in hoofdstuk 2 beschreven zeolitatieproces aan te passen. Dit blijkt mogelijk te zijn door voorafgaand aan het zeolitatieproces de kolenvliegashoudend stof te onderwerpen aan een silica extractie. Op deze wijze is het mogelijk tot 70 gram puur zeoliet uit 1 kg kolenvliegashoudend stof te synthetiseren.

Voor de toepasbaarheid is het van groot belang dat de gezeolitiseerde vliegashoudend stof aan de geldende milieuregels voldoet. Dit aspect is bestudeerd in **hoofdstuk 4**. Het gedrag van zware metalen gedurende het zeolitatieproces is gevolgd, en het uitlooggedrag van de gezeolitiseerde vliegashoudend stof is met behulp van standaard kolomtesten (volgens NEN) onderzocht. Het blijkt dat de uitloging van milieugevaarlijke elementen uit vliegashoudend stof door de zeolitatie sterk is gereduceerd en dat deze reductie nog groter is indien de vliegashoudend stof voorafgaand aan de zeolitatie is gewassen met organische oplossingen. De uitloging van zeoliet dat is gesynthetiseerd uit op deze manier voorbehandeld vliegashoudend stof overschrijdt op geen enkel punt de Nederlandse norm.

Een analysetechniek die speciaal van belang is voor 'geochemical engineering' is kwantitatieve röntgendiffractie (QXRD). De reden hiervoor is dat deze techniek de mogelijkheid biedt om de mate van succes van een omzettingsproces vast te stellen. Voor dit onderzoek wil dat zeggen dat bepaald wordt hoeveel van de in de vliegase aanwezige glasfase is omgezet en hoeveel zeoliet hierbij is gevormd. In **hoofdstuk 5** wordt de toepasbaarheid van een conventionele QXRD methode met standaard additie vergeleken met een relatief nieuwe techniek, de Rietveld methode. Met deze laatste methode wordt op basis van instrumentele en kristallografische parameters een diffractiepatroon berekend dat zo goed mogelijk past op het gemeten diffractiepatroon. Beide QXRD methoden gaven soortgelijke resultaten voor kolenvliegase en gezeolitiseerd vliegase, met uitzondering voor kwarts. De gehalten van deze laatste zijn in de uitkomsten van de Rietveld methode veel hoger zijn dan in die van de conventionele methode. Gezien het feit dat de conventionele methode vele malen arbeidsintensiever is dan de Rietveld methode, is de conclusie dat de Rietveld methode inderdaad vele voordelen biedt ten opzichte van de conventionele methode, indien geschikte structuurdata beschikbaar zijn van de aanwezige mineralogische fasen.

Chapter 1

Introduction

Partially published as:

"The synthesis of zeolites from fly ash and the properties of the zeolite products"

by G. Steenbruggen and G.G. Hollman

Journal of Geochemical Exploration 62 (1998) pp. 305-309

At present, approximately 900 000 ton of fly ash is produced by coal combustion in the Netherlands each year. The fly ash is used mainly in the production of building materials. In 1996 68% of the coal fly ash produced was used for manufacturing cement and concrete, 18% for producing artificial gravel (Lytag granules) and the remaining 14% in other applications such as filler materials for asphalt (Aalbers et al., 1998). The present use of coal fly ash (CFA) is mainly based on its pozzolanic properties, which entail a reaction between calcium oxides, silica and water to form calcium silicate hydrates which contributes significantly to the strength of building materials like cement and concrete (RIVM, 1993).

At the beginning of the 90's part of the applications for CFA seemed to come to an end as a result of stricter environmental regulations, changes in the CFA quality due to co-combustion of organic waste material, changes in combustion techniques, and additional fears for reduced possibilities of fly ash applications due to competition with other residues. To avoid future disposal problems for this kind of combustion residues, an interest in new applications for CFA arose. In addition, new applications of coal fly ash would preferably have higher margins of profit than the present ones and would contribute to a diversification of the applications.

One possible new application for CFA is the synthesis of zeolite products: a process analogous to the formation of natural zeolites from volcanic ash deposits. Both volcanic ash and CFA are fine-grained and contain a large amount of aluminosilicate glass. Under the right natural conditions, e.g. under the influence of percolating hot groundwater (Barrer, 1982), this glass fraction may be converted into zeolites, and these subsequently into analcime and feldspar, i.e.

glass → zeolite → analcime → feldspar

This conversion process may take tens to thousands of years under natural conditions but can be speeded up to merely days or even hours under controlled laboratory conditions, both for volcanic ash and coal fly ash (see e.g. Höller and Wirsching, 1985; Singer and Berkgaot, 1995; Amrhein et al., 1996).

To examine the possibilities of zeolite formation from Dutch coal fly ash, a research project at the Utrecht University was started in 1994 in cooperation with and financed by KEMA (Arnhem), with additional financial support of the Dutch Ministry of Economic Affairs (PBTS Environmental Technology grant, Senter MIL 93188). The aims of this project were:

- 1) To establish the optimal conditions for the formation of zeolite products from CFA;
- 2) To examine the applicability of the synthesized zeolite for the immobilization of environmental pollutants.

This thesis has the first of these two aims as subject, i.e. the synthesis of zeolite from fly ash. Research on the application of the zeolites synthesized was carried out in the same period and had many interactions with the research published here, which is logical as sorption characteristics of the zeolite product can be influenced by changes in the zeolitization process. The applicability part of the project is the subject of a thesis by Steenbruggen (1999).

This introductory chapter will present background information on the characteristics and origin of fly ash and zeolites and will conclude with an outline of this thesis.

FLY ASH

Origin of fly ash

Fly ash is produced by a number of processes, such as the combustion of coal in power stations, the gasification of coal and the combustion of waste, each of which may lead to fly ashes with specific characteristics. The subject of this thesis is restricted to fly ashes that originate from the combustion of powdered coal in electricity power plants.

Essentially, in a power station, coal is mixed with air and converted into energy, carbon dioxide, water and an incombustible inorganic fraction. For this purpose mainly so-called low-NO_x furnaces are used in the Netherlands, in which a temperature of 1300-1500°C is reached (Pietersen, 1993). Figure 1.1 presents a flow diagram of the combustion process. The pulverized coal is injected in the burning zone by a flow of pre-heated air that causes a rapid increase in temperature of the coal particles. This leads at first instance to dehydration reactions as well as the development of CO₂, SO₂, and NO_x gases. At a temperature of about 450°C the bound water in the clay (one of the mineral phases in coal) has been removed. Upon a further increase of temperature, combustible volatiles in the coal will inflame and coke particles are formed. As combustion proceeds, an increasing amount of coke particles become oxidized and part of the alkalis evaporates (Fraay, 1990). The coarser mineral particles will (partially) melt and drop to the bottom of the oven where they are recuperated as bottom ash. The finer mineral parts remain in the hot air stream where they melt and form droplets. These droplets leave the combustion zone with the combustion gases that rapidly cool down. Some of the volatile elements condense during cooling and will be incorporated in the matrix of the fly ash particles. However, because of the sudden temperature decrease no equilibrium will be reached and a part of these elements, especially the more volatile ones, will condense on the surface of the fly ash particles. Finally, the fly ash particles are removed from the combustion gases with the aid of electrostatic precipitators (efficiency ca. 99%).

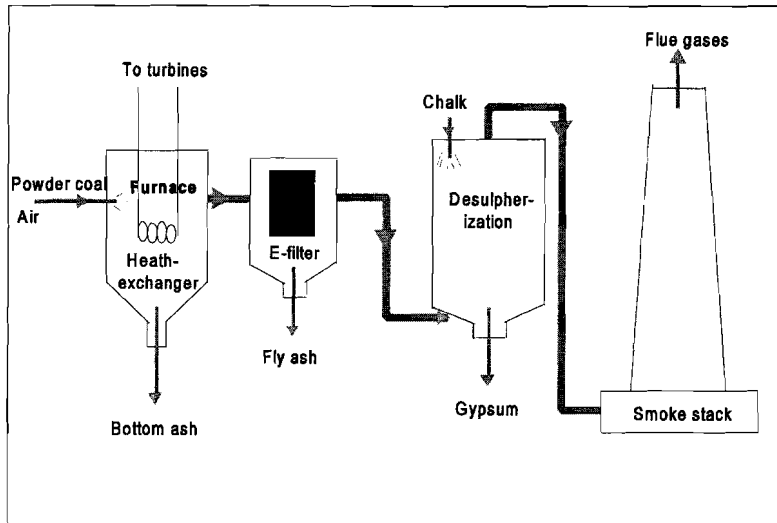


Figure 1.1 Flow diagram of the coal combustion process in a power station

Physical characteristics

The physical characteristics of CFA depend on a number of factors, such as the characteristics of the coal combusted, the grinding efficiency of the coal, the combustion regime and temperature, the volume of air forced into the oven, and the method of precipitation (Fraay, 1990). Typically CFA is a finely powdered material consisting of spherical particles that range in diameter from less than 1 to 200 μm but with ca. 80% having a diameter of 63 μm or less. A typical particle size distribution of CFA is presented in figure 1.2. Other physical characteristics are (RIVM, 1993):

- bulk density of ca. 1000 kg/m^3 ;
- specific density of 2000-2400 kg/m^3 ;
- specific surface of 300-400 m^2/kg ;
- melting point 1200-1600 $^{\circ}\text{C}$.

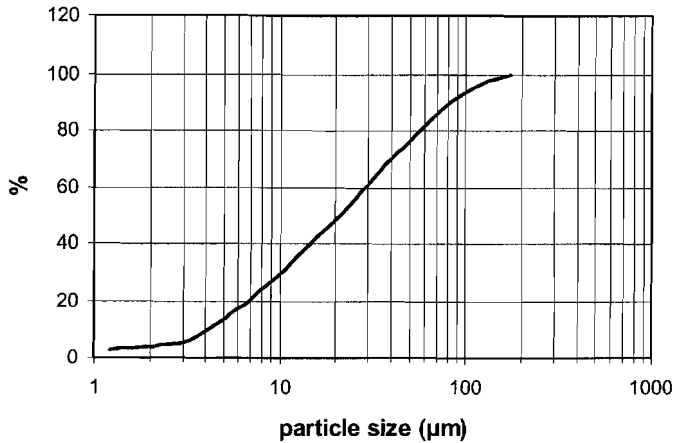


Figure 1.2 Particle size distribution of CFA (analyzed by Malvern 2600C analyzer)

Structural and mineralogical characteristics

Coal fly ash originates from the inorganic fraction of the combusted coal. At the macro-structural level coal fly ash consists of a heterogeneous mixture of different mineral phases, the most important of which are (Pietersen, 1993):

- aluminosilicate glass;
- mullite, $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ with x varying between 0.18 and 0.55 (Fischer et al., 1994);
- quartz;
- iron oxides (magnetite, hematite);
- salts and earth-alkali oxides (CaO, MgO).

Glass and mullite originate from the aluminosilicates (clays) present in coal. In addition mullite may form by devitrification of glass. Quartz is believed to be mainly of detrital origin while iron oxides, salt and oxides of Ca and Mg are formed after decomposition and volatilization of sulphides, chlorides and carbonates.

The distribution of these phases varies not only per CFA particle, but also within individual particles. Magnetite e.g. is known to occur as separate particles but also intergrown with glass, showing exsolution phenomena (Pietersen, 1993). Mullite occurs as needles embedded in glass and glass itself is known to show zones with different compositions.

Different types of particles can also be discerned on a macrostructural level, i.e.:

- solid particles;
- hollow particles (cenospheres);
- hollow particles filled with other particles (plerospheres);
- porous particles (bloated by gases during the combustion process).

Dudas and Warren (1987) proposed a structural model for coal fly ash in which the particles consist of a core of interior glass, with embedded mullite crystals, surrounded by a hull of exterior glass. Because of the enrichment in salts and a large number of metals and metalloids, the outer layer of exterior glass is relatively reactive compared to the inner glass matrix. Figure 1.3 shows a schematic representation of this model.

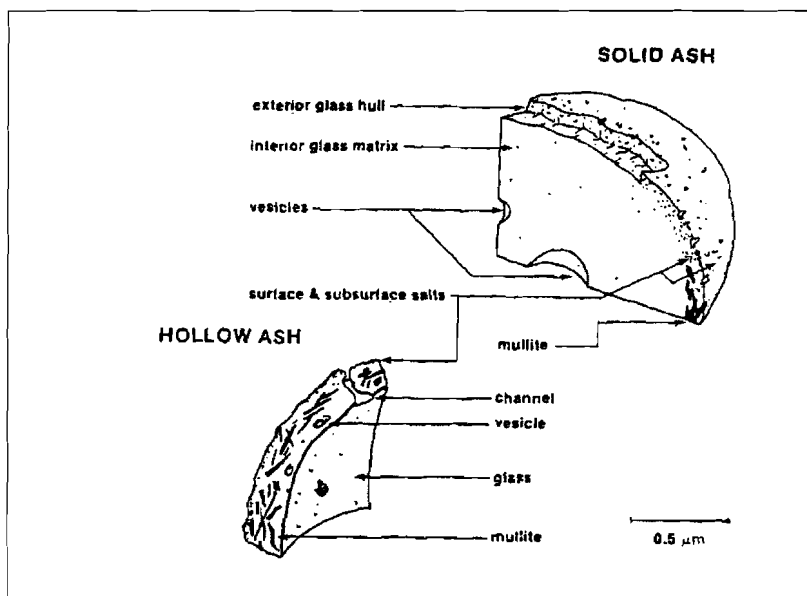


Figure 1.3 Structural model of CFA particles by Dudas and Warren (1987)

Chemical characteristics

Macro-chemically, fly ash consists of 85% aluminosilicates, 8% iron-, alkalis and earth alkali oxides, 1% sulphates, and 5% unburned carbon. CFA also contains a large number of trace elements (table 1). The more volatile elements (e.g. Se, V, Mo) which condense relatively late, are enriched on the surface of CFA particles. This surface layer plays an important role in the leaching of elements from fly ash.

Table 1 Content of trace elements in fly ash (RIVM, 1993)

Element	Concentration range in mg/kg
B, Ba, Cu, Mn, Sr, Zn	100-1000
As, Cr, Mo, Ni, Pb, Th, U	10-100
Cd, Sb, Se, Ti, V	1-10
Hg	< 1

Applications of coal fly ash

As already stated, CFA is used in cement and concrete as a pozzolane and filling material. Application of CFA in unbounded form (e.g. under roads) is not allowed because of a too high leachability. Especially the trace elements that are condensed on the surface of the fly ash particles will leach quite easily from the fly ash and form an environmental threat.

An important incentive to start in 1994 the zeolitization research described in this thesis was the expected Dutch Decree on Building Materials. There was concern that this decree would pose stricter regulations on the use of fly ash. At the 1st of January 1999 this decree came into effect and was enforced from the 1st of July 1999. It states that standard leaching tests (NEN 7341, 7343 and 7345) have to be carried out to determine whether the material to be used is in compliance with the regulations. At present, however, the restrictions posed by the decree on the use of coal fly ash seem to be very limited and are certainly not as large as feared at the beginning. The use of CFA as a secondary raw material for building materials will be continued. If by unforeseen changes this would change in the future, a special category in the Decree will be established for coal fly ash (VROM, 1998).

ZEOLITES

Zeolites are aluminosilicates with a skeletal structure that contains channels and cavities occupied by ions and water molecules. These ions and water molecules have a considerable freedom of movement and can be exchanged or reversibly dehydrated (Breck, 1974). The primary building block of the zeolite framework is the tetrahedron. The center of this tetrahedron is usually occupied by a silicon or aluminum atom surrounded by four atoms of oxygen at the apices of the tetrahedron (Tsitsihvili et al., 1992). Each of these oxygen atoms is shared between two tetrahedral. Hence, the tetrahedral form a continuous framework. Substitution of Si^{4+} by Al^{3+} leads to a negative charge of this framework, which is compensated for by monovalent or divalent cations located in structural channels together with water molecules. Typically zeolites are characterized by a large internal pore volume composed of cavities that are interconnected by one or more channel systems. Figure 1.4 presents some examples of this.

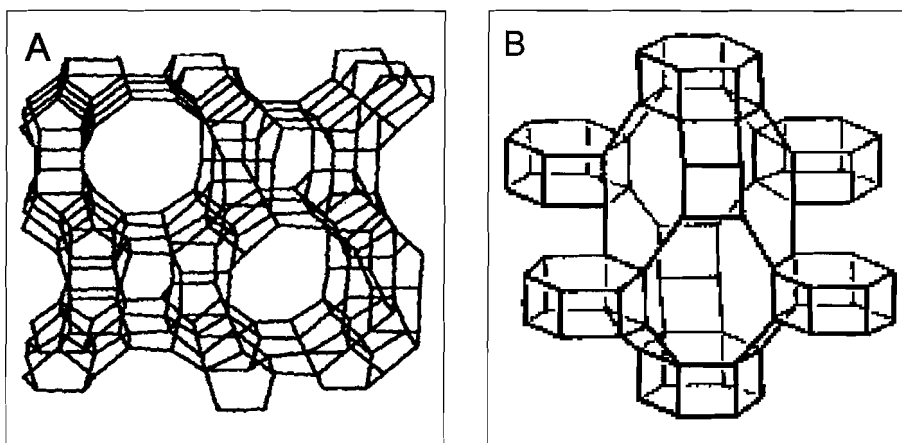
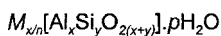


Figure 1.4 Examples of zeolite structures (Manly and Holmes, 1989):
A) mordenite, B) chabazite

Cations in the channels are easily substituted, and are therefore called exchange cations, unlike Si and Al, which are not exchanged under ordinary conditions and are called framework elements.

The idealized chemical formula of the zeolites is (Breck, 1974):



Where M is (Na, K, Li) and /or (Ca, Mg, Ba, Sr), n is cation charge, y/x is 1 to 6, p/x is 1 to 4.

The lower limit of the Si/Al ratio of zeolites is determined by Löwenstein's rule, according to which an AlO_4 tetrahedron cannot be directly connected to another AlO_4 tetrahedron. At a Si/Al ratio of 1, the silicon and aluminum tetrahedral alternate to form the ordered framework. The upper limit of the Si/Al ratio is found to be 5 to 6 for natural zeolites (clinoptilolite, mordenite, ferrierite, dachiardite), but higher ratios are possible for synthetic zeolites. The Si/Al ratio can vary considerably within the limits of one structural type, depending upon the composition of original solutions and crystallization conditions (Tsitsihvili et al., 1992).

The water content also varies within certain limits depending upon the character of the exchange cations and crystallization conditions. Under ordinary conditions, the water molecules completely fill the free volume of channels and voids in the zeolite structure. The free inner volume, which for some types of zeolite can be up to 50 %, can be determined by measuring the volumes of water released under heating *in vacuo* or calculated from structural data.

The linking of the framework tetrahedra may occur in numerous ways and produces a huge variety of different zeolites. These can be classified according to their structure (topology), Si/Al ratio, Si-Al ordering, cation population and cation locations. Further distinction can be made between natural zeolites (ca. 40 different kinds), and synthetic zeolites (over 150 different kinds) (Manly and Holmes, 1989).

Natural zeolites are associated with volcanic deposits in hydrothermal or saline alkaline environments. In a number of countries, especially the USA, Japan, China and Eastern European countries, mining of natural zeolites occurs (Gottardi and Galli, 1985). For example, in 1994 production in the USA amounted to 52800 tonnes, while Japan is reported to produce 60000 tpa, Bulgaria 45000 tpa and China over 2 millions tpa (personal communication professor Kalló).

Attempts to synthesize silicates began already in 1845, and the synthesis of the first zeolite, analcime, was reported in 1882 (Breck, 1974). Over a period of many decades, geologists and mineralogists have been interested in reproducing the formation of minerals in the laboratory by methods simulating natural processes. Nowadays, synthetic zeolites are manufactured in bulk quantities, most of which are used as an additive to detergents.

Properties and use of zeolites

Because of the channel-like structure and negatively charged framework, zeolites have high cation exchange capacities, in the order of 2-5 meq/g. The magnitude and selectivity of the cation exchange capacity (CEC) of a specific zeolite depend upon a number of factors:

- 1) the nature of the cation species, in particular the cation size, cation charge;
- 2) the structural characteristics of the particular zeolite (e.g. aperture of the internal channels);
- 3) the concentration of the cation species in the solution and in the zeolite;
- 4) the anion species associated with the cation in solution;
- 5) the solvent;
- 6) the temperature.

As a result of these factors, cation selectivity do not follow the typical rules that are evidenced by other ion exchangers. With their internal channel system, zeolite structures have unique features that lead to unusual types of cation selectivity and molecular sieving varying from zeolite to zeolite.

The cation exchange properties of zeolite were first observed about 100 years ago (Breck, 1974). The ease of cation exchange in zeolites led to an early interest in their application as water softening agents. Nowadays, zeolites are used for a wide variety of applications, especially for their ion exchange, absorption and catalytic properties.

In general a distinction can be made between synthetic and natural zeolites. Synthetic (pure) zeolites mainly find use as water softening agents in detergents, as catalyzers (especially in the petrochemical industry) and as desiccants. Compared to synthetic zeolites, natural zeolites are used on a much smaller scale. Their applications include uses in animal nutrition, odor control, soil amendment (slow release of fertilizers), desiccation and treatment of waste waters (adsorption of heavy metals, radioactive isotopes and ammonium).

OUTLINE OF THIS THESIS

As stated above, stricter environmental regulations and competition with other residual material may require new applications of coal fly ash in order to avoid a future surplus. Therefore, this research on the synthesis of zeolite from fly ash was carried out.

In **Chapter 2** the focus is on the research carried out to establish the optimal conditions for the formation of zeolites from Dutch CFA. A large number of zeolitization experiments was carried out to examine the influence of the different reaction parameters such as reaction time, temperature, molarity and type of alkaline solution, on the formation of different types of zeolites, on the cation exchange capacity of the zeolites, and on the zeolite contents.

The presence of non-zeolite phases in the conversion products, limits the cation exchange capacity of the zeolitized fly ash and reduces their value for application in the field of ad- and absorption. The research described in **Chapter 3** was carried out to examine if it is possible to synthesize pure zeolites from CFA by modification of the 'traditional' zeolitization process described in chapter 2. This was done by the application of a silica extraction before the zeolite was formed and synthesize pure zeolite from this extract.

For its applicability, the zeolitized fly ash has to comply with the environmental regulations. This is discussed in **Chapter 4**. The behavior of heavy metals during the zeolitization process was examined, and the leaching behavior of the zeolitized fly ash was tested by standard column experiments. Investigated was if the potential hazard to the environment, posed by the leaching of metals from the CFA, is reduced by zeolitization, and how this is influenced by treatment of the CFA with organic extractants prior to zeolitization. In all cases, the leaching of elements was compared to the Dutch norms.

One of the analytical techniques that is of special interest to geochemical engineering is quantitative X-ray powder diffraction (QXRD), because it offers the possibility to assess the degree of success of a conversion process involving crystalline phases, in this case how much of the glass phase in CFA has been converted in to zeolite. Conventional methods of QXRD relate the intensities of diffraction peaks of crystalline phases to absolute quantities by comparing them to the intensities of diffraction peaks of an external or internal standard. However, this technique is laborious as series of samples have to be prepared and analyzed, and peak overlap is a problem. In **Chapter 5**, the applicability of the conventional QXRD method was compared to a newer technique, the Rietveld method. This latter method comprises the calculation of the diffraction pattern from the instrumental and crystallographic structural parameters and fits this pattern to the observed diffraction pattern.

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Chapter 2

Single step conversion of coal fly ash into zeolite

ABSTRACT

Coal fly ash is partly converted into zeolite by treatment with hot alkali solutions. By using NaOH and KOH solutions different types of zeolite are synthesized from CFA, such as zeolite Na-P1, zeolite K-G and zeolite ZK19. The type of zeolite that is formed depends on composition and molarity of the hydroxide solution used, and parameters such as temperature, time and liquid/solid ratio. Conversion results in a sharp increase of the cation exchange capacity from 1.9 to ca. 200 meq/100 g. For zeolite Na-P1 a content of 40 wt. % is measured after conversion. Theoretically a conversion of ca. 50 wt. % should be possible. Lack of sufficiently reactive Al probably prevents this degree of conversion to be reached.

key words: coal fly ash, zeolite, conversion, cation exchange capacity

1 INTRODUCTION

At present, almost all fly ash produced by coal combustion in the Netherlands (about 900 000 ton/year) is used in the production of building materials. This application is mainly based on the pozzolanic properties of the coal fly ash (CFA). This entails a reaction between calcium oxide, silica and water, that leads to the formation of calcium silicate hydrates (CSH) and improves the strength of concrete. However, present possibilities for the use of combustion residues, such as CFA, may decrease in the near future because of stricter environmental regulations and changes in CFA quality due to the co-combustion of organic waste material and changes in combustion techniques. New applications for this kind of combustion residues may very well be needed in the near future to avoid disposal problems. One possible new application for CFA is the synthesis of zeolite products. The results of single step conversion experiments carried out to examine the possibilities to synthesize zeolite from coal fly ash, are presented in this chapter.

The need for new applications is felt in other countries as well, where the use of CFA is far from complete and large quantities are dumped in landfills. This is reflected in the increasing rate at which publications on the zeolitization of CFA appear, e.g. Kato et al. (1984, 1987), Höller and Wirsching (1985), Henmi (1987), Singer and Bergaut (1995), Lin and Hsi (1995), Querol et al. (1995), Park and Choi (1995) and Amrhein et al. (1996). A short overview of the research on the zeolitization of CFA, found in literature, is presented in Appendix A. This overview shows that the possibilities for zeolitizing CFA are studied world-wide (e.g. Austria, Spain, Korea, Japan, Colombia and USA), covering a broad range of conditions of zeolitization. However, because of this variation in the conditions, results from different studies are often difficult to compare with each other. Especially the origin (e.g. coal composition and combustion temperature) and ensuing composition of the CFA, which varies from study to study, influences the outcome of the zeolitization process and makes it difficult to extrapolate results from literature to other settings.

This study forms part of a research program that started in 1994 to examine the possibilities for developing a zeolitization process for Dutch CFA. Starting-point was that the zeolitization process should be economically feasible which meant that a balance had to be found between an as high as possible content of (useful) zeolite in the conversion product and as low as possible costs. For this purpose, the research program carried out aimed at establishing 1) the optimal conditions for the formation of zeolite from Dutch CFA, 2) the economic viability of the process and 3) the possible applications of the synthesized zeolite products. This paper presents results on the first of these aims. For this purpose over 150 zeolitization experiments were carried out in which the influence of different reaction parameters on the conversion process was tested, i.e. reaction time, temperature, type and strength of the alkaline solution, liquid/solid ratio (L/S ratio), stirring and the influence of some additives and pretreatments. After a description of the experimental methods, the results of these experiments are presented and discussed. Finally a summary is given of the influence of these parameters and a comparison made with data from literature.

2 MATERIALS AND METHODS

Starting materials

Experiments were carried out with an alkaline fly ash obtained in 1990 from the Dutch “Amercentrale” where it was formed as a result of the combustion of powdered coal at a temperature of circa 1500°C. This particular coal fly ash (CFA) was chosen because it was already fairly well described in a previous research project (1990-1993) on soil formation in CFA deposits (KEMA, 1994). In the Netherlands, at least until recently, most of the coals imported for combustion in power plants are mixed with each other to ensure a constant coal quality. This also results in a relatively constant quality of CFA, necessary for its application in building materials, and makes it possible to carry this study out with a single representative CFA.

Alkaline reaction solutions of NaOH, KOH, LiOH, up to 5 molar, were prepared from reagent grade chemicals (MERCK) and demineralized water. Solutions of 0.1 M and 1 M TMAOH (tetramethylammonium hydroxide), a substance forming complexes with silica and frequently used in the zeolite sciences as a template (i.e. a structure directing agent), were prepared from 97% tetramethylammonium hydroxide pentahydrate (Janssen Chimica). Solutions of 0.25 M and 1 M NaF were also prepared from reagent grade chemicals (MERCK) and aluminate solutions were prepared by dissolution of aluminum band (99.99% Al p.a., MERCK) in a 5 M NaOH solution.

Experimental set-up

Fly ash was converted into zeolite by mixing it with a hydroxide solution in a sealed vessel for a certain period at temperatures up to 150°C, while under autogenous pressure. Table 2.1 lists the chosen ranges of reaction parameters, however, not necessarily every variation was tested in combination with all the others. The choice of parameter ranges was guided by the outcome of the experiments and by what was considered still realistic for an economically feasible process.

Table 2.1 Variation in experimental parameters applied

Parameter	Variation
reaction time (t)	1-120 hour
temperature (T)	40-150°C
type and molarity of alkaline solutions	1-5 M NaOH 1-4 M KOH 0-2.5 M NaOH + 0-2.5 M KOH 2 M LiOH (suspension)
liquid/solid ratio (L/S ratio)	1-20 l/kg
stirring	0-800 rpm
additives (for higher degree of conversion)	TMAOH, aluminate, seeding, NaF
pretreatments (for zeolite enrichment)	extraction with acid or water removal of magnetite grinding

Different experimental set-ups were used during this study, as increasing amounts of zeolitized CFA were required for further examination, demanding the use of larger reaction vessels. Used were the following set-ups:

- 1) Teflon reaction vessels with a volume of 8 or 40 ml were placed in a steel bomb which in its turn was placed in a stove for heating. Reaction vessels could be rotated in the longitudinal direction with a speed of 3.75 rpm. This set-up permits a maximum reaction temperature of 200°C;
- 2) A Teflon beaker with a volume of 2 liter was placed in a heated water bath. The vessel was equipped with a IKA propeller stirrer for mixing (<2500 rpm). The maximum reaction temperature used is 100°C. This set-up, in contrast to the previous one, allows sampling of the reaction mixture while the reaction is in progress;
- 3) A 100 l stirred autoclave coupled to an expansion vessel that can be used for rapid cooling of the reaction mixture, as described by Borst and Krijgsman (1991). This set-up was used to treat 8 kg CFA during 24 h with a 2 M NaOH solution (L/S 3.5) at 150°C, applying a stirring speed of 90 rpm.

At the end of the experiments the reaction mixtures were filtrated and the residues washed with water at a L/S ratio of 3 to 10 and dried at 75°C.

Analytical techniques

X-ray diffraction (XRD) was used for the identification of the mineral phases in the original and zeolitized fly ash (CuK α radiation at 40 kV using a Philips PW1050/25 diffractometer and PW1710 control system). Quantitative mineralogical analyses were carried out for quartz, mullite and zeolite Na-P1 by standard addition methods (Brindley, 1980; Snyder and Bish, 1989). For this purpose a standard of zeolite Na-P1 was synthesized following the

prescription by Milton (1961). Standard materials for quartz and mullite were obtained respectively from Merck (Darmstadt, Germany) and Vuurvast Keramiek (Gouda, the Netherlands). An extensive treatise on the quantitative mineralogical techniques employed is given in chapter 5 of this thesis.

The cation exchange capacity (CEC) of selected samples was determined by the International Soil Reference and Information Center (ISRIC) in Wageningen (The Netherlands), applying the ammonium acetate method (ISRIC, 1992) after treatment of the samples with 80% alcohol in order to remove excess salt. In addition, particle size distributions were measured with a Malvern 2600C analyzer while specific surface was measured with a Micromeritics Rapid Surface Analyser 2205, that measures the amount of argon gas needed to form a monolayer on the sample surface (BET-principle). A JEOL JSM 6300 scanning electron microscope (SEM), equipped with NORAN Voyager III M3200 energy-dispersive X-ray analysis system (EDS) was used for the further chemical and morphological characterization of the residues. Polished sections were prepared by mixing samples of CFA or zeolitized CFA with araldite CY219 (SPI Supplies, West Chester USA) which were subsequently hardened at room temperature in a pressure cooker, cut, polished and analyzed by SEM.

The chemical composition of liquids was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES; elements Al, B, Ba, Ca, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr, Ti, V, Zn), hydride-atomic absorption spectrometry (hydride-AAS; elements: As, Sb, Se) and Graphite Furnace-AAS with Zeeman background correction (ZGF-AAS; element: Mo). Prior to the analysis, liquids were acidified with concentrated HNO_3 to a pH of 1 to 2. Prior to acidification and analysis, it was necessary to dilute the reaction liquids obtained from the zeolitization process by a factor 10 to 100 in order to avoid interferences of the high alkali concentrations and to avoid the formation of silicate precipitates upon acidification. The pH of solutions was measured with an Orion solid state sure flow pHuture electrode (model 61-65) connected to an Orion ISE/pH meter (model 940). This pH electrode contains no glass but a Si sensor which leads to a more stable signal when measuring highly alkaline solutions. Precision of pH measurements was ± 0.03 up to pH 14.3 when no new calibration was carried out. Comparing results from different calibration runs, however, showed a precision of only ± 0.2 . Solids were analyzed following standard decomposition procedures which included dissolution of solid samples at 90°C with $\text{HF}/\text{HClO}_4/\text{HNO}_3$ mixed acid in closed Teflon vessels or by the use of a lithium metaborate melt, and subsequent analysis by ICP-AES, hydride-AAS and ZGF-AAS.

3 RESULTS

Appendix B at the end of this chapter gives an extensive overview of the zeolite products that were obtained from CFA under the various conditions applied. In total 6 different zeolites were synthesized, i.e. zeolite Na-P1 (gismondine type), zeolite K-G (chabazite type), zeolite K-M (phillipsite type), zeolite ZK19 (phillipsite type), zeolite Li-ABW (linde type) and hydroxysodalite (HS, sodalite type, often not considered to be a real zeolite). Table 2.2 summarizes the (range of) conditions that resulted in the synthesis of each of these zeolites.

Table 2.2 Conditions of formation for different zeolites synthesized

Type of zeolite	T (°C)	t (h)	Solution	L/S ratio
Na-P1	80-150	12-24	1-2.5 M NaOH	2.5-10
K-G	90-150	24-50	1-4 M KOH	2.5-3.5
ZK19	90-150	6-160	2 M NaOH+KOH (2:1, 1:1)	2.5-3
K-M	150	24	2 M KOH	3-5
Li-ABW	150	24	2 M LiOH	3.5
HS	150	24	3M NaOH	2.5-20

In Appendix C at the end of this chapter some important characteristics of these zeolites are listed. Application of zeolites as absorbent or adsorbent depend mainly on characteristics like cation exchange capacity and apertures of the internal channels. Taking these qualities into account but also considering the relative ease with which the different zeolites can be synthesized, it was decided to focus this research primarily on the conversion of CFA into zeolite Na-P1 and to carry out additional experiments to study the conversion into zeolite K-G, K-M and ZK19. This is reflected in the number of experiments in which these zeolites were involved, i.e. approximately 100 for zeolite Na-P1 and 15 for each of the other three zeolites.

Table 2.3 presents a quantitative mineralogical analysis of CFA before and after conversion into zeolite Na-P1 at 93°C. Glass is the predominant phase in CFA. Other important mineralogical phases are mullite, quartz and iron oxides (magnetite and others). Quantitative XRD analyses show that by single step conversion at 93°C, a yield of zeolite Na-P1 of ca. 35 wt. % is feasible. At the same time, the glass content decreases from 70 to ca. 20%. At 150°C (including the experiment carried out with the 100 l autoclave) feasible yields of zeolite Na-P1 are slightly higher, i.e. ca. 40 wt. %. Figure 2.1 presents representative X-ray diffraction patterns of the zeolite products obtained.

Table 2.3 Mineralogical composition (wt. %)¹⁾ of coal fly ash before and after conversion into zeolite Na-P1. Reaction conditions: 24 h, 93°C, 2 M NaOH solution, L/S ratio of 2.5, 240 rpm

Mineral phase	CFA	Zeolitized CFA
zeolite Na-P1	0	32
glass (including reactive oxides and salts)	71	33
quartz	4	3
mullite	16	14
iron oxides (hematite, magnetite)	6	4
calcium and magnesium hydroxides	0	10
loss on ignition (carbon, water, excl. zeolitic water and water in Ca,Mg-hydroxides)	3	3

¹⁾ Concentrations of quartz, mullite and zeolite Na-P1 were determined by XRD standard additions. Those of iron oxides and calcium and magnesium hydroxides were estimated from chemical analysis and sequential extractions (KEMA/UU, 1992). Glass content was calculated by completion to 100%

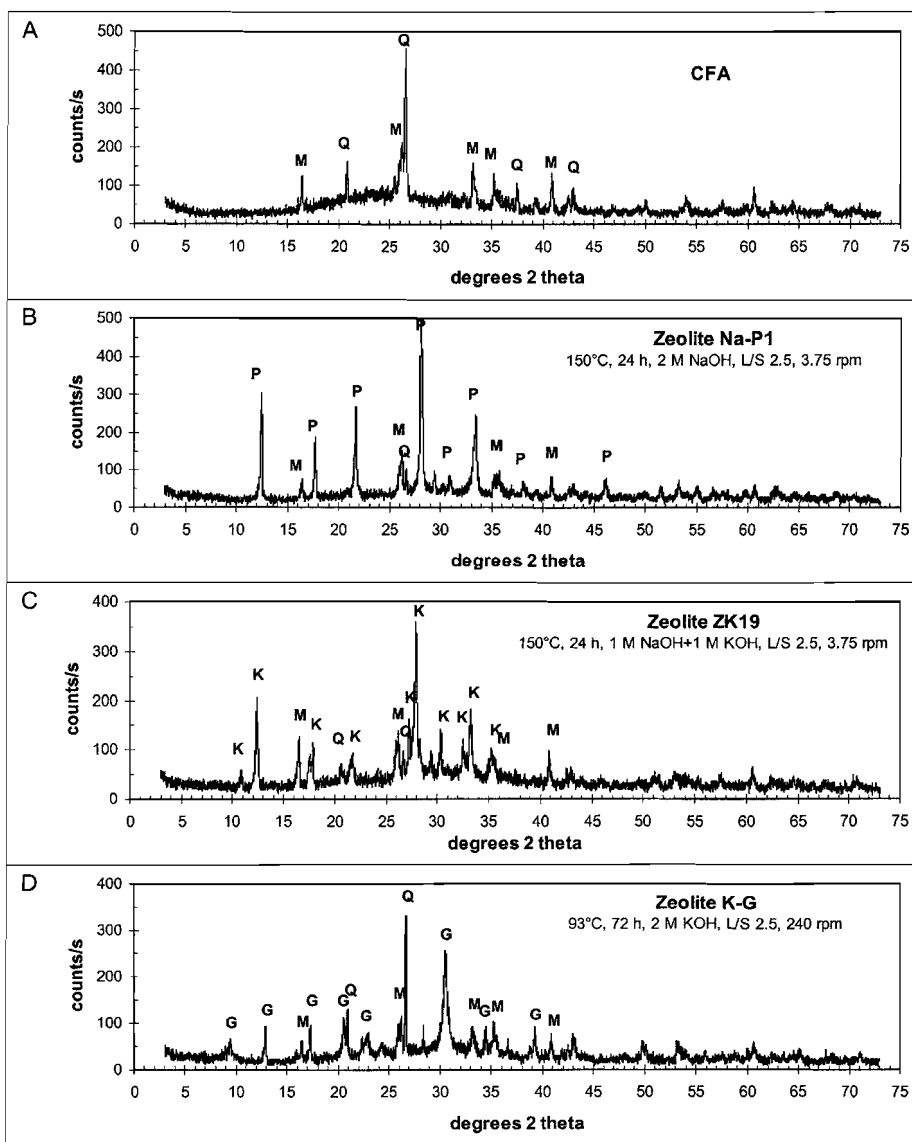


Figure 2.1 X-ray diffraction patterns of the coal fly ash (A) before and after conversion to different zeolites (B-F). Q=quartz; M=mullite; P=zeolite Na-P1; K=zeolite ZK19; G=zeolite K-G. Indicated are the conditions of zeolite synthesis, i.e. temperature, duration reagent, liquid/solid ratio and intensity of mixing.
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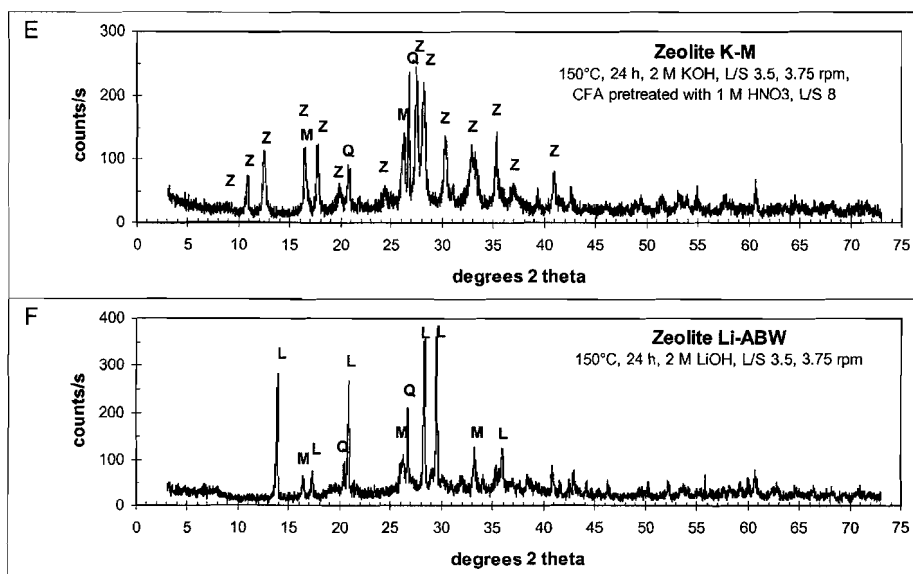


Figure 2.1 Continuation

Q=quartz; M=mullite; Z=zeolite K-M; L=zeolite Li-ABW. Indicated are the conditions of zeolite synthesis, i.e. temperature, duration reagent, liquid/solid ratio and intensity of mixing.

Representative chemical compositions of CFA and zeolitized CFA are presented in table 2.4. Most important differences concern the loss on ignition (LOI) and the alkali content. Table 2.5 lists chemical compositions of some resulting process and washing waters. Except for the concentrations of alkali elements, concentrations of elements in the process water do not vary significantly with the type of reaction fluid used. In general, the metallic elements present as cations (e.g. Ba, Cd, Co, Cu, Zn) prove to be relatively insoluble during the zeolitization process while elements present as anions (metal oxy-anions such as As, Mo, Se and V, and others like S and P) are fairly soluble. Si concentrations (3000-6000 mg/l) may also vary depending on the type of reaction liquid used. Filtrating the reaction mixture at the end of the zeolitization reaction under a pressure of 5-6 bar, retrieves only about half of the water present. The remaining water is held by the zeolitized CFA and with this water also dissolved salts that will crystallize if the zeolitized CFA is dried. To remove these the zeolitized CFA may be washed with water. Table 2.5 lists concentrations in 9 batches of washing water retrieved consecutively from washing the zeolitized CFA on the filter. The data show that especially anions are extracted up to a L/S ratio of 9.

Table 2.4 Chemical compositions of CFA before and after conversion into different zeolites¹⁾

	CFA	zeolite Na-P1	zeolite K-G	zeolite ZK19
kg/kg CFA	1	1.1	1.15	1.2
Oxides (wt. %)				
SiO ₂	46.9	39.1	36.0	33.1
Al ₂ O ₃	24.9	21.8	20.0	18.0
Fe ₂ O ₃	8.8	7.7	7.8	7.2
CaO	6.9	6.1	5.7	5.1
MgO	3.8	3.5	3.2	2.9
K ₂ O	2.1	1.3	8.8	4.9
Na ₂ O	1.2	6.5	0.3	3.6
TiO ₂	0.9	0.9	0.9	0.8
P ₂ O ₅	0.7	0.4	0.4	0.3
SO ₃	1.0	0.1	0.1	0.1
LOI	2.0	10.3	13.3	23.3
Sum	99.4	97.9	96.7	99.5
Minor and trace elements (mg/kg)				
As	28	n.a.	n.a.	n.a.
B	310	n.a.	n.a.	n.a.
Ba	2170	1950	1820	1620
Cd	1	n.a.	n.a.	n.a.
Co	66	59	54	48
Cr	155	145	140	125
Cu	215	185	175	155
Mn	1030	920	885	800
Mo	9	n.a.	n.a.	n.a.
Ni	140	135	125	110
Pb	125	n.a.	< 18	< 18
Sb	16	<12	<12	<12
Se	16	<6	<6	<6
Sn	6	n.a.	n.a.	n.a.
Sr	1390	1070	1010	915
V	320	95	100	95
Zn	215	180	170	155

¹⁾ Analysis by ICP-AES, hydride-AAS and ZGF-AAS after dissolution by mixed acid (HF/HNO₃/HClO₄) or a lithium metaborate melt. Conditions of synthesis: zeolite Na-P1: 2 M NaOH, 48 h, 93°C, L/S 2.5, 240 rpm; zeolite K-G: 2 M KOH, 96 h, 93°C, L/S 2.5, 240 rpm; zeolite ZK19: 1.33 M NaOH+0.67 M KOH, 168 h, 90°C, L/S 2.5, 3.75 rpm. n.a. = not analyzed

Table 2.5 Chemical compositions (mg/l) of typical process and washing waters obtained from the zeolitization process¹⁾

	Reaction liquids		Washing water of CFA converted into zeolite Na-P1								
	zeolite Na-P1	zeolite K-G									
liter per kg CFA	1.1	1.1	1	1	1	1	1	1	1	1	1
pH	13.7	13.6	13.6	13.6	13.4	12.9	12.8	12.6	12.5	12.4	12.3
Al	18	20	8.6	7.9	7.0	7.7	4.2	4.2	2.4	2.7	1.9
As	2.8	3.0	1.2	1.1	0.3	0.2	0.2	0.2	0.1	0.2	0.1
B	40	38	15.7	15.3	6.0	3.1	2.8	2.9	2.7	2.8	2.5
Ca	<0.6	<0.6	<0.03	<0.03	1.4	3.4	0.9	1.5	<0.03	3.6	0.1
Cr	<0.6	<0.6	<0.03	<0.03	<0.03	0.2	0.2	0.3	0.2	0.3	0.2
Fe	0.7	<0.3	0.2	0.1	0.7	1.0	0.1	0.4	0.2	0.2	0.0
K	2146	23410	830	810	315	125	75	60	47	43	35
Mo	3.0	2.9	1.0	0.9	0.3	0.1	0.06	0.06	0.04	0.06	0.05
Na	26430	3040	>1500	>1500	>1500	>1500	890	730	590	540	450
P	490	470	220	210	62	17	10	10	9	10	8
S	1870	1850	700	665	190	40	15	13	10	12	9
Sb	<1.0	1.9	0.2	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Se	5.8	6.0	2.8	2.7	0.7	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Si	5850	3050	2300	2250	1010	470	300	250	210	195	170
Sn	<0.6	<0.6	0.2	0.2	0.1	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Ti	<0.6	<0.6	0.09	0.08	0.2	0.24	0.14	0.14	0.08	0.09	0.06
V	77	81	28.3	27.2	9.7	2.5	1.1	1.0	0.8	1.0	0.8

¹⁾ Analysis by ICP-AES, hydride-AAS and ZGF-AAS. Conditions of synthesis: zeolite Na-P1: 2 M NaOH, 48 h, 93°C, L/S 2.5, 240 rpm; zeolite K-G: 2 M KOH, 96 h, 93°C, L/S 2.5, 240 rpm; Washing carried out on vacuum filter, catching consecutive samples of 1 L/S ratio. The concentration of a number of elements was in all cases below the detection limit (d.l.) of the analytical method applied, i.e. of (with d.l. valid for respectively reaction fluid and washing water between brackets): Ba (0.3, 0.01), Cd (0.6, 0.01), Co (0.6, 0.02), Cu (0.3, 0.01), Mg (0.6, 0.02), Mn (0.3, 0.01), Ni (0.3, 0.03), Pb (0.9, 0.1), Sr (0.3, 0.01) and Zn (0.3, 0.02)

A micrograph of the fly ash is presented by photo 2.1 which shows glassy spherical particles with salts on the surface. Photo 2.2 shows micrographs of CFA converted into zeolite Na-P1 and zeolite K-G. Examination by SEM/EDS and XRD of CFA samples taken within the first few hours of zeolitization, indicate that the crystallization of the zeolite is preceded by the formation of an amorphous aluminosilicate phase on the surface of the CFA particles. Examination of polished sections by SEM shows that the zeolite crystals have indeed mostly formed on the surface of fly ash particles (photo 2.3A). In addition newly formed Ca and Mg phases are visible in polished sections (photo 2.3B), presumably hydroxides, though analysis by EDS also suggests the presence of some carbonate.

Residual phases are mostly associated with mullite, visible as needle-like crystals that have a Si/Al ratio of 0.25-0.33, and large (40-100 µm diameter) porous fly ash particles with a Si/Al ratio of 0.5-0.6 (photo 2.3C). The nature of these latter particles is not completely clear. Possibly they are made up of a sillimanite-like phase. Sillimanite has a Si/Al ratio of

0.5 and a crystalline structure and X-ray diffraction pattern which resembles that of mullite and is indeed considered by some to represent an end member of the mullite composition range (Sadanaga et al., 1962; Saalfeld, 1979; Deer et al, 1982).

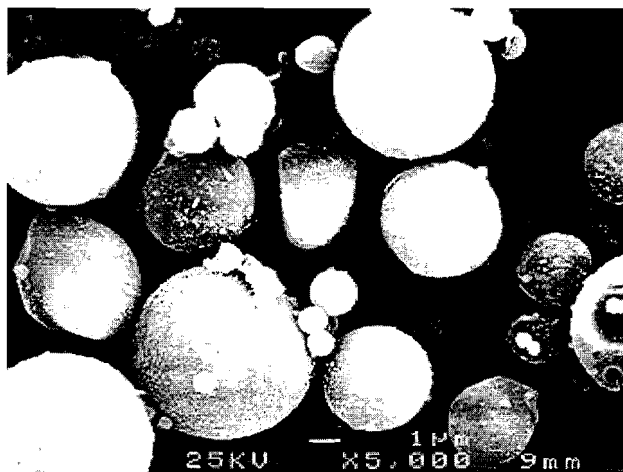
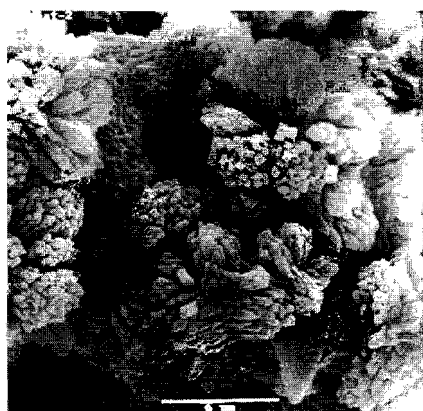
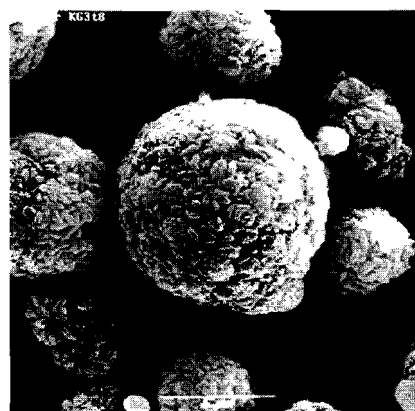


Photo 2.1 Micrograph of CFA, originating from the power plant in Geertruidenberg (NL)

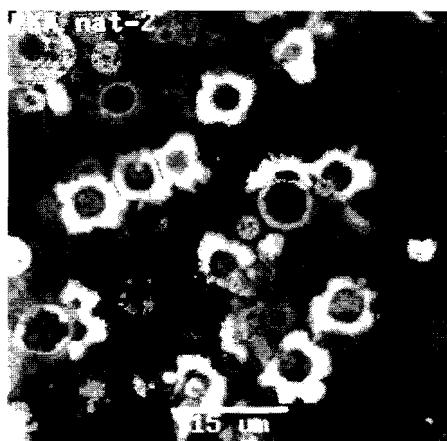


A

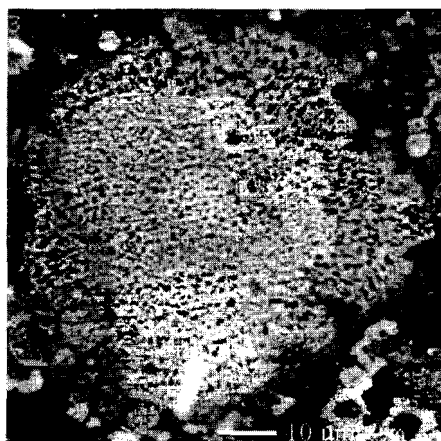


B

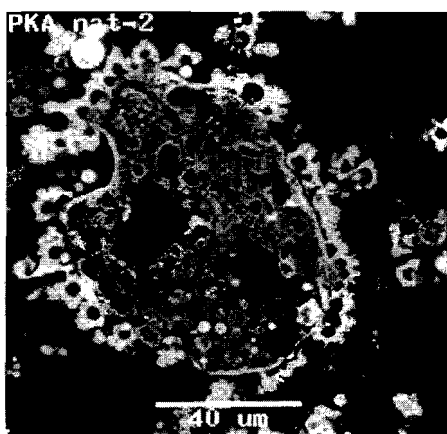
Photo 2.2 Micrograph of zeolitized CFA with zeolite Na-P1 (A) and zeolite K-G (B). Synthesized at 93°C, L/S 2.5 with either a 2 M NaOH (Na-P1) or 2 M KOH (K-G) solution



A



B



C

Photo 2.3 Micrographs of polished sections of zeolitized CFA showing zeolite Na-P1 on the surface of residual CFA particles (A), a newly formed Ca- and Mg phase (B), and a residual phase consisting possibly of a sillimanite-like phase (C)

As a result of the conversion into zeolite the CEC increased from 1.3 meq/100 g for the original CFA to values of 190 to 240 meq/100 g. Likewise the specific surface increased from 0.7 m²/g to 45 to 70 m²/g. Assuming that no other phases than the synthesized zeolites contribute to the measured CEC and assuming an ideal composition of the zeolite, the measured CEC's can also be used to quantify the zeolite content of the conversion products by comparing it with the theoretical CEC a pure zeolite would possess. Table 2.6 shows this for a number of products. However, because of the assumptions made, the zeolite concentrations calculated in this way can be no more than indicative. Especially the zeolite composition, and thus the CEC they actually possess, may vary significantly (Breck, 1974) and should be measured for an accurate calculation of their real CEC (when pure) and their ensuing content. Analyses available indicate that the zeolite concentrations obtained by calculation from the CEC's are higher than those obtained with direct measurement by XRD.

Adsorption experiments carried out by Steenbruggen (1999) showed that the adsorption capacity created by conversion of CFA into zeolite, can indeed be used for the adsorption of pollutants like e.g. heavy metals and ammonium.

Table 2.6 CEC and calculated zeolite content

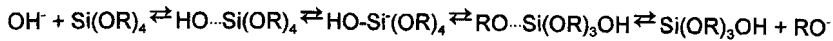
Zeolite	Theoretical composition ¹⁾	T _{synthesis} (°C)	CEC (meq/g)		zeolite content (wt. %)		exp. code
			measured	theoretical for pure zeolite	calculated from CEC	measured by XRD	
Na-P1	Na ₆ Al ₆ Si ₁₀ O ₃₂ •15H ₂ O	150	2.4	4.4	55	43	63.1
		90	2.1	4.4	48	39	al1
K-G	K ₂ Al ₂ Si ₄ O _{11.8} •13H ₂ O	150	1.9	3.6	53	-	56.1
		90	2.1	3.6	58	-	zkg2
K-M	K ₂ Al ₂ Si _{3.6} O _{11.2} •5.1H ₂ O	150	2.0	4.0	50	-	62.2
ZK19	K ₂ Na ₄ Al ₆ Si ₁₃ O ₃₂ •12H ₂ O	150	2.1	3.9	54	-	64.1

¹⁾ From Breck (1974)

4 DISCUSSION

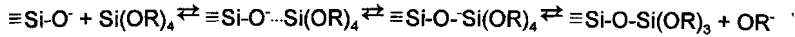
Generally, zeolites are synthesized from a silicate or aluminosilicate gel and an alkaline solution. Upon mixing of these reactants at room temperature hydrolysis reactions cause the release of monomeric silica species into solution. This dissolution process is promoted by the coordination of the hydroxide ion with Si which weakens the Si-O bonds in the gel structure. This nucleophilic mechanism (Brinker 1988; Jansen, 1991) can be presented by

the following scheme :



In which R represents H, Si or an alkoxy group.

In addition at high pH condensation reactions may take place in which nucleophilic deprotonated silanol groups bind to neutral monomeric species as presented in the following scheme (Brinker, 1988; Jansen, 1991):



This condensation reaction leads to large branched clusters which reorganize into larger particles that are stabilized by dissolved cations like Na^+ and form the zeolite nuclei. As the reaction mixture is heated, the rate of dissolution increases and polymeric silicate species dissociate into monomeric and dimeric silicate species. This and the continuing hydrolysis and condensation processes cause a constantly changing phase, consisting of gel, monomers and increasing amounts of clusters. As these clusters continue to rearrange into larger particles, zeolite nuclei, large enough to be stable, form and zeolite crystallization starts. The growing crystals consume then the precursor species and limit their availability for the formation of new nuclei (Barrer, 1982).

Generally four cases of nucleation followed by crystallization are discerned (Jansen, 1991):

- homogeneous nucleation in a clear solution, followed by crystallization with a driving force that is equal in all directions;
- heterogeneous nucleation on a dispersed low density gel, followed by crystallization with a driving force that is also equal in all directions;
- heterogeneous nucleation on a high density gel, followed by crystallization that proceeds into the gel;
- heterogeneous nucleation in a metastable solid phase, leading to recrystallization into a more stable phase.

The processes described by Jansen (1991) and Barrer (1982) also take place when CFA is treated with alkaline solutions, with the provision that the glass phase present in the CFA, and not a gel phase, is the major initial source of Si and Al. In addition, because of the composition of CFA, a range of other dissolution and precipitation processes takes place (e.g. dissolution of salts, precipitation of hydroxides).

From the observations by SEM, which show that zeolite crystals form exclusively on the surface of CFA particles, it can be concluded that this formation process proceeds by heterogeneous nucleation. The formation of an amorphous aluminosilicate phase prior to the formation of zeolite crystals, furthermore indicates that the glass phase in CFA is solubilized and reorganized into a gel-like phase into which subsequently zeolite nuclei form and crystallization proceeds, conform the heterogeneous nucleation of case c) above.

The dissolution and precipitation reactions lead to a sigmoidal crystallization curve that is typical for the formation of zeolites (Barrer, 1982). Only when from the start crystallization sites are readily available, e.g. by seeding, is it possible that the induction period is skipped and that formation of zeolite crystals starts at once. Figure 2.2 presents examples of crystallization curves obtained for the zeolitization of CFA at 40, 70 and 93°C. They show that respectively three phases can be discerned in the zeolitization process, i.e.:

- 1) an induction period during which glass is dissolved and zeolite nuclei are being formed;
- 2) a relative short period in which the actual crystallization of zeolite takes place;
- 3) an extended period in which the zeolite content does not increase significantly.

In the following, the influence of the different reaction parameters on the conversion of CFA are examined more closely. Discussed are consecutively the influence of temperature and reaction time, of molarity and type of hydroxide concentration, of the L/S ratio and of mixing. This is followed by a discussion on ways to increase the zeolite content in the conversion product.

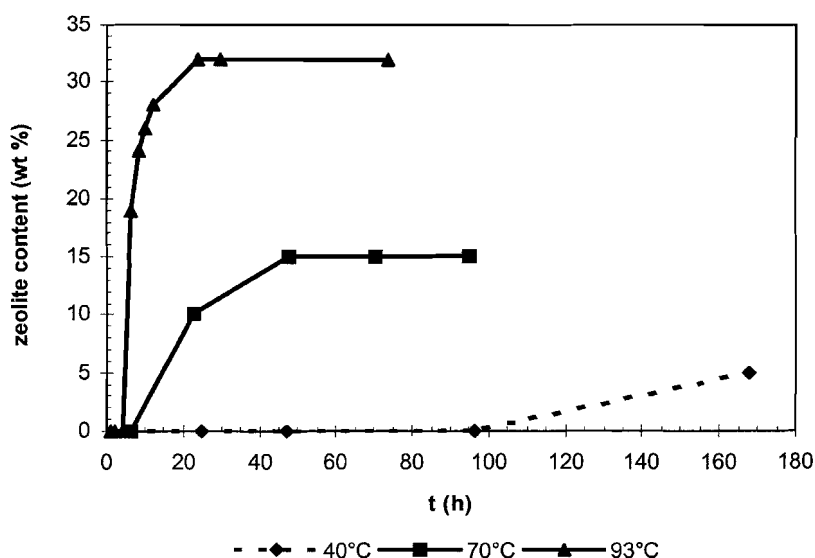


Figure 2.2 Conversion of coal fly ash into zeolite Na-P1: crystallization curves obtained at 40, 70 and 93°C. In all cases a 2 M NaOH solution was used at a L/S ratio of 2.5. The reaction mixture was stirred at 240 rpm. The crystallization curve for 40°C is dotted to indicate the large uncertainty on the exact moment that zeolite starts to crystallize at that temperature

Temperature and reaction time

The selected temperature of zeolitization directly influences the rate of the reaction. Decreasing the temperature slows the reaction down and vice versa, and consequently influences the time needed to reach the maximum degree of conversion achievable at that temperature. This is illustrated by figure 2.2 above. From this figure three effects can be discerned from an increase of the reaction temperature, viz.:

- 1) a shortening of the induction period
- 2) an increase of the crystallization rate (represented by the slope of the central part of the crystallization curve)
- 3) an increase of the final zeolite content, supposedly because of a more extensive dissolution of the glass phase. However, as indicated by the data in table 2.7 the difference in content between 150°C and 93°C is much smaller than between 93°C and 70°C. Apparently, above 100°C the increase is relatively small.

Increasing the reaction temperature beyond 150°C thus seems mainly to benefit the reaction rate. However, the temperature can not be increased infinitely. Ultimately, the crystallization field of zeolite is left and other phases will form. For example, the synthesis of zeolite Na-P1 will give way to that of analcime between 180 and 200°C (Barrer, 1982). In addition, the choice of temperature affects the costs involved with the zeolitization process as temperatures above 100°C result in a more complicated and expensive process, demanding the use of autoclaves.

Table 2.7 Maximum contents of zeolite Na-P1 at different process temperatures

Content of zeolite Na-P1 ¹⁾ (%)	T (°C)	Reaction time (h)
5 ²⁾	40	97<t<167
15	70	23<t<48
32	90	24
42	150	12

¹⁾ Measured by means of XRD standard addition techniques (see ch. 5 for an extensive description). All syntheses were carried out with a 2 M NaOH solution, L/S 2.5 and stirring at 240 rpm

²⁾ No data points available beyond 167 h, possibly a higher content is achievable at 40°C

The temperature dependence of the synthesis of the zeolites K-G, K-M and ZK19 has been examined less extensively. Semi-quantitative XRD analyses showed that the conversion of CFA to zeolite K-G is higher at a temperature of 93°C than at 150°C. Furthermore, conditions which at 150 °C lead to the synthesis of zeolite K-M and to the synthesis of zeolite ZK19, resulted at 93°C in the formation of respectively zeolite K-G and a mixture of zeolite K-G and zeolite ZK19. This suggests that the stability of zeolite K-G increases with a decreasing temperature and that in this case the temperature is also of influence on the type of zeolite that is formed.

Molarity and type of hydroxide solution

The data in table 2.2 show that the type of zeolite formed by conversion of CFA is largely determined by the type and strength of the hydroxide solution. Depending on the dominant cation in the hydroxide solution used, zeolite Na-P1 (Na), zeolite ZK19 (Na and K), zeolite K-G (K) or zeolite Li-ABW (Li) is formed. An increase of the hydroxide concentrations to values larger than 2.5 M enhances the formation of hydroxy-sodalite.

Furthermore, the type of hydroxide solution used is of influence on the rate of zeolite formation. This has been examined for zeolite Na-P1 and zeolite K-G by carrying out experiments at 93°C with respectively a 2 M NaOH and 2 M KOH solution in which samples were taken at regular time intervals. In figure 2.3 the relative increase in the zeolite contents measured by XRD in the subsequent samples is shown. It is clear that the induction period is much longer if a 2 M KOH solution is used than if a 2 M NaOH solution is used, i.e. respectively 44 hours and 6 hours. Also the crystallization rate under these conditions is somewhat higher for zeolite Na-P1 than for zeolite K-G.

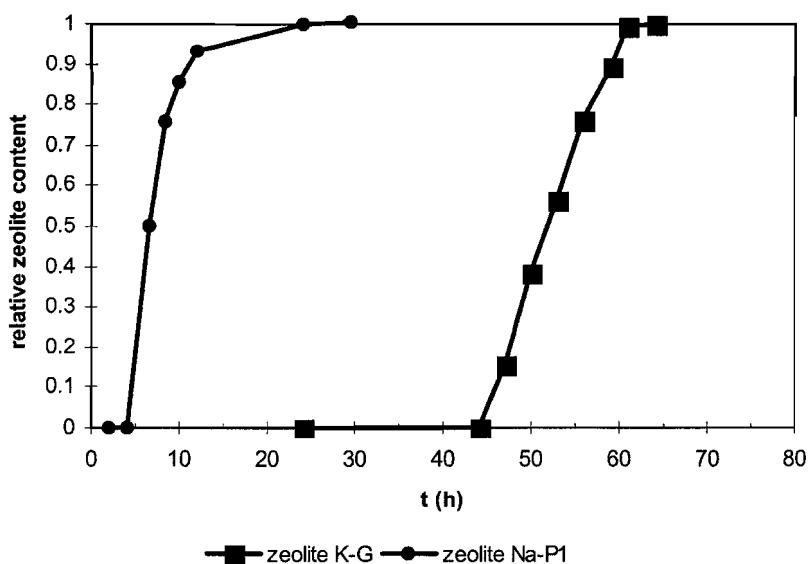


Figure 2.3 Single step conversion of CFA to zeolite: relative increase in contents of zeolite Na-P1 and zeolite K-G as a function of time, during synthesis experiments carried out at 93°C with respectively a 2 M NaOH and a 2 M KOH solution

Induction periods may be shortened by providing readily available nucleation sites in the reaction mixture (Barrer, 1982). This effect was tested for the conversion into zeolite K-G. It was found that by replacing at $t=0$ 10% of the CFA by CFA already converted to zeolite K-G that the length of the induction period was decreased from 44 to 34 hours, bringing the total reaction time for conversion on 50 h. This is still a considerably longer period than needed for the conversion into zeolite Na-P1, for which, without seeding, a reaction time of 24 h suffices at 93°C.

The longer induction period observed for the conversion to zeolite K-G is also reflected in the slower increase of silica concentrations and slower decrease of Al concentrations, as is shown by the graphs in figure 2.4. It is likely that the lower rate for the synthesis of zeolite K-G is caused by the larger size of the potassium cation in comparison to the sodium cation which results in a slower penetration of alkalis into the glass framework of the CFA particles and thus in slower dissolution rates of the Si in the glass. As a result the addition of nucleation sites can only have a limited effect.

Though higher hydroxide concentrations were expected to increase the zeolitization rate (Barrer, 1982) in this study they mainly influenced the type of conversion product. Results of experiments carried out at 150°C and 100°C with a L/S ratio of 5 and a 1 M NaOH solution and with a L/S ratio of 2.5 and a 2 M NaOH solution showed no differences in the conversion to zeolite. For this reason, the major part of the experiments was carried out with L/S 2.5 and 2 molar hydroxide solutions, which allowed the treatment of more CFA per run. In addition, zeolitization experiments, carried out at 150°C with L/S 2.5 and different hydroxide concentrations in the solution, showed that:

- at hydroxide concentrations of 2.5 M or less, zeolite Na-P1 was the only crystalline phase formed
- at hydroxide concentrations of 3 M, a mixture of zeolite Na-P1 and sodalite was formed
- at hydroxide concentrations of 4 M and higher, sodalite or noseane-cancrinite phases were formed.

Because the sorption properties of the phases as sodalite, noseane and cancrinite are considered less useful than those of zeolite, their formation was avoided as much as possible. The upper limit of hydroxide concentrations in the experiments was therefore set at 2.5 molar.

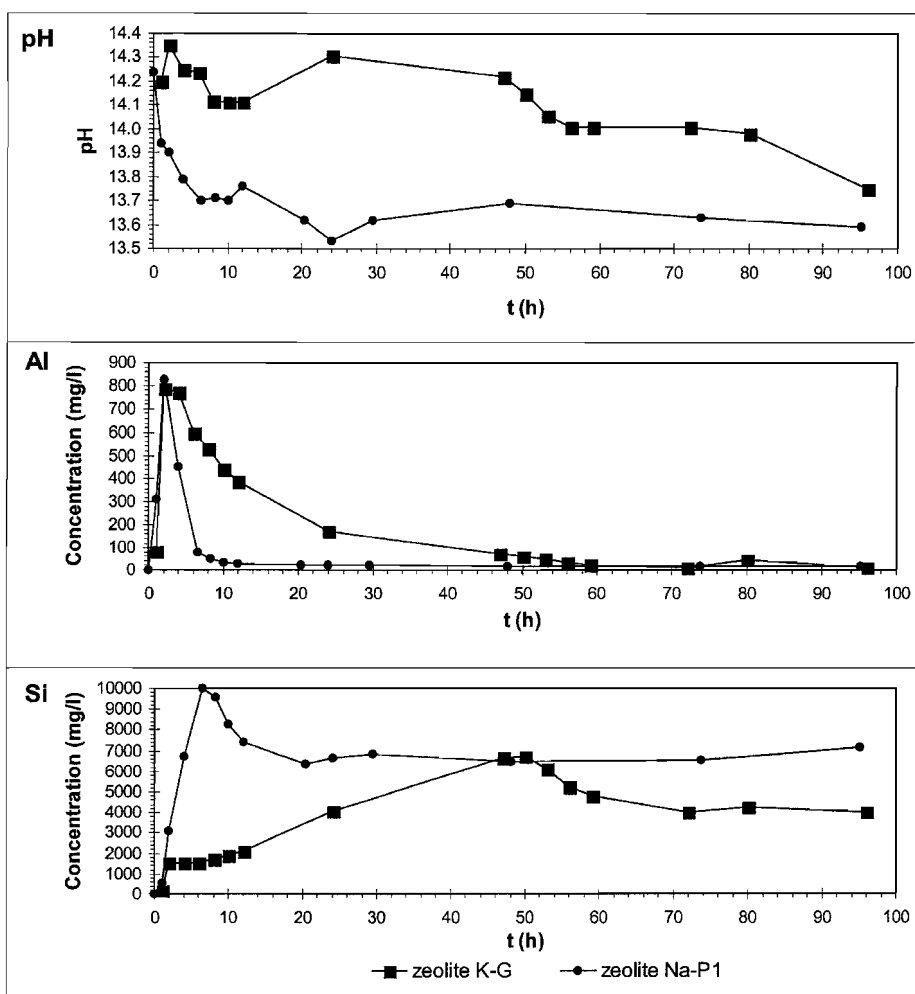


Figure 2.4 Conversion of coal fly ash into zeolite Na-P1 and zeolite K-G: pH of solution, concentration of Al and Si in the process water as a function of time

Liquid/solid ratio

An increase of the L/S ratio of the reaction mixture from 2.5 to 7 had no clear influence on the conversion process (when using a 2 M NaOH solution). In experiments carried out at 150°C with L/S ratios in this range and otherwise comparable conditions, the content of zeolite Na-P1 was circa 20% after 6 h of reaction and 40% after 24 h of reaction. At L/S ratios of 10 and higher sodalite was formed at the expense of zeolite Na-P1. Therefore the

maximum L/S ratio for an optimal conversion to zeolite Na-P1 lies between 7 and 10. The minimum L/S ratio is not primarily defined by the desired product of conversion but by the intensity of mixing of the suspension in the reaction vessel, design of the reaction vessel and the increasing viscosity of the mixture during reaction. A low L/S ratio in combination with a too low intensity of mixing will result in cementation of the reaction mixture on the bottom of the vessel. In the set-up used for experiments below 100°C this occurred at a stirring rate of 125 rpm with a L/S ratio of 2.5.

Mixing

The influence of mixing was examined by carrying out zeolitization experiments (at 93°C with a 2 M NaOH solution) with an IKA stirrer equipped with a propeller head and adjusted to 125, 240 and 500/800 rpm (in the latter case the experiment was started with a speed of 800 rpm but later decreased to 500 rpm to diminish vibrations). Table 2.8 gives a synopsis of the results of these experiments.

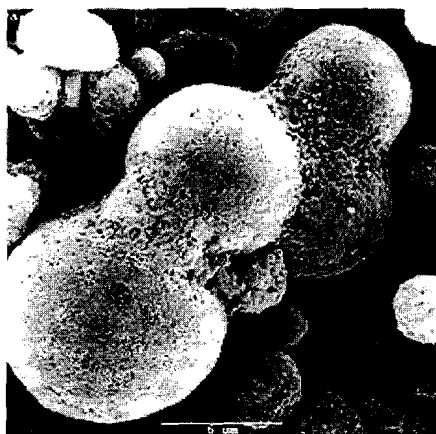
Table 2.8 Influence of the speed of stirring on the synthesis of zeolite Na-P1 at 93°C

Speed of stirring (rpm)	Time interval of zeolite crystallization (h)		Zeolite content (%)	Morphology of zeolite crystals
	Start	End		
800 ->500	2-4	12-24	40	rounded relatively smooth spherules with skins of zeolite. No clear crystals visible with SEM
240	4-6	20-24	40	small crystals of ca. 1 µm length, lying closely together on the surface of residual fly ash particles
125	6-8	24-48	40 ¹⁾	As at 240 rpm. However, in the cemented part smaller and larger crystals (0.1-3 µm length)

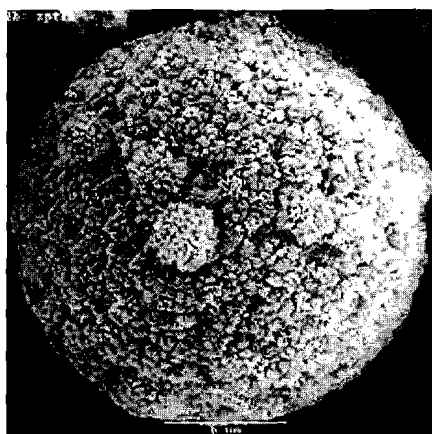
¹⁾ in suspension, content in cemented part was 20%, average value was 32 %

It appears that the stirring speed does not have a significant influence on the final zeolite content which in all cases amounted to circa 40% of zeolite Na-P1 formed. An increase in speed does result however in shorter induction periods and thus in a shorter reaction time necessary to reach the maximum zeolite content. Presumably this is due to an increase in the rate of dissolution of silica. In addition the speed of stirring proves to be of influence on the morphology of the zeolites formed. At higher speeds newly formed crystals appear to be smaller. In fact at a speed of 500/800 rpm no clear zeolite crystals could be discerned up to a magnification of 20 000, and particles appeared to be very streamlined. A speed of stirring of 125 rpm, on the other hand, proved to be insufficient to keep all particles in suspension with the set-up used. This resulted in hard cemented aggregates on the bottom of the reaction vessel which contained crystals of zeolite Na-P1 with a length of 0.1-3 µm. At 240

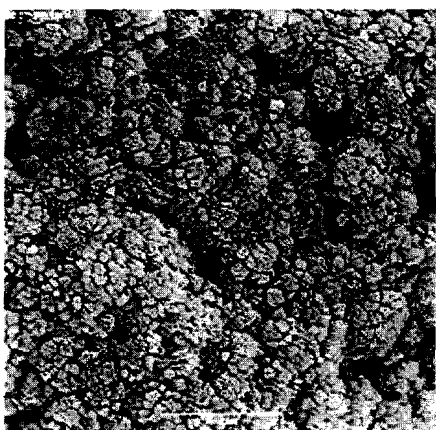
rpm, the speed of stirring used in most experiments carried out below 100°C, the length of zeolite crystals was approximately 1 μm . Photos 2.4A-D present examples of the morphology observed.



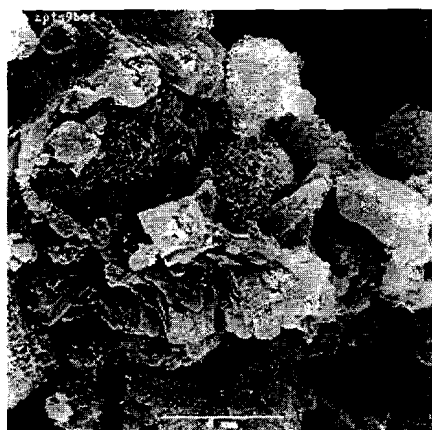
A



B



C



D

Photo 2.4 Morphology of zeolite Na-P1 synthesized at 93°C with a 2 M NaOH solution (L/S ratio 2.5) at different speeds of stirring: A) 500-800 rpm, reaction time 48 hours; B) 240 rpm, reaction time 48 hours; C) 125 rpm, reaction time 48 hours; D) 125 rpm, reaction time 72 hours, cemented part

The influence of stirring, and related to this, the turbulence of the reaction mixture still need further investigation. These factors do not only depend on the rheology of the mixture but also on the design of the reaction vessel, e.g. geometry of the vessel and type and placement of stirrer (Thoenes, 1994). These aspects should be examined and taken into consideration prior to any upscaling of the conversion process, in order to increase the efficiency of the process and prevent the formation of hard cemented aggregates.

Degree of conversion

Table 2.9 presents a mass balance for the conversion of CFA into zeolite at a temperature of circa 95°C. Results show that 1 kg CFA converts into ca. 1.1 kg product with zeolite Na-P1. As mullite and quartz are still present in the zeolitized CFA, one can assume that these two phases remain more or less inert during the zeolitization reaction. Taking this into account it can be calculated from the chemical and mineralogical analysis of the CFA (table 2.3 and 2.4) that per kg CFA 125 g Al_2O_3 and 393 g SiO_2 are available for zeolite formation. Analyses by SEM/EDS have shown that the composition of the synthesized zeolite Na-P1 is very close to the theoretical composition of $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$. This means that for a conversion product with 40 wt. % zeolite Na-P1, which is the about the highest content measured without applying enrichment procedures, ca. 103 g Al_2O_3 and 202 g SiO_2 are needed. In other words, for a conversion product with 40 wt. % zeolite Na-P1, 82 % of available Al_2O_3 and 51 % of available SiO_2 are used. However, sequential extractions, involving the subsequent treatment of CFA with a 1.2 M HCl solution and a boiling 4.5 M KOH solution, carried out in a previous research (KEMA/UU, 1992), and also described by Pietersen (1993), showed that part of the silica in the glass phase (ca. 70 g SiO_2 /kg CFA) may be considered inert during the zeolitization process. This means that per kg CFA not 387 but 317 g of SiO_2 is available for zeolite formation and that for a conversion product with 40 wt. % zeolite Na-P1 82% of the available Al_2O_3 and 63% of the available SiO_2 is used.

Table 2.9 Single step CFA conversion: mass balance¹⁾

REACTANTS →	CONVERSION	→ PRODUCTS
1.0 kg CFA	t = 24 h	1.1-1.2 kg zeolitized CFA
0-0.2 kg NaOH ²⁾	T = 95°C	1.3 kg residual water ³⁾
0-0.3 kg KOH ²⁾	p = 1 bar	1.1 kg process water
2.4 kg (process) water		9.1 kg washing water
9.0 kg (washing) water		
12.6-12.7 kg	sum	12.6-12.7 kg

¹⁾ Mass balance is normalized to 1 kg CFA, but is based on experiments carried out with 500 g CFA.

²⁾ Dependent on type of zeolite synthesized

³⁾ Residual water is the solution that stays behind in the conversion product after its filtration at 6 bar, but that is removed when drying the sample at 75°C

From the previous it appears that based on the Si and Al availability in CFA, at a zeolite content of 40 wt. %, the formation of an additional 110 g of zeolite Na-P1 per kg of CFA is in

principle possible. The maximum conversion was not reached, as was confirmed by experiments in which the zeolite was removed from zeolitized CFA by acid treatment and the remaining residue again zeolitized. By the acid treatment, carried out batchwise with a 1 M HCl solution at L/S ratio of 500, 60 wt. % of the zeolitized sample was removed, including all previously formed zeolite and Ca and Mg hydroxides. The XRD pattern of the residue in fact resembles that of the original untreated CFA, with mullite, quartz and magnetite present as the only crystalline phases, and a broad band between 15 and 35°2 θ indicating the presence of glass. Reaction of this residue with a 2 M NaOH solution at 150°C for 24 h, leads to the formation of zeolite Na-P1 and some analcime. Though no quantitative analysis exists of the zeolitized residue, semi-quantitative X-ray diffraction analysis shows that its zeolite content is clearly larger than normally reached by zeolitization of CFA, i.e. above 40 wt. %.

For the application as an adsorbent, a conversion product with the highest possible zeolite content is desirable. To examine if a higher degree of conversion is attainable a number of experiments were carried out which involved:

- 1) addition of aluminum hydroxide (23 g per 500 g of CFA) to the reaction mixture to test if availability of Al is of importance;
- 2) addition of agents like tetramethylammonium hydroxide and sodium fluoride, that form complexes with Si, increasing its solubility, in order to postpone the formation of zeolites on the surface of the fly ash particles, enclosing them and possibly isolating them from further reaction;
- 3) grinding of fly ash particles prior to zeolitization to improve the availability of both Al and Si and to test if encapsulation of particles by newly formed phases is of importance.
- 4) addition of NaOH to the reaction mixture to restore the pH to its initial value of 14.3 and to test if this improves the aggressiveness of the solution sufficiently to solubilize residual CFA particles.

However, none of these variations resulted in higher yields of zeolite. Instead they lead to the formation of sodalite or cancrinite-like phases in the experiments under 1) and 4), a lengthening of the induction period in the experiments under 2), or showed no influence on the degree of conversion at all in the experiments under 3). Nevertheless it is believed that availability of suitable Al, of which the concentration in solution is steeply decreasing at the end of the induction period, is the key problem. Addition of Al as a sodium aluminate or as a suspension of gibbsite, was not successful because it brought the reaction mixture out of the crystallization field of zeolite Na-P1 and into that of sodalite. Possibly this can be solved by a fine tuning of the rate at which the Al was added. At present it was added at different rates, varying from 23 g of Al(OH)₃ at once to 2.3 g of Al(OH)₃ per hour. Another possibility, that was not examined, is that it is not the quantity of Al added but that of hydroxide that causes the formation of sodalite. In that case the addition of AlCl₃ or some other aluminum salt may increase the degree of conversion.

Zeolite enrichment by pretreatment of CFA

Another possibility to attain higher zeolite concentrations in the conversion product is by way of enrichment, i.e. by removing those components in the CFA that do not contribute to the zeolite formation. The most prominent of these are the Ca-, Mg-, Fe- and S-phases.

The easiest way to attain this is by the removal of magnetite from CFA (before or after conversion). This can be simply done by leading a suspension with the (converted) CFA along a (electro)magnet to remove magnetite (and phases intergrown with magnetite), in total about 10% of the CFA. It was found that the zeolite content in the conversion product is raised by this from 40 to 45 wt. %.

From several studies on CFA, e.g. Dudas and Warren (1987), it is known that part of the Ca and Mg is concentrated in the exterior glass hull of CFA particles as oxides or soluble salts. To remove this Ca and Mg CFA was treated with a 1 M HNO₃ solution (batchwise at L/S ratio of 8) prior to zeolitization. During this treatment, with a final pH in solution of 0.5, circa 20 wt. % of the CFA is solubilized, including significant parts of Ca (60-82%), Mg (17-68%: inconsistent results), Fe (10-20%) and S (70-100%) but also of Al (9%) and Si (4-8%). For comparison, a similar treatment with water at L/S 20 results in the extraction of 16% of Ca, 40% of S and 0% of Mg, Fe, Al and Si (final pH in solution 11.2).

Subsequent zeolitization of the nitric acid treated CFA at 150 or 93°C with a 2 M NaOH solution, leads to conversion products with ca. 50 wt. % of zeolite Na-P1. Pretreatment of CFA with an acid thus indeed results in higher zeolite concentrations during subsequent zeolitization.

Extracting the CFA prior to zeolitization with nitric acid and also with other extractants such as EDTA, was also examined as a way to improve the environmental quality of the zeolitized CFA. Results on this topic are discussed in chapter 4.

Comparison with literature

The formation of the reported zeolites and ensuing cation exchange capacities correspond fairly well with those found in literature. The number of different types of zeolites reported in literature is, however, somewhat larger. For example, the formation of zeolite A (linde type) is reported by Bergk et al. (1985) and that of zeolite X (faujasite type) by Höller and Wirsching (1985), Henmi (1987) and Amrhein et al. (1996). The cause of these differences may be found in the specific conditions of zeolitization used, applied pretreatments or additives, and in the characteristics of the CFA used. Especially the Si and Al content and crystallinity of the CFA, i.e. the availability of Si and Al to take part in the zeolite synthesis, will have a large influence on the type and amount of zeolites produced.

One peculiar finding when examining the literature on zeolitization of CFA, is the apparent lack of attention for mixing of the suspension of CFA and alkali solution. Except by Bergk et al. (1985a-b, 1986a-b, 1987a-b), who confirm its influence on the rate of reaction, this aspect is simply not mentioned. The present study shows that if the CFA is not kept in suspension

during the zeolitization reaction, cementation is very likely to occur under the influence of high Si concentrations in solution. This may result in a lower zeolite content and will diminish the uniformity of the crystal size. When planning a scale-up of the zeolitization process this aspect most certainly needs to be reckoned with.

5 CONCLUSIONS

- Alkaline treatment of Dutch coal fly ash leads to the synthesis of zeolites, resulting in a conversion product with up to 40 wt. % zeolite and an increase of cation exchange capacities from 1.9 meq/100 g to 190-240 meq/100 g;
- The conversion process is characterized by heterogeneous nucleation followed by rapid zeolite crystallization resulting in sigmoidal crystallization curves;
- Different types of zeolite can be formed from CFA by varying the type of alkali solution used. The use of NaOH, KOH and mixed NaOH/KOH solutions leads to the synthesis of respectively zeolite Na-P1, zeolite K-G and zeolite ZK19;
- The temperature of reaction influences the rate at which the zeolite formation proceeds and the degree of conversion attained, higher temperatures leading to a higher rate and, especially up to 100°C, to higher yields of zeolite;
- A total hydroxide concentration of 2 M was found to be optimal for the zeolite synthesis. Using hydroxide concentrations of 3 M or more leads to the formation of sodalitic or cancrinite-like phases instead of zeolite. A similar shift was observed when applying liquid/solid ratios of 10 and higher;
- It is found that in batch reactors zeolite Na-P1 can best be formed in ca. 12 h at 150°C, using a 2 M NaOH solution at a L/S ratio of 2.5 or alternatively in ca. 24 h at 93-100°C and otherwise similar conditions. Zeolite K-G can best be formed in 50 h at 93-100°C, using a 2 M KOH solution at L/S 2.5 and replacing 10% CFA by CFA already converted into zeolite K-G;
- It is imperative that during conversion the reaction mixture is kept in suspension, as cementation reactions will occur under the influence of high Si concentrations in solution.
- By removing magnetite the zeolite content in the final product may be raised to 40 to 45 wt. %. Extracting significant parts of the Ca, Mg and Fe present in the CFA raised the zeolite content in the final product to ca. 50 wt. %;
- Based on analysis and calculations a conversion into zeolite of ca. 50 wt. % should be possible. The limiting factor which prevents this percentage to be reached in the experiments described here, is believed to be the availability of sufficiently reactive Al;
- Possibly the degree of conversion can be improved by adding aluminum salt other than hydroxide, or by fine tuning of the rate at which aluminate is added;
- Generally, results compare well with those in literature.

Acknowledgments

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Authors	Fly ash type	Reaction solution	L/S (ml/g)	T (°C)	Reaction time	Zeolites produced	Adsorption data product	Remarks
Bergk et al. (1985, 1986, 1987)	brown coal	2.2-7.4 M NaOH (use of seeding)	3-16	90	3-6 h	zeolite A	not specified	mixing: 225 and 3000 rpm.
Höller and Wirsching (1985)	brown coal	0.1-5.0 M NaOH/KOH 0.1/1.0 M NaCl/KCl/CaCl ₂ 0.1-4 M NaOH 0.1-5 M KOH 1-4 M NaOH+KOH (1:1) 0.1-1 M NaCl 0.1-1 M KCl, CaCl ₂	50	50-250	40-72 d	analcite, chabazite faujasite, phillipsite zeolite F, zeolite J zeolite M, zeolite Na-P zeolite Na,K-P hydroxysodalite montmorillonite	not specified	open and closed systems
Kato et al. (1984, 1987)	fly ash clinker ash (formed at 800-900°C)	1-5 M NaOH 1, 2, 3 M NaOH filtrate 1st step+NaOH+NaAlO ₂	20	35-95	12-42 h	zeolite P (60%) hydroxysodalite zeolite A zeolite X	NH ₄ 35 mg/g Pb, Cd, Sr >70 mg/g Co, Cu, Mn 40-70 mg/g Cr, Ni, Zn <25 mg/g	mixing
Japan IERE Council (1992)	fly ash clinker ash	1.0-6.3 M NaOH 1.0-4.0 M KOH 1.0-3.0 M LiOH 2.0 M Ca(OH) ₂ 2.0 M Mg(OH) ₂ 2.0 M NaOH + NaAlO ₂ 2.0 M NaOH +Na ₂ SiO ₃	10	100	18 h	zeolite Na-P, zeolite Na-A hydroxysodalite zeolite Li-A	highest CEC for zeolite Na-P (3 meq/g) which adsorbs ammonium and has a high capacity for the adsorption of heavy metals (Fe, Pb)	
Mondragon et al. (1990)	fly ash	2-13 M NaOH	ns	90-100	8-48 h	hydroxysodalite 50-75% zeolite X en P	not specified	pretreatment with acid
Koloušek (1994)	fly ash natural glass	2 M NaOH + 2 M KOH 2 M Na ₂ CO ₃ + 2 M K ₂ CO ₃	24	130	6 h 1-5 d 1-7 d	ca. 60% phillipsite chabazite, phillipsite K-feldspar, analcite	not specified	mixing

Authors	Fly ash type	Reaction solution	L/S (ml/g)	T (°C)	Reaction time	Zeolites produced	Adsorption data product	Remarks
Henmi (1987)	Japanese CFA fraction < 44 µm F-I: high-T ash F-II: low-T ash (F-I more amorphous)	3.5 M NaOH --> -->	8 --> -->	80-90 --> -->	24 h --> -->	dried at room-T (hydroxy)sodalite faujasite+phillipsite	CEC (Ca-Na): 3.6 meq/g 1.6 meq/g	reflux set-up used
Lin and Hsi (1995)	Taiwanese CFA 55.2% SiO ₂ 25.4% Al ₂ O ₃	2 M NaOH 3.5-10 M NaOH 2 M NaOH 2 M NaOH 2 M NaOH 0.5-2.5 M Na ₂ CO ₃	10 10 10 10 10 10	90 (1 bar) 90 (1 bar) 70 (34 bar) 150 (34 bar) 170 (34 bar) 200 (34 bar) 90-200	24 h 24 h 24 h 24 h 24 h 24 and 120 h 24 and 120 h	zeolite P hydroxysodalite zeolite P analcime hydroxysodalite cancrinite no zeolite	CEC (NH ₄ -Na): 1.9 meq/g <1.9 meq/g 1.6-2.1 meq/g 0.2 meq/g 0.2 meq/g 0.2 meq/g 0.2 meq/g Cu and Cd tested	10-90% addition of silicic acid no influence of pressure noticed
Querol et al. (1995)	Spanish CFA (Teruel) SiO ₂ /Al ₂ O ₃ = 1.8	0.1-1 M NaOH 0.1-1 M NaOH+KOH 0.1-1 M KOH	5-33 --> -->	60-200 --> -->	8-100 h --> -->	zeolite Na-P1 and analcime zeolite Na-P1, analcime and phillipsite phillipsite	not specified	
Park and Choi (1995)	Korean CFA fraction <100µm 29.3% SiO ₂ 52.4% Al ₂ O ₃	2 M NaOH	4	105	2-48 h	zeolite Na-P1 (called phillipsite by authors)	CEC (NH ₄ -K): 2 meq/g	
Shin et al. (1995)	Korean CFA magnetic fraction removed (6-10%) 55.2% SiO ₂ 21.5% Al ₂ O ₃	1-5 M NaOH (optimum at 4 molar)	2.5	60, 80, 100	3-96 h	zeolite Na-P1	CEC (couple not specified) 1.8-2.4 meq/g NH ₄ , Pb, Cu, Cd en Or tested	

Authors	Fly ash type	Reaction solution	L/S (ml/g)	T (°C)	Reaction time	Zeolites produced	Adsorption data product	Remarks
Singer and Berggaut (1995)	Israeli CFA fraction < 25 µm 1: 61.6% SiO ₂ 21.3% Al ₂ O ₃ 2: 44.7% SiO ₂ 32.3% Al ₂ O ₃	3.5 M NaOH	8	100	2-48 h	1: zeolite Na-P, (converts to sodalite) 2: sodalite	CEC (NH ₄ -Na): 1.8-2.1 meq/g NH ₄ and heavy metals tested	reflux set-up used synthesis of pure zeolite from process water of 45 min.
Amrhein et al. (1996)	USA CFA 51.5% SiO ₂ 19.0% Al ₂ O ₃	3.5 M NaOH 3 M NaOH 0-4 M NaOH 1-4 M KOH 3 M NaOH+KOH 3 M NH ₄ OH	8	40 60 100 50 100 150 200 250 100 100 100 100	24-240 h -> -> 72 h -> -> -> -> 72 h 72 h 72 h 72 h	zeolite Na-P1 zeolite Na-P1 zeolite Na-P1 zeolite Na-P1 zeolite Na-X zeolite Na-X zeolite Na-X zeolite Na-P1+P2 zeolite K-G zeolite K-G no zeolite	CEC (NH ₄ -Na): 1.3 meq/g after 10d 2.2 meq/g after 10d 2.4 meq/g after 6d 2.5 meq/g 3 meq/g 0.5 meq/g 0.5 meq/g 0.5 meq/g 3 meq/g 3 meq/g 3 meq/g <0.1 meq/g	oven and reflux set-up used; reuse of NaOH tested
KEMA/UU this study (1994-1997)	Dutch CFA 46.9% SiO ₂ 24.9% Al ₂ O ₃	1-4 M NaOH 2 M (NaOH+KOH) 1-4 M KOH	2-20	40-150	1-167 h	zeolite Na-P1 zeolite K-G zeolite ZK19 zeolite K-M sodalite	CEC (NH ₄ -Na): 2-2.5 meq/g (max. 4.3 meq/g for pure zeolite) NH ₄ and heavy metals tested Environmental quality tested	also synthesis of pure zeolite from process water obtained at end induction period or from final process water (see chapter 3 for this).

B.1 Treatment of CFA with NaOH solutions

T (°C)	t (h)	NaOH (mol/l)	L/S (ml/g)	stirring (rpm)	product	exp. code
150	24	5	5	3.75	sodalite	5.2
		3	3.5	3.75	sodalite + zeolite Na-P1	44.2
		2.5	3.5	3.75	zeolite Na-P1	27.4
		2	3.5	90	zeolite Na-P1	wap1
		2	7	3.75	zeolite Na-P1	9.4
		2	5	3.75	zeolite Na-P1	5.1
		2	3.5	3.75	zeolite Na-P1	9.3/15.1/63.1/al1
		2	2.5	3.75	zeolite Na-P1	1.1
		1	5	3.75	zeolite Na-P1	1.4
		18	2	7	zeolite Na-P1	9.2
		2	3.5	3.75	zeolite Na-P1	9.1
	12	2	3.5	3.75	zeolite Na-P1	10.3
		2	7	3.75	zeolite Na-P1	10.4
	8	2	3.5	3.75	zeolite Na-P1	10.1
		2	7	3.75	zeolite Na-P1	10.2
	6	4	3.5	3.75	sodalite	22.4
		3	3.5	3.75	zeolite Na-P1 + sodalite	22.3
		2.5	3.5	3.75	zeolite Na-P1	27.3
		2	3.5	3.75	zeolite Na-P1	12.3
		2	7	3.75	zeolite Na-P1	12.4
		2	2.5	3.75	zeolite Na-P1	30.1
		2	5	3.75	zeolite Na-P1	30.2
		2	10	3.75	zeolite Na-P1 + sodalite	30.3
		2	20	3.75	zeolite Na-P1 + sodalite	30.4
		1	5	3.75	zeolite Na-P1	2.4
		1	3.5	3.75	zeolite Na-P1	22.1
	4	2	3.5	3.75	amorphous	11.3
		2	7	3.75	amorphous	11.4
	3	2	3.5	3.75	amorphous	12.1
		2	7	3.75	amorphous	12.2
	2	2	3.5	3.75	amorphous	13.1
		2	7	3.75	amorphous	13.2
	1	2	3.5	3.75	amorphous	11.1
		2	7	3.75	amorphous	11.2
140	6	2	3.5	3.75	zeolite Na-P1	21.1
130	6	2	3.5	3.75	zeolite Na-P1	21.2
120	6	2	3.5	3.75	amorphous	21.3
110	6	2	3.5	3.75	amorphous	21.4
100	24	2	2.5	3.75	zeolite Na-P1	3.1
	24	1	5	3.75	zeolite Na-P1	3.4
	6	5	2.5	3.75	sodalite	6.1
	6	5	5	3.75	sodalite	6.2
	6	2	2.5	3.75	amorphous	4.1
	6	1	5	3.75	amorphous	4.4
93	96	2	2.5	240	zeolite Na-P1	zpt
	49	2	2.5	800>500	zeolite Na-P1	zptf
	51	2	2.5	125	zeolite Na-P1	zpts
	48	2	2.5	240	zeolite Na-P1	960528
80	24	2	2.5	3.75	zeolite Na-P1	8.1
		2	5	3.75	zeolite Na-P1	8.2
70	96	2	2.5	240	zeolite Na-P1	ext70
40	167	2	2.5	240	zeolite Na-P1	ext40

B.2 Treatment of CFA with NaOH solutions and additional treatment

T (°C)	t (h)	NaOH (mol/l)	L/S (ml/g)	stirring (rpm)	pretreatment or additions ¹⁾	product	exp. code
150	24	4	3.5	3.75	z, a	zeolite Na-P1 + analcime	58.3
		3	3.5	3.75	a	zeolite Na-P1	43.2
		3	3.5	3.75	g	sodalite	43.4
		2	5	3.75	g	zeolite Na-P1	35.4
		2	3.5	3.75	z, a	zeolite Na-P1 + analcime	58.1
		2	3.5	3.75	m	zeolite Na-P1	14.4
		2	3.5	3.75	g	zeolite Na-P1	43.3
		2	3.5	3.75	f	zeolite Na-P1 (trace of sodalite)	32.3
		2	3.5	3.75	al	zeolite Na-P1 + sodalite	27.2
		2	3.5	3.75	a, m	zeolite Na-P1	55.1
		2	3.5	3.75	a	zeolite Na-P1	41.1
		2	3.2	3.75	al	zeolite Na-P1	23.2
		2	3.2	3.75	a	zeolite Na-P1	62.1
		2	3	3.75	q	zeolite Na-P1 (trace of chabazite)	44.3
		2	3	3.75	a	zeolite Na-P1	45.2
		1.9	3.5	3.75	t	zeolite Na-P1	40.4
		1	3.5	3.75	t	zeolite Na-P1	40.2
	6	ca. 2	3.5	3.75	r	zeolite Na-P1	18.2
		2	5	3.75	g	zeolite Na-P1	35.3
		2	3.5	3.75	s	zeolite Na-P1	25.1
		2	3.5	3.75	m	zeolite Na-P1	15.4
		2	3.5	3.75	g	zeolite Na-P1	31.2
		2	3.5	3.75	f	zeolite Na-P1 (trace of sodalite)	31.3
		2	3.5	3.75	al	zeolite Na-P1 + sodalite	27.1
		2	3.2	3.75	al	zeolite Na-P1	23.1
		1.9	3.5	3.75	t	amorphous	40.3
		1	3.5	3.75	t	amorphous	40.1
93	40	2	2.5	240	o	zeolite Na-P1	ow1-5
	40	2	2.5	240	w	zeolite Na-P1	ww1,2
	48	2	2.5	240	al	zeolite Na-P1 + gibbsite	adal
	24	2	2.5	240	m	zeolite Na-P1	demag
	48	2	2.5	240	a	zeolite Na-P1	73.1

¹⁾ a=acid treatment; m=removal of magnetite from CFA; s=10% seeding with CFA already converted into zeolite; g=grinding; z=zeolitised; f=fluoride added; t=TMAOH added; q=quartz added; al=Na-aluminate added; o=CFA prewashed with organic extractant (EDTA, citric acid or oxalic acid); w=CFA prewashed with water; r=process water upto four times recycled

B.3 Treatment of CFA with LiOH suspension

T (°C)	t (h)	LiOH (mol/l)	L/S (ml/g)	stirring (rpm)	product	exp. code	
150	6	2		3.5	3.75	zeolite Li-ABW	li1
	24	2		3.5	3.75	zeolite Li-ABW	li2

B.4 Treatment of CFA with KOH solutions (in some cases with pretreated CFA)

T (°C)	t (h)	KOH (mol/l)	L/S (ml/g)	stirring (rpm)	pretreatment or additions ¹⁾	product	exp. code
150	24	4	3.5	3.75	-	zeolite K-G	56.2
		3	3.5	3.75	-	zeolite K-G	56.1
		2	5	3.75	-	zeolite K-M	66.2
		2	3.5	3.75	-	zeolite K-G	35.2, 67.1
		2	3.2	3.75	-	zeolite K-M	63.4
		2	3	3.75	s	zeolite K-G	48.1
		2	3	3.75	-	zeolite K-M	68.1-4
		2	3.5	3.75	a, m	zeolite K-M	55.3
		2	3.2	3.75	a	zeolite K-M	62.2
	6	2	3.5	3.75	-	amorphous	35.1
93	96	2	2.5	240	-	zeolite K-G	kg
	72	2	2.5	240	-	zeolite K-G	ZKG2
	72	2	2.5	240	-	zeolite K-G	zkt
	72	2	2.7	240	a	zeolite K-M	zkm
	55	2	2.5	240	s	zeolite K-G	kg4,5
	7	2	2.5	240	-	amorphous	961904

¹⁾ a=acid treatment; m=removal of magnetite; s=10% seeding with chabazite or CFA already converted to zeolite K-G

B.5 Treatment of CFA with NaOH+KOH solutions

T (°C)	t (h)	NaOH (mol/l)	KOH (mol/l)	L/S (ml/g)	stirring (rpm)	product	exp. code
150	24	2.5	2.5	5	3.75	cancrinite	5.4
		1.33	0.67	2.5	3.75	zeolite ZK19	1.2
		1	1	2.5	3.75	zeolite ZK19	1.3
		1	1	5	3.75	zeolite Na-P1	5.3
		1	1	3.2	3.75	zeolite ZK19	64.1-3
		0.5	1.5	3	3.75	zeolite ZK19 + zeolite K-M	46.2
		0.25	1.75	3	3.75	zeolite ZK19 + zeolite K-M	46.1
	6	1.33	0.67	2.5	3.75	zeolite ZK19	2.2
		1	1	2.5	3.75	zeolite ZK19	2.3
	100	24	1.33	0.67	2.5	3.75	zeolite ZK19
1			1	2.5	3.75	zeolite ZK19	3.3
6		2.5	2.5	2.5	3.75	amorphous	6.3
		2.5	2.5	5	3.75	amorphous	6.4
		1.33	0.67	2.5	3.75	amorphous	4.2
		1	1	2.5	3.75	amorphous	4.3
90		168	1.33	0.67	3	3.75	zeolite ZK19

Appendix C Characteristics of zeolites encountered in this study (Breck, 1974; Barrer, 1982)

Zeolite	Typical unit cell contents	Variation Si/Al ratio	CEC ¹ (meq/g)	Natural counterpart	Density (g/cc)	Void volume (cc/cc)	Free apertures (Å)		Largest molecule adsorbed	Kinetic diameter (Å)
							hydrated	dehydrated		
zeolite Na-P1	$\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{10}] \cdot 15\text{H}_2\text{O}$	1.1-2.5	4.4	Gismondine	2.01	0.41	3.1 x 4.4 2.8 x 4.9	2.6	H ₂ O	2.6
zeolite ZK19	$(\text{Ca}, \text{Na}_2\text{K}_2)_6[(\text{AlO}_2)_{10}(\text{SiO}_2)_{22}] \cdot 20\text{H}_2\text{O}$	1.7-2.4	3.9	Phillipsite	2.15	0.31	4.2 x 4.4 2.8 x 4.8 3.3	?	H ₂ O	2.6
zeolite K-G	$\text{K}_4[(\text{AlO}_2)_4(\text{SiO}_2)_8] \cdot 13\text{H}_2\text{O}$	1.6-3	3.6	Chabazite	2.1	0.47	3.7 x 4.2 2.6	3.1 x 4.4	n-paraffins	4.3
zeolite K-M	$\text{K}_{42}[(\text{AlO}_2)_{42}(\text{SiO}_2)_{76}] \cdot 107\text{H}_2\text{O}$?	4.0	Phillipsite	2.18	0.22	3.6	?	SO ₂	3.6
zeolite Li-ABW	$\text{Li}_4[(\text{AlO}_2)_4(\text{SiO}_2)_4] \cdot 4\text{H}_2\text{O}$?	6.9	none	2.27	0.28	?	?	NH ₃ (but not N ₂)	2.6
sodalite	$\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 8\text{H}_2\text{O}$?	6.0	Sodalite	2.03	0.35	2.2	2.2	H ₂ O	2.6

¹ CEC calculated from presented unit cell composition. Changes in composition will result in changes in CEC

?= unknown

Chapter 3

Synthesis of pure zeolites from powder coal fly ash

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"A two-step process for the synthesis of zeolites from coal fly ash"

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ABSTRACT

The well known single step conversion of coal fly ash into zeolite can be extended to a two-step process whereby besides zeolite that still contains residual fly ash, also pure zeolite can be synthesized. This is achieved by: 1) the application of a silica extraction to skim off the surplus of Si available in fly ash; 2) the synthesis of pure zeolite from the extracted silica and additional aluminum obtained from an industrial residual source; 3) the conversion of the remaining fly ash residue resulting in a similar zeolite product as obtained from the "regular" single step process. In this study up to 70 g of pure zeolite was synthesized per kg of coal fly ash treated. The measured cation exchange capacities of these zeolites ranged from 3.6 to 4.3 meq/g.

Keywords: fly ash, zeolite, synthesis, silica, residual aluminate

1 INTRODUCTION

The production of zeolites from powder coal fly ash (CFA) by batchwise treatment with alkaline solutions at temperatures of 50 to 200°C is a well known process which shows a strong similarity to the natural formation of zeolites from volcanic ashes. Research on this subject has been published by many authors, e.g. Höller and Wirsching (1985), Henmi (1987), Singer and Bergaut (1995), Lin and Hsi (1995), Querol et al. (1995), Park and Choi (1995) and Amrhein et al. (1996). All these publications showed the formation of a zeolite product that still contains significant amounts of residual fly ash. Likewise, our own results (see chapter 2) showed that by the current single step conversion methods a product may be obtained from CFA with circa 40 wt % of zeolite and a cation exchange capacity (CEC) of 2-2.5 meq/g. Figure 3.1 presents an example of a X-ray diffraction pattern (XRD) of CFA zeolitized with a 2 M NaOH solution at 93°C. The diffraction peaks of residual quartz and mullite are clearly visible. Examination of polished sections of zeolitized CFA by SEM (see chapter 2) showed that the zeolite crystals were formed on the surface of CFA particles, but also that Ca, Mg-hydroxides had precipitated. The presence of these non-zeolite phases in the conversion products, limits the cation exchange capacity of the zeolitized fly ash and reduces their value for application in the field of adsorption and absorption. Therefore it was examined if it is possible to synthesize pure zeolites from CFA by modification of the 'traditional' zeolitization process. Patent on this newly developed process, which is not fully optimized yet, has been applied for by KEMA (No. NL1004729). In this paper an overview of this process is presented.

2 MATERIALS AND METHODS

Starting Materials

Experiments were carried out with an alkaline fly ash obtained in 1990 from the Dutch "Amercentrale" where it was formed as a result of the combustion of powdered coal at a temperature of circa 1500 °C. This particular coal fly ash (CFA) was chosen for this research project because it was already fairly well described in a previous research project (1990-1993) on soil formation in CFA deposits (KEMA, 1994).

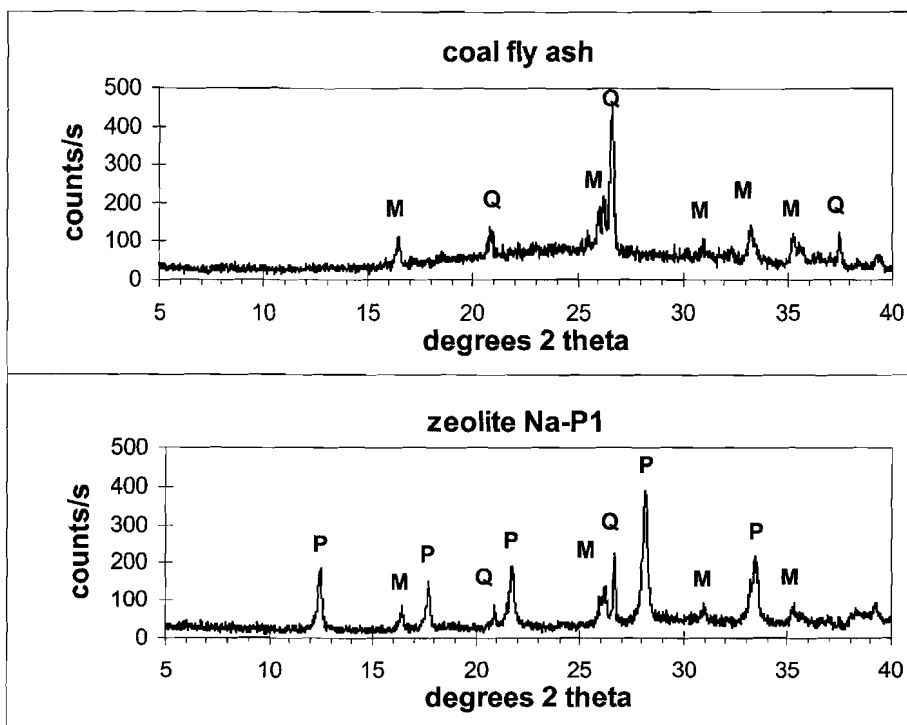


Figure 3.1 X-ray diffraction patterns of coal fly ash before and after zeolitization. Synthesis of zeolite was carried out with a 2 M NaOH solution at 93°C in 24 hours. P = zeolite Na-P1, M = mullite, Q = quartz

As sources of alumina for zeolite synthesis $\text{Al}(\text{OH})_3$ obtained from MERCK (Darmstadt, Germany) was used as well as alkaline aluminate solutions from AKZO (Apeldoorn, The Netherlands) and Alumat (Etten-Leur, The Netherlands). These solutions are residues of the aluminum finishing industry and are produced during the polishing of aluminum. They contain circa 115000 mg/l Al, 5 molar equivalents of NaOH and some sorbitol which forms complexes with the dissolved aluminum and serves to increase the aluminum solubility (pers. comm. van der Heuvel, Aladin B.V.). Furthermore these solutions originally contain a black suspension of sulfides of heavy metals, such as Zn, released from the aluminum. However, in the aluminate solution obtained from AKZO this sulfide suspension was already removed by microfiltration. From the solution obtained from Alumat it was removed by sedimentation and decantation upon receipt. At present this type of residual aluminate solutions is used for the removal of phosphates from waste waters.

Sodium hydroxide solutions used in this study were prepared from reagent grade chemicals and demineralized water.

Experimental methods

One-step zeolitization process

CFA was zeolitized by mixing 500 g CFA with 1.25 liter 2 M NaOH solution and heating this mixture to 93°C for 96 h. At regular time intervals 10-15 ml aliquots were taken by pipette of the reaction mixture that were analysed on pH and concentrations of Si and Al. The reaction was carried out in a Teflon beaker with a volume of 2 liter that was placed in a water bath. An IKA propeller stirrer tuned to 240 rpm, was used to keep the reaction mixture in suspension. Filtration of the reaction mixtures was carried out by pressure filtration (2-6 bar) using S&S 595 paper filters.

Two-step zeolitization process

Reaction liquids were obtained by filtration from the above described one step zeolitization process (step 1). Added to these were the aluminate solutions obtained from AKZO or Alumet, or aluminum hydroxide (MERCK) to adjust the Si/Al ratio of these reaction liquids. These optimized mixtures were used for the synthesis of pure zeolites. For this purpose they were heated in a stove to 90-95°C for 44 to 163 h in closed 40 ml Teflon vessels without any stirring (step 2). At the end of this reaction period the mixture was filtrated and the recovered residues dried and analyzed by XRD. In addition a number of experiments was carried out with stirring (150 rpm) using the set-up described above and a reaction time of 24 h. Solids retrieved by filtration were washed with water (L/S 3-9), dried (75°C) and analyzed by XRD.

Analytical techniques

XRD was used for the identification of the mineral phases in the original and zeolitized fly ash (CuK α radiation at 40 kV using a Philips PW1730 diffractometer coupled to a PW1710 control system). Quantitative mineralogical analysis was carried out for zeolite Na-P1 by standard addition method (Brindley, 1980; Snyder and Bish, 1989). For this purpose a standard of zeolite Na-P1 was synthesized following the prescription by Milton (1961). See chapter 5 of this thesis for a more extensive treatment of this subject.

The CEC of selected samples was determined by the International Soil Reference and Information Center (ISRIC) in Wageningen (The Netherlands), using the ammonium acetate method (ISRIC, 1992), after the samples were washed with 80% alcohol to remove excess salt. In addition, a JEOL JSM 6300 scanning electron microscope (SEM) was used for further characterization of the solids.

The concentration of Si in the reaction liquids obtained during the zeolitization of CFA was measured by spectrometry (Dr. Lange LCW028) for instant analysis. A more complete chemical analysis was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES; elements Al, B, Ba, Ca, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr, Ti, V, Zn). Prior to the analysis, liquids were acidified with concentrated HNO₃ to a pH of 1 to 2. To prevent interference of the high alkali concentrations with the analyses and to avoid the formation of silicate precipitates upon acidification, reaction liquids were diluted by a factor 10 to 100. The pH of solutions was measured with an Orion solid state sure flow

pHutere electrode (model 61-65) connected to an Orion ISE/pH meter (model 940). This pH electrode contains instead of a glass electrode, a silicon sensor which leads to a more stable signal when measuring highly alkaline solutions. The relative accuracy of the pH measurement proved to be ± 0.03 up to pH 14.3 if no new calibration was carried out. Comparing results from different calibration runs, however, showed a relative precision of only ± 0.2 .

Solids were analyzed following standard procedures which including dissolution in closed Teflon vessels by heating with a mixture of HF/HClO₄/HNO₃ or by fusion with a mixture of lithium metaborate and tetraborate, and subsequent analysis by ICP-AES.

3 RESULTS AND DISCUSSION

Behavior of Si and Al in solution during zeolitization

The analytical results of the aliquots taken at regular time intervals from the reaction vessel in which CFA was being converted into zeolite by current single step methods, show that the concentration of Si in solution reaches a maximum of circa 10000 mg/l before stabilizing at circa 6800 mg/l after zeolite crystallization. Analyses by XRD of the solids obtained at the same time intervals show that the maximum in the concentration of Si coincides with the start of crystallization of zeolite Na-P1. The concentration of Al in solution on the other hand, reaches a maximum concentration of circa 840 mg/l solution within the first hour of the conversion process and subsequently decreases to nearly zero.

These reaction patterns, which are shown for reaction temperatures of 40, 70 and 93°C in figure 3.2, indicate the presence of an induction period prior to the real zeolite crystallization. During this induction period part of the fly ash dissolves, zeolite nuclei form on the surface of the residual fly ash particles and the solution becomes supersaturated with Si in respect to zeolite. Crystallization then starts at the moment the size of these nuclei reaches a certain minimum from which point on further growth is advantageous for minimizing the surface energy (Barrer, 1982). From figure 3.2 it is clear that both the rate of this process and the final zeolite content, increase with an increase of the temperature of reaction.

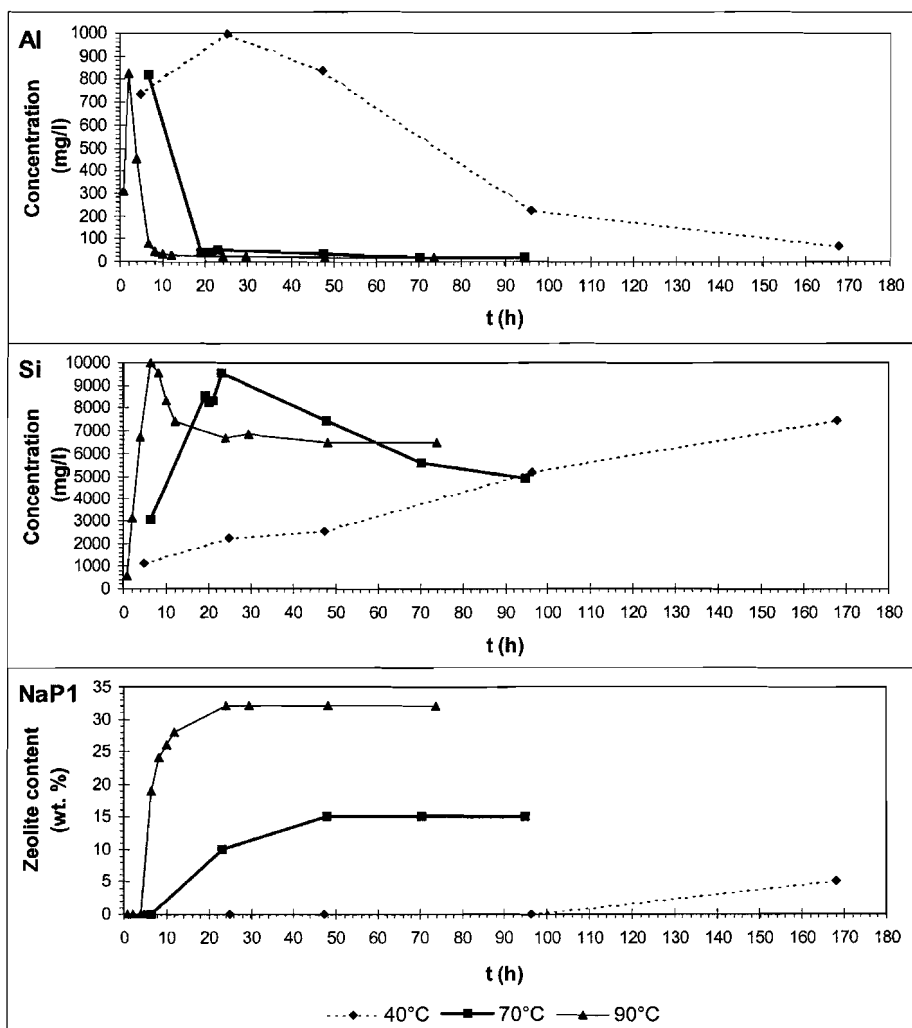


Figure 3.2 Al and Si concentration in solution and content of zeolite Na-P1 as a function of time for the treatment of coal fly with a 2 M NaOH solution at reaction temperatures of 40, 70 and 93°C

Step 1: extraction of Si

The high concentrations of Si present in solution at the end of the induction period can be used for the synthesis of pure zeolites. For this purpose an additional filtration and zeolitization step are necessary. The reaction mixture of CFA and hydroxide solution is filtrated at the moment the concentration of Si in solution is nearing its maximum. Thus the

zeolite synthesis is stopped and, in effect, a silica-extraction is being carried out. This silica-extract can then be used for the synthesis of pure zeolite.

Step 2: synthesis of pure zeolite

Pure zeolites can be synthesized from the silica-extract by adding Al in a reactive form and subsequently heating this new mixture. This has been carried out for a range of Si/Al ratios at 90°C. Table 3.1 presents chemical analyses of the residual aluminate solutions that have been used. Over time the organic Al-complex appeared to be unstable as gibbsite precipitated from the originally received residual aluminate solutions. This caused a gradual drop in the concentration of Al in the residual solutions used to circa 65000 mg/l.

Table 3.1 Chemical composition (mg/l) of residual aluminate solution¹⁾ obtained from AKZO and Alumet. Both contain ca. 5 eq of NaOH per liter.

Element	AKZO	Alumet	Element	AKZO	Alumet
Al	143000	112200	Mn	5.3	<60
B	n.a.	<180	Na	115769	123400
Ba	1.4	<60	Ni	21	<60
Ca	124	<240	P	2.8	<480
Cd	n.a.	<60	Pb	147	<300
Co	n.a.	<60	S	8419	476
Cr	16	<60	Si	<400	266
Cu	1.1	<60	Sr	3.8	<60
Fe	62	<60	Ti	13	<120
K	8930	<360	V	n.a.	<60
Mg	37	<60	Zn	635	<120

¹⁾ Excluding organic components; n.a. = not analyzed

Alternatively, instead of to the silica-extract, Al may be added to the final process waters, that are left over from the zeolitization of CFA by the current single step procedure, and contain ca. 6500 mg/l Si. Pure zeolites can also be synthesized from these mixtures (see table 3.3) but in lower amounts. It should be noted that zeolite K-G, mentioned in table 3.3, was synthesized from a process water obtained from the zeolitization of acid pretreated CFA which had an unusually high concentration of Si (ca. 9000 mg/l). Also, the relatively heavy weight of the K contributes to the high amounts of zeolite K-G synthesized.

The application of a silica-extraction thus makes it possible to synthesize pure zeolite from CFA. As far as known this has not been described before. Closest to the procedure described here, is the synthesis by Singer and Berggaut (1995) of mixtures of zeolite Na-P1 and sodalite, without any further impurities, from the reaction solution filtrated prior to the end of the induction phase. In this case, however, no external Al was added, only the Si and

Al dissolved from CFA was used. Therefore quantities of zeolite produced were presumably very low. These were, however, not specified.

Because our interest was primarily in the application of zeolite as an adsorbent, the synthesis of zeolites with a large cation exchange capacity (CEC) was aimed for, i.e. of zeolites with a low Si/Al ratio, such as zeolite Na-P1, zeolite Na-A, zeolite K-G and zeolite Na-X. Table 3.2 presents molar ratios of reaction mixtures used for the synthesis of these zeolites from gels as reported by Breck (1974). These ratios were used as a first guideline for adjustment of the Si/Al ratios of the silica-extract.

Table 3.2 Molar composition of reaction mixtures generally used for the synthesis of zeolites (Breck, 1974)

Type of zeolite	Typical reactant composition (mol/mol Al_2O_3)			
	Na_2O	K_2O	SiO_2	H_2O
Na-A	2	-	2	35
Na-P1	2	-	3.8	94
Na-P2	6	-	8	L/S=6
Na-X	3.6	-	3	144
sodalite	2.8	-	3	34
K-G	-	2.5	5	ns ¹⁾

¹⁾ ns = not specified

In table 3.3 an overview of the results of the experiments is presented. It proved to be possible to synthesize different types of zeolite from the silica-extract. Synthesized were zeolite Na-P1, zeolite Na-X, zeolite Na-A, zeolite K-G and sodalite. Figure 3.3 presents examples of XRD patterns of the zeolites synthesized from the silica-extract. Photo 3.1a and 3.1b present micrographs of respectively zeolite Na-P1 and zeolite Na-X. Analysis by XRD and SEM shows that a high purity for the products with zeolite Na-P1 and zeolite Na-X is possible (>95% by estimation) but also that these two zeolites often coexist in the same product. Synthesized zeolite Na-A usually contains some sodalite or amorphous material.

Table 3.3 Overview of zeolites synthesized at 90°C from silica-extracts or process waters, obtained from the zeolitization of CFA, and aluminate solutions. Experiments are listed in order of increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

	Type of zeolite synthesized ¹⁾	Yield of zeolite (g/kg CFA)	Al-source ²⁾	Molar ratios (mol/mol Al_2O_3)				t (h)	exp.code
				Na_2O	K_2O	SiO_2	H_2O		
silica-extract	sodalite (A, am)	87	a	4.0	0.2	2.2	340	163	z1-15271
	sodalite (am)	86	a	5.2	0.2	2.2	340	163	z1-25271
	sodalite	80	s	5.0	0.2	2.2	360	72	z1p2-8c
	zeolite Na-X (P)	73	l	5.8	0.2	2.2	370	72	z1p2-6c
	zeolite Na-A	74	l	6.0	0.3	2.2	485	72	z4-4142
	zeolite Na-A (S, am)	78	l	6.5	0.4	2.5	535	67	z4-572
	sodalite (A)	58	l	7.4	0.3	2.8	475	44	alad4
	zeolite Na-X (S, P)	43	m	7.4	0.3	2.8	475	44	alad8
	sodalite (A)	74	l	7.2	0.3	2.9	490	72	z1-271
	sodalite (am)	76	l	7.2	0.3	2.9	490	163	z1-10271
	zeolite Na-P1	39	l	7.5	0.3	3.0	590	48	A3A4
	zeolite Na-X (P)	27	m	8.3	0.4	3.2	535	44	alad7
	sodalite (X)	52	l	8.3	0.4	3.2	535	44	alad3
	zeolite Na-X+Na-P1	25	s	8.2	0.3	3.2	660	48	z3z5
	zeolite Na-X (A)	60	l	8.4	0.5	3.5	735	67	z4-472
	zeolite Na-X	67	l	8.3	0.4	3.5	580	50	z1-532
	zeolite Na-X	67	l	8.7	0.4	3.6	600	50	z1-432
	zeolite Na-P1	48	l	9.1	0.4	3.6	600	44	alad2
	zeolite Na-X (P)	34	m	9.1	0.4	3.6	600	44	alad6
	zeolite Na-P1 (X)	39	l	9.3	0.4	3.6	760	28	A1A2
	zeolite Na-P1	40	l	9.2	0.5	3.7	670	28	A5A6
	zeolite Na-P1	43	l	9.6	0.5	3.8	635	24	A7A8
	zeolite Na-X (P)	64	l	10.2	0.4	3.8	780	50	z3-1332
	zeolite Na-X (S)	52	s	8.1	0.3	3.9	620	72	z1p2-11
	zeolite Na-P1+Na-X	45	l	8.9	0.4	3.9	630	72	z1p2-6
	zeolite Na-P1	46	a	7.5	0.4	4.0	790	48	z4-11
	zeolite Na-X+Na-P1	32	m	10.0	0.5	4.0	665	44	alad5
	zeolite Na-X+Na-P1	40	l	10.0	0.5	4.0	665	44	alad1
	zeolite Na-X (P)	51	l	10.3	0.6	4.3	910	72	z4-1532
	zeolite Na-X (P)	65	l	10.2	0.6	4.4	925	72	z4-5142
	zeolite Na-X (P)	29	s	9.5	0.5	4.5	920	48	z4-16
	zeolite Na-X+Na-P1 (A)	54	l	10.3	0.4	4.6	750	50	z1-632
	zeolite Na-X (P)	30	s	14.9	0.6	7.5	1180	72	z1p2-16
	zeolite Na-P1+Na-X	25	l	15.6	0.7	7.5	1190	72	z1p2-8
	zeolite Na-P1	27	a	16.4	0.7	8.7	1736	92	gib 6
	zeolite Na-P1	27	a	17.4	0.7	8.7	1737	92	gib12
	zeolite Na-P1	27	a	18.4	1.0	8.7	1738	92	gib8
process water	sodalite (A)	48	s	7.2	0.3	2.3	540	72	bet3-11
	zeolite Na-A (S)	41	l	8.0	0.4	2.3	555	72	bet3-12
	zeolite K-G	74	l	2.2	3.3	4.0	407	48	zk2-8
	zeolite K-G	76	s	1.4	3.3	4.0	395	48	zk2-12

¹⁾ in brackets phases of which traces are present: P=zeolite Na-P1, X=zeolite Na-X, A=zeolite Na-A, S=sodalite, am=amorphous

²⁾ a= $\text{Al}(\text{OH})_3$ (MERCK), l=residual aluminate solution, s=residual aluminate solution with precipitated gibbsite, m=residual aluminate solution, including suspension of metal sulfides

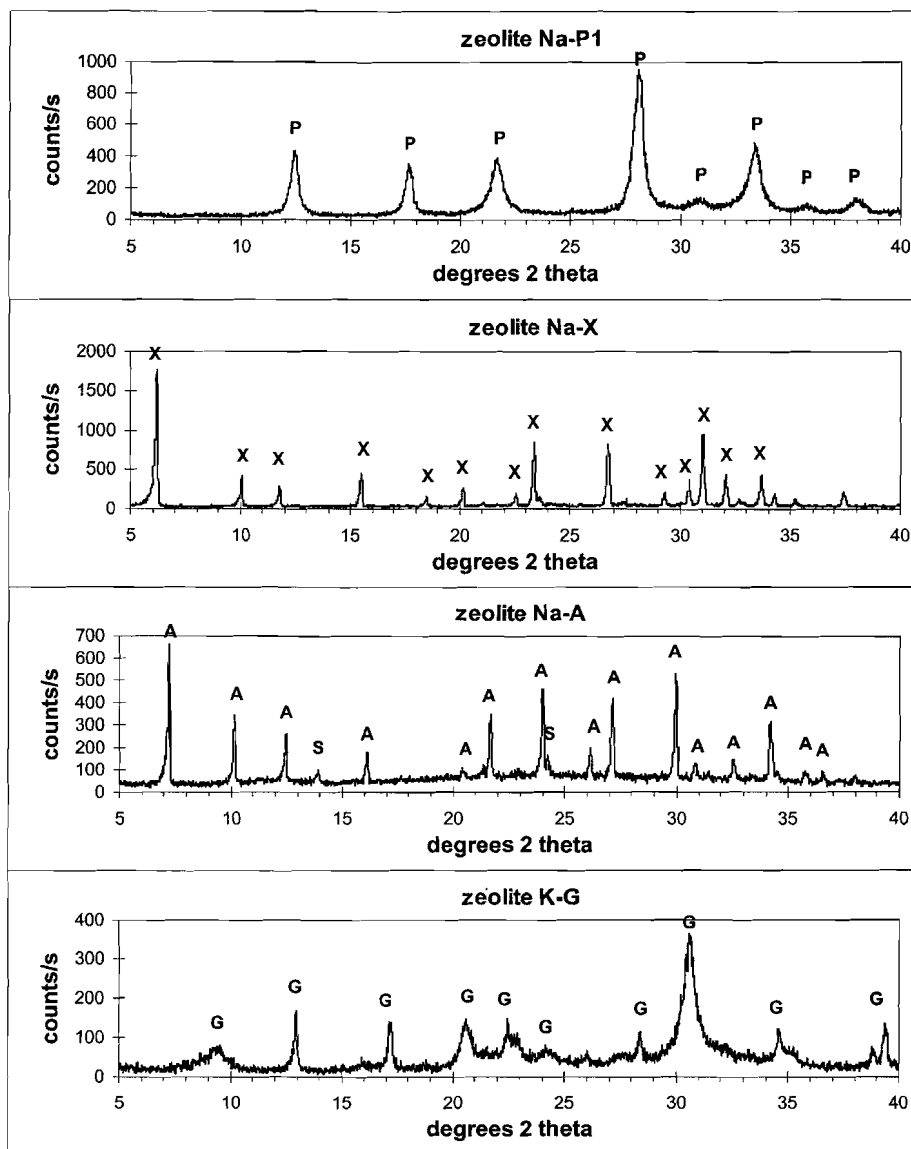
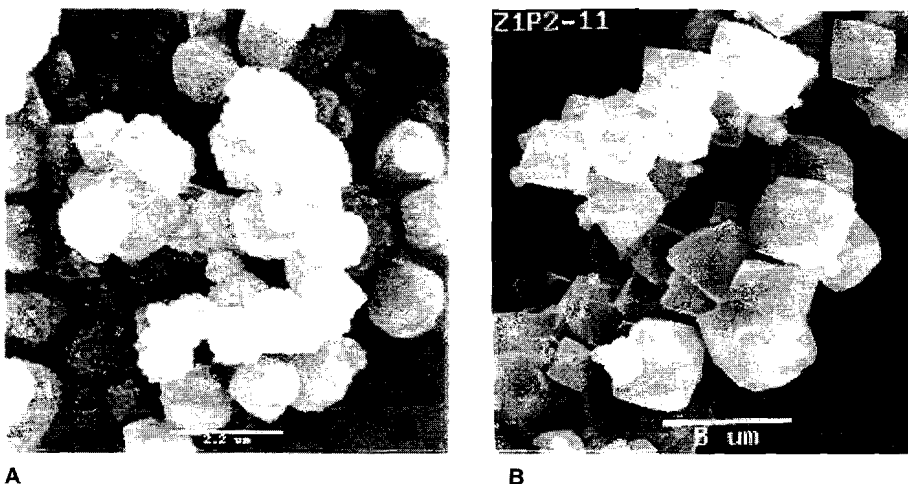


Figure 3.3 Examples of X-ray diffraction patterns of zeolites synthesized at 90°C from coal fly ash and aluminate solution. P = zeolite Na-P1, X = zeolite Na-X, A = zeolite Na-A, G = zeolite K-G. From top to bottom are shown the diffraction patterns of the products from experiments A5A6, z1-532, z4-4142 and zk2-12 (see table 3.3 for further specifications)



A Photo 3.1 Micrographs of zeolite Na-P1 (A) and zeolite Na-X (B). Both zeolites were synthesized at 90°C from silica-extracts and residual aluminate solution, respectively in experiment A5A6 and z1p2-11 (see table 3.3 for further specifications)

The yield of zeolite produced varied from 25 to 90 g per kg of fly ash. The highest yields are, however, measured for the products with sodalite, which, because of its structure, has only limited value as an exchanger (Barrer, 1982). From the results it can be concluded that for zeolite Na-P1, zeolite Na-X and zeolite Na-A, all valuable exchangers, a yield of 50-70 g/kg CFA is very well possible. Calculations, based on the amount of zeolite Na-P1 synthesized from CFA in the current single step process, and on the amount of mullite, quartz and concentration of SiO_2 and Al_2O_3 in CFA, indicate that theoretically the synthesis of circa 100 g of pure zeolite per kg of CFA is possible without disrupting the zeolitization of the residual CFA. To achieve this the efficiency of the silica-extraction must be improved. This will also lower the price per ton of zeolite synthesized.

Cation exchange capacities, measured for the products of the experiments z4-11 (zeolite Na-P1), z1p2-6c (zeolite Na-X), z4-572 (zeolite Na-A and sodalite) and zk2-8 (zeolite K-G), varied from 3.6 to 4.3 meq/g. The chemical composition of zeolite K-G and zeolite Na-X, respectively synthesized in the experiments zk2-8 and z1p2-6c, are given in appendix A. Measured compositions serve as a check of measured CEC's. Unfortunately no analyses for zeolite Na-P1 and zeolite Na-A are available or for the products of any other runs. A comparison (table 3.4) of the compositions and CEC that were measured with the theoretical composition and CEC, reveals that the analyzed zeolites differ slightly in their $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from the expected theoretical value. The CEC measured for zeolite Na-X is 1.5 meq/g lower than that expected for pure zeolite Na-X while that for zeolite K-G reasonably fits the expected value.

Table 3.4 Comparison between the theoretical expected¹⁾ and measured composition of zeolite Na-X and zeolite K-G from experimental runs zk2-8 and z1p2-6c

		Oxides of major elements (mol/kg)					CEC (meq/g)
		K ₂ O	Na ₂ O	SiO ₂	Al ₂ O ₃	H ₂ O	
zeolite Na-X	z1p2-6	0.2	2.1	6.5	2.3	13.4	3.6
	theoretical	0.0	2.5	6.0	2.5	12.6	5.1
zeolite K-G	zk2-8	1.6	0.4	6.4	2.2	11.7	3.7
	theoretical	2.0	0.0	7.6	2.0	9.0	3.9

¹⁾ Based on Breck (1974)

Zeolitization of the CFA residue

The CFA residue remaining from the silica-extraction was converted into zeolite Na-P1 following the method of the one-step zeolitization process, but replacing the reaction solution of clean hydroxide solution by the process water remaining from the synthesis of pure zeolite. XRD in combination with standard addition methods showed that the resulting zeolite contents were similar to the content reached in the original one-step conversion process, i.e. about 32% at 93°C, before applying enrichment procedures. Table 3.5 presents a mass balance of the two-step zeolitization process.

Table 3.5 Mass balance of the two-step zeolitization process¹⁾

Reactants →	Zeolite synthesis	→ Products
1.0 kg coal fly ash	Reaction time: 24 to 30 h	1.04 kg zeolite with residual fly ash
0.35 kg NaOH	T = 90-100°C	0.06 kg pure zeolite
0.05 kg aluminate solution (115000 mg Al/l)	p = 1 atm	1.8 kg residual water ²⁾
4.3 kg process water		2.7 kg process water
9.2 kg washing water		9.3 kg washing water
14.9 kg	Sum	14.9 kg

¹⁾ Mass balance is normalized to 1 kg CFA, but is based on experiments carried out with 500 g CFA.

²⁾ Residual water is the solution that stays behind in the conversion product after its filtration at 6 bar, but that is removed when drying the sample at 75°C

In figure 3.4 a schematic is presented of the resulting overall two-step zeolitization process. In this graphic visualization of the process, the silica-extraction is assumed to be carried out in a continuous flow reactor. Batchwise processes may, however, in practice be preferred for simplicity of operation.

Integrated in the schematic is a black box which represents pretreatment of the CFA. Research (KEMA/UU, 1998) indicates that washing of the CFA with water or organic extractants and magnetic separation of the magnetic fraction, are beneficial for the synthesis of zeolite from CFA. These treatments are, however, not included in this chapter.

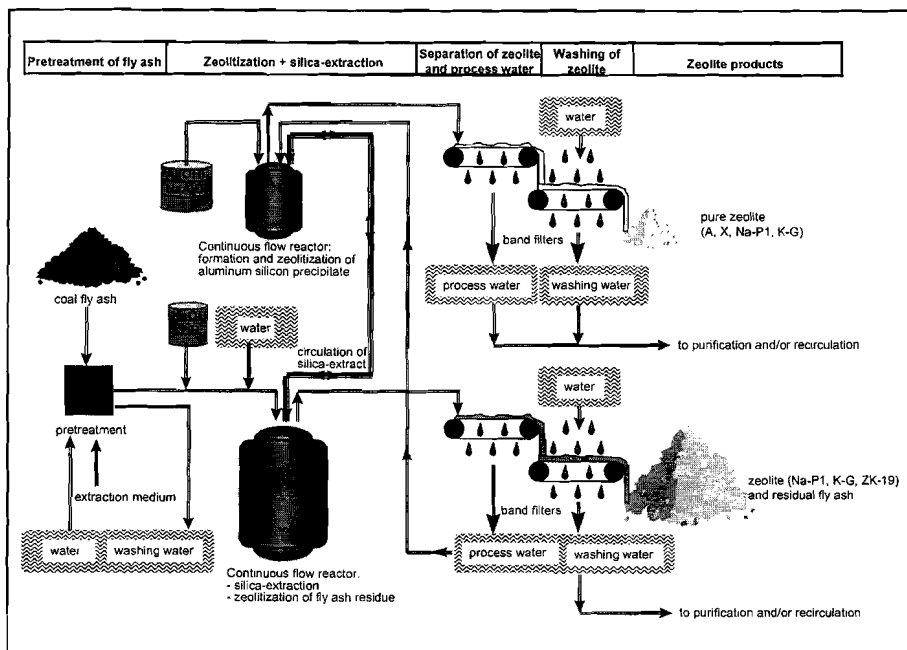


Figure 3.4 Schematic presentation of the overall two-step zeolitization for coal fly ash, which results in the synthesis of pure zeolite and zeolite polluted with residual fly ash

Control of the type of zeolite synthesized and their purity

The synthesis of pure zeolite proceeds through the formation of a gel-like substance which precipitates instantly when aluminate is added to the silica-extract, resulting in a decrease of the concentration of Si in solution to ca. 2500 mg/l. Synthesis of zeolites from gels is common procedure in zeolite science and generally allows the synthesis to be directed towards the formation of particular zeolites by manipulation of the reaction parameters, such as type of reactants and their mutual ratio, pH, temperature and use of structure directing molecules (e.g. Breck, 1974; Barrer, 1982; Jansen, 1991). For the synthesis of pure zeolites from CFA, however, the extent to which the reaction parameters can be varied, is restricted by the Si-source, i.e. the silica-extract. This extract fixes the amount of Si in the mixture and determines the predominant type of cation (Na and/or K) and the minimum amount in which they are present. Also fixed is the minimum amount of water present, which is rather high compared to the examples from Breck (1974) that are listed in table 3.2. The consequence is that the major means by which the synthesis process can be directed towards the formation of specific zeolites is the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, i.e. the amount of Al that is added to the mixture.

As already shown in table 3.3, the variation in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio results in different zeolite products. A graphical overview of this is presented in figure 3.5 in which the type of product obtained is plotted as a function of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ ratio of the reaction mixture. It shows that roughly two crystallization fields can be distinguished. One for zeolite Na-A and sodalite at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios smaller than 3, and one for zeolite Na-P and zeolite Na-X at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios larger than 3.

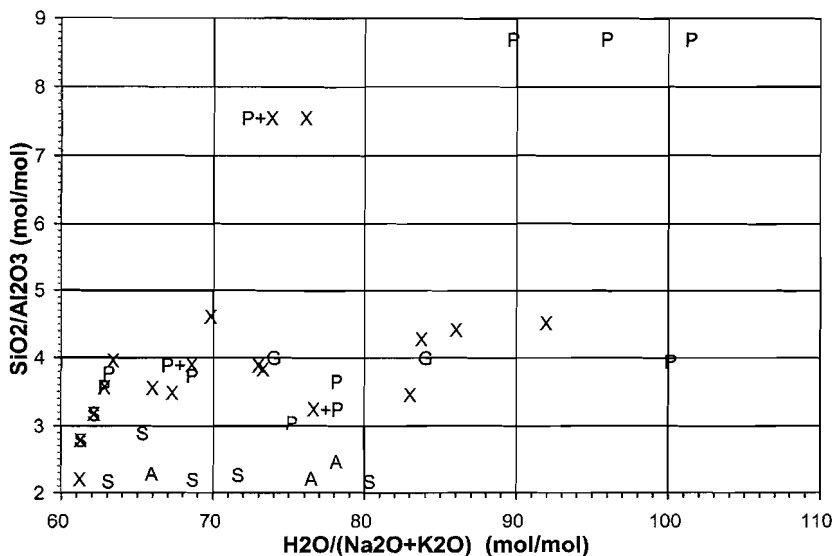


Figure 3.5 Reactant composition and zeolites synthesized from silica-extracts and residual aluminate solutions or $\text{Al}(\text{OH})_3$. See table 3.3 for further specifications

Though data of chemical composition and CEC are too scarce to confirm this, analyses by XRD and SEM indicate that a high purity for the products with zeolite Na-P1 and zeolite Na-X is possible, but also that these two zeolites often coexist in the same product. Similarly, products with zeolite Na-A usually also contain some sodalite. This is in agreement with observations by Freund (1976) that competitive crystallization exists between zeolite Na-A, zeolite Na-P1 and sodalite and between zeolite Na-X and zeolite Na-P1. Both zeolite Na-A and zeolite Na-X are known to be metastable relative to zeolite Na-P1 (Breck, 1974). This means that, provided that the reaction time is sufficiently long, both zeolite Na-A and zeolite Na-X will recrystallize to zeolite Na-P1. Also, in case of an excess of NaOH, zeolite Na-A is known to transform to sodalite (Breck 1974). This is in compliance with the Oswald step rule which states that the most likely phase to form is not necessarily thermodynamically the most stable one and that equilibrium will be gradually approached through a series of irreversible steps (Dibble and Tiller, 1981). The reason for this is that in a system

supersaturated in many solids, the phase with the highest growth rate (zeolite Na-X in our case) will dominate the initial solid phase assemblage. Though this may suppress temporarily the formation of more stable solids (zeolite Na-P), this does not exclude their formation. The selectivity for the crystallization of zeolite Na-X, zeolite Na-A or zeolite Na-P1 depends on the number of nuclei formed prior to crystallization, i.e. during the induction period, and thus on the rate of nucleation and crystallization. According to Freund (1976) there are three major factors that are decisive in this respect:

- 1) the type of silica source: the use of inactive sources, such as solids and colloid suspensions, yields zeolite Na-P1, while the use of active silica sources, such as hydrated sodium silicates tends to yield zeolite Na-X;
- 2) the reaction temperature: the rate of nucleation of zeolite Na-X at room temperature is much faster than that of zeolite Na-P1, while the opposite is true at temperatures of 80°C and higher;
- 3) the rate of stirring: this determines the thickness of the layer surrounding a nucleus in which no foreign nucleus can form. The thickness of this layer decreases as the rate of stirring increases. This implies that at higher rates of stirring, a larger number of nuclei is needed to obtain selective zeolite crystallization.

The findings of Freund (1976) explain for a large part why from mixtures with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios greater than 3, predominantly zeolite Na-X was formed, unless stirring was applied. The silica-extracts used in this study can be considered as active silica-sources. They were usually cooled to room temperature before adding the aluminate solutions. This procedure thus enhanced the formation of zeolite Na-X nuclei. Synthesis was, however, carried out at 90°C. Though this promotes the nucleation of zeolite Na-P1, the absence of stirring in most experiments slows down the nucleation of zeolite Na-P1 and enhances the crystallization of zeolite Na-X of which already more nuclei will have been formed at that time. If stirring is applied, as in the experiments A1A2, A3A4, A5A6 and A7A8 in this study, then within the 24 h of reaction time applied, indeed, zeolite Na-P1 is formed, without any trace of zeolite Na-X in the product. Thus if the objective is the formation of zeolite Na-X, stirring should be avoided. Because stirring also increases the rates of nucleation and crystallization (Freund, 1976), this also means that the synthesis of zeolite Na-X will take more time than that of zeolite Na-P1 and will thus be more expensive. According to Freund (1976) his findings can be extended to the competitive formation of zeolite Na-A and sodalite. The formation of the latter may, however, also be promoted by higher hydroxide concentrations.

Another factor that may affect the formation of zeolite Na-P1 and zeolite Na-X is the presence of impurities. The residual aluminate solution contains some components which may be of influence on the zeolite synthesis, especially the sorbitol type of substance that is used to increase the solubility of Al. The characteristics of this substance are not extensively examined. As already mentioned it does not appear to be very stable which causes the precipitation of gibbsite. When this is the case it is indicated in table 3.3, though this does not seem to be of influence on the zeolite synthesis. Experiments carried out with and without the metal sulfide suspension originally present in the residual aluminate solution (exp. codes alad5 to alad8 in table 3.3), indicate that this impurity is of influence on the zeolite synthesis. The results from these experiments suggest that these sulfides enhance

the formation of zeolite Na-X. The mechanism behind this has, however, not been examined. The residual aluminate solution has been shown to be a suitable source of Al for the synthesis of zeolite. If the removal of the metal sulfide suspension is not necessary for this application, it will be of great interest to the aluminum finishing industry (pers. comm. Van der Heuvel, Aladin B.V.).

Economic Perspective

At present the process for synthesizing pure zeolites from CFA should still be optimized. Given the quantities of pure zeolite that were synthesized, they can at present be no more than a byproduct in the zeolitization process, though possibly a valuable one. Tentative calculations by APM Consultants B.V. (KEMA/UU, 1998) show that the cost of the two-step process amounts to circa \$40,- per keq exchange capacity generated. For the one-step process this would be circa \$25,- per keq exchange capacity generated. This difference should be compensated by the high purity of part of the zeolites synthesized and the more intricate applications they should be suitable for. In the end it will depend on the production costs and the market value whether or not the two-step synthesis process is worthwhile. At present the use of zeolite, natural or synthetic, in The Netherlands for the adsorption of pollutants is practically nonexistent which means that the market for zeolites from CFA still has to be created.

4 CONCLUSIONS

- Current single step zeolitization methods for CFA can be extended to a two-step process in which besides zeolite that still contains residual fly ash, also pure zeolite can be synthesized. The extension consists of a silica-extraction carried out at the end of the induction time, just before zeolite crystallization starts when the concentration of Si in solution is at its maximum. Pure zeolite can be synthesized from the silica-extract after addition of Al in a reactive form to adjust its Si/Al ratio.
- Synthesized were zeolite Na-P1, zeolite Na-A, zeolite Na-X and zeolite K-G. CEC's of the pure zeolites ranged, as far as measured, from 3.6 to 4.3 meq/g, and are approximately twice as high as the CEC of zeolitized CFA obtained in a single step process, i.e. ca. 2 meq/g.
- A less costly alternative to the use of the silica-extract, is the synthesis of pure zeolite from the process water left over from the current single step zeolitization process for CFA. Because of the lower amounts of dissolved Si, this leads to circa half the yield of zeolite synthesized.
- The type of zeolite that is formed can be directed by the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the solution and the rate of stirring. For the synthesis of zeolite K-G the use of KOH instead of NaOH solutions is imperative.
- Thus far pure zeolites were synthesized in amounts of 25 to 90 g per kg of CFA treated. The highest amounts were, however, measured for the products with sodalite. A yield of zeolite Na-P1, zeolite Na-X and zeolite Na-A from the silica-extract of 50 to 70 g per kg of

CFA is possible. Theoretically the synthesis of circa 100 g of pure zeolite per kg of CFA is possible, without disrupting the zeolitization of the residual CFA.

- The residual aluminate solutions from the aluminum finishing industry appear to be a suitable source of Al for the synthesis of zeolite from silica solutions. Zeolite synthesis is an interesting new application for these residuals, certainly if the metal sulfides they originally contain need not to be removed. However, this aspect still has to be examined more closely.
- In view of the quantities synthesized, the pure zeolite can be, in spite of its high CEC, no more than a byproduct in the zeolitization process. The main product remains the zeolitized CFA consisting of zeolite and residual fly ash particles. Whether or not the synthesis of pure zeolite from CFA is worthwhile depends on the production costs and their future market value.

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Appendix A Chemical analyses of zeolite Na-X and zeolite K-G synthesized from silica-extracts and residual aluminate solutions. Respectively synthesized in experiment z1p2-6 and zk2-8. See table 3.3 for specifications of the synthesis

Oxides of major elements (wt %)	zeolite Na-X	zeolite K-G	Minor and trace elements (mg/kg)	zeolite Na-X	zeolite K-G
SiO ₂	39.0	38.2	Ba	< 6.2	15
Al ₂ O ₃	23.9	22.6	Ca	< 12.4	< 12.0
Na ₂ O	12.9	2.7	Cd	< 12.4	< 11.9
K ₂ O	1.5	14.9	Co	< 12.4	< 12.0
			Cr	< 12.4	< 12.0
LOI	24.1	21.0	Cu	< 6.2	< 6.0
			Fe	< 6.2	< 6.0
Total	101.3	99.5	Mg	< 6.2	< 6.0
			Mn	< 6.2	< 6.0
			Ni	8	< 6.0
			P	< 44	113
			S	< 31	< 30
			Sr	< 6.2	< 6.0
			Ti	< 12.4	< 12.0
			V	< 6.2	20
			Zn	< 6.2	< 6.2

Chapter 4

Behavior of heavy metals during zeolitization of coal fly ash and leachability of the zeolitized product

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Appeared also in:

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Thesis Utrecht University by G. Steenbruggen*

Submitted to Fuel

ABSTRACT

Coal fly ash (CFA) was zeolitized with a 2 M NaOH solution to examine the behavior of the heavy metals it contains. Results showed that the metallic cations (Ba, Co, Cu, Ni, Pb, Zn) remain immobile during this process while those elements that form oxy-anions (As, B, Se, Mo, V) can be significantly extracted. By means of the standard column leaching test NEN 7343, the leachability of elements from the zeolitized CFA was examined. It was shown that compliance of CFA to the legal norms is improved by its conversion to zeolite. The leachability of As, Se and V is, however, increased after zeolitization due to the inheritance of these elements from the residual reaction fluid and to the competition for metallic cations that are now adsorbed by the zeolite or precipitated as hydroxides. Treatment of the CFA, prior to zeolitization, with organic extractants like EDTA and citric or oxalic acid solutions, removes significant parts (30-80%) of those heavy metals that are critical for the Dutch Decree on Building Materials. Standard column leaching tests with this zeolitized pretreated CFA show that it complies with the norms posed by the Dutch Decree on Building Materials when assuming that the zeolitized CFA is applied in a layer of 1 m thickness. Pretreatment of CFA with organic extractants has no clear influence on the zeolite content.

key words: coal fly ash, zeolite, heavy metals, leaching, column leaching experiments

1 INTRODUCTION

Coal fly ash (CFA) is an inhomogeneous substance consisting of particles of different composition and sizes, ranging from smaller than $0.1\ \mu\text{m}$ up to circa $200\ \mu\text{m}$, which have been formed by the melting and condensation of the inorganic components in coal during the combustion process, and their subsequent solidification and condensation. The leachability of heavy metals contained by CFA, is related to their distribution on the submicroscopic scale. This distribution in its turn is determined by the mineralogical or organic source of the specific elements in the coal and by the condensation processes that take place in the flue gases of an electric power station. In general, volatile elements and those associated with the organic fraction tend to be enriched on the surface of CFA particles (Dudas and Warren, 1987; EPRI, 1987). The most volatile elements are the last to condense and become especially enriched on the smaller particles that have the highest surface area/volume ratio. The less volatile elements and those associated with the inorganic fraction, on the other hand, become especially incorporated in the glassy matrix or are associated with the mullite or the iron oxides present in CFA. Different studies (Van der Sloot, 1982; EPRI, 1987, Eary et al., 1990) report varying degrees of enrichment for different elements. All agree though that more than 50% of the As, Mo and Se is present on the surface of CFA particles while varying degrees of enrichment are reported for B, Ba, Cd, Cr, Cu, Ni, V and Zn.

Because of the potential threat that the heavy metals in CFA pose to the environment, the use of coal fly ash (CFA) is in most countries restricted by environmental regulations. In the Dutch situation this means that CFA may only be used if the amount of heavy metals that is expected to leach from it, and thus enter the environment, remains below the norms specified in the Dutch Decree on Building Materials (DDBM). This decree is applicable for all construction materials containing at least a total of 10 wt. % of Al+Si+Ca that are or can come in contact with rainwater, groundwater, or surface water. The purpose of the DDBM is to protect soil and surface waters, and to stimulate the re-use of secondary building materials. To this effect, the DDBM uses the concept of 'marginal soil loading', which means that the input of polluting components leached from construction materials may, after 100 years, not exceed 1% of the target concentrations ('streefwaarde', i.e. the concentration of elements in soil thought natural) over 1 m of soil. In the DDBM this concept is translated into immission norms, that present for a number of components the maximum input to soil in mg/m^2 per 100 years. Distinguished are norms for category 1 and for category 2 materials. Category 1 materials can be used in practice without any further restrictions, category 2 materials may only be used under specific isolation criteria.

Standard tests have been developed to assess whether materials comply with the DDBM. Construction materials have to be submitted to these tests before they may be applied in order to assess the amounts of hazardous components that may be emitted and compare these to the norms posed. The tests in use are a column leaching test for fine grained material (e.g. loose, not-bounded CFA) and a diffusion test for coarse materials (e.g. blocks of concrete). Procedures for both tests have been established by the Netherlands Standardization Institute (1995). In this study the column leaching test (NEN 7343) was used to test the leaching from

CFA and zeolitized CFA. However, the leaching data obtained by submitting a material to the column leaching test can not be compared directly with the immission norms specified by the DDBM, as the first are obtained in mg/kg and the latter are specified in mg/(m²·100y). For not-bounded loose materials like fly ash, a number of correction factors have to be taken into account as well as the thickness of the layer at which the material will be applied in practice. The immission I specified by the DDBM is related to the leaching observed in the column leaching (NEN 7343) by the formula:

$$I = 1550 * (E_{L/S=10} - a) * h * f_{ext} \quad (1)$$

In which

$$f_{ext} = \frac{1 - e^{\left(-\frac{\kappa * t * N_i}{1550 * h}\right)}}{1 - e^{(-\kappa * 10)}} \quad (2)$$

and:

$E_{L/S=10}$ is the cumulative leaching (mg/kg) at a liquid/solid ratio of 10, determined by standard column leaching test, in accordance to NEN 7340 and NEN 7343

a is a correction factor related to the difference in leaching occurring under laboratory and field conditions

h is the thickness at which the building material will be applied

f_{ext} is an extrapolation factor that translates the leaching observed at L/S 10 in the column leaching tests to leaching occurring over 100 years under field conditions

κ is a constant determined by the rate of leaching of a component

N_i is the effective infiltration (mm/year)

t is the time (years)

e is the ground number of natural logarithms

Both the values of a and κ can be read from tables published by the Ministry of Housing, Spatial Planning and Environment (VROM, 1998). The time factor t is taken as 1 year for chloride and sulphate and as 100 years for other components.

At present, virtually all CFA produced in The Netherlands is used for the manufacturing of building materials. This situation may, however, change as combustion practice changes, e.g. by the co-combustion of organic waste. Newly developed applications for CFA to counter a possible surplus of CFA, also will have to comply with the regulations and the norms specified by them. One possible new application for CFA is its use for the synthesis of zeolite. By treatment with hot alkaline solutions, CFA can be converted into zeolite, which results in a product containing up to 40 wt. % zeolite. Results on the influence of different reaction parameters for this conversion process were discussed earlier in Chapter 2 of this thesis. The properties of the zeolitized CFA are discussed by Steenbruggen (1999). In the following it will be discussed how the zeolitized CFA complies with the environmental regulations. For this purpose, the behavior of heavy metals during the synthesis of zeolite and their leachability afterwards, as tested by the column leaching test, will be examined and discussed.

2 MATERIALS AND METHODS

Starting materials

Experiments were carried out with an alkaline fly ash obtained in 1990 from the Dutch "Amercentrale" where it was formed as a result of the combustion of powdered coal at a temperature of 1500°C. Alkaline solutions used in this study for the conversion of CFA to zeolite were prepared from reagent grade chemicals and demineralized water.

Experimental set-up for zeolitization experiments

Fly ash was converted into zeolite by mixing it with a 2 M NaOH solution for 30 h at a temperature of 93 or 150°C while under autogenous pressure. For this purpose two different experimental set-ups were used:

1. Experiments at 150°C were carried out in Teflon reaction vessels with a volume of 40 ml that were placed inside a steel bomb that in its turn was placed in a stove. Reaction vessels could be rotated in the longitudinal direction with a speed of 3.75 rpm. The experiments were carried out with either 9 g of CFA and 31.5 ml 2 M NaOH solution (L/S 3.5) or 5 g of CFA and 35 ml 2 M NaOH solution (L/S 7).
2. Experiments at 93°C were carried out in a Teflon beaker with a volume of 2 liter that was placed in a heated water bath. The vessel was equipped with an IKA propeller stirrer for mixing (240 rpm). This set-up, in contrast to the previous one, allows sampling of the reaction mixture while the reaction is in progress. The experiments were carried out with 500 g of CFA to which 1250 ml 2 M NaOH was added (L/S 2.5).

Prior to zeolitization, CFA was washed with water, a 1 M HNO₃ solution or organic extractants to test whether this would lead to a reduction of the leachability of oxy-anions from the CFA or zeolitized CFA. Table 4.1 gives an overview of these pretreatments carried out. Washing with the organic extractants was carried out at the Technical University of Delft as part of another research project (KEMA 1998, 1999). Pretreated CFA was also zeolitized at 93 or 150°C as specified in table 4.1.

At the end of the zeolitization experiments the reaction mixtures were filtrated and the residues washed with water at a L/S ratio of 10 and dried at 75°C.

Table 4.1 Conditions of pretreatment and subsequent zeolitization with a 2 M NaOH solution

Pretreatment			Zeolitization			Column leaching test (yes/no)
Extractant	L/S	t (h)	T(°C)	L/S	t	
demineralized water	2	0.5	-	-	-	no
demineralized water	20	0.5	-	-	-	no
0.05 M H ₄ EDTA	5	4	93	2.5	30	yes
0.06 M citric acid/0.1M NH ₄ -citrate ¹⁾	5	4	93	2.5	30	yes
0.06 M oxalic acid//0.1M NH ₄ -	5	4	93	2.5	30	yes
0.25 M NH ₄ -carbonate ¹⁾	5	4	93	2.5	30	yes
1 M HNO ₃ ²⁾	8	16	150	3.2	24	no

¹⁾ followed by washing twice with demineralized water at L/S 2

²⁾ followed by washing once with demineralized water at L/S 2

Experimental set-up for column leaching experiments

The leaching of elements from CFA and a number of zeolitized CFA's was tested in accordance to the Dutch Standard NEN 7343, that is titled: 'Leaching characteristics of solid earthy and stony building and waste materials. Leaching tests. Determination of the leaching of inorganic components from granular materials with the column test'. This standard is drafted by the Netherlands Standardization Institute (1995) and is used to decide if any possible leaching of elements from granular materials poses a threat to the quality of the environment. In table 4.1 it is indicated which zeolitized CFA's were exposed to the column leaching test. Compared to the NEN 7343 standard column test, the leaching tests carried out were expanded with one addition: instead of collecting only the cumulative percolate fractions L/S 0.1, 0.2, 0.5, 1, 2, 5 and 10 as described by the standard test, the cumulative fractions, L/S 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 were collected. For the calculation of the total cumulative leaching this makes no difference, but the higher number of fractions, allows to gain more insight in the leaching behavior of the elements during the duration of the column test.

Figure 4.1 presents the set-up used for the column leaching test. In a column (diameter 5 cm, length 50 cm, Pharmacia) the material to be tested (300-600 g) is percolated up-flow with demineralized water that is acidified with nitric acid to a pH of 4 to simulate rainwater. The column is percolated with a constant flow rate (circa 0.5 L/S per day in l/kg). The percolate is filtrated (0.45 µm) when it leaves the column and collected in fractions. The L/S ratio reflects the amount water (L liter), which during the duration (t) of the column experiment passes the S kg material in the column. In practice, the L/S ratio is related to the leaching period. At specific cumulative L/S-ratios the pH is measured in the collected fraction and a representative sample is taken for analysis.

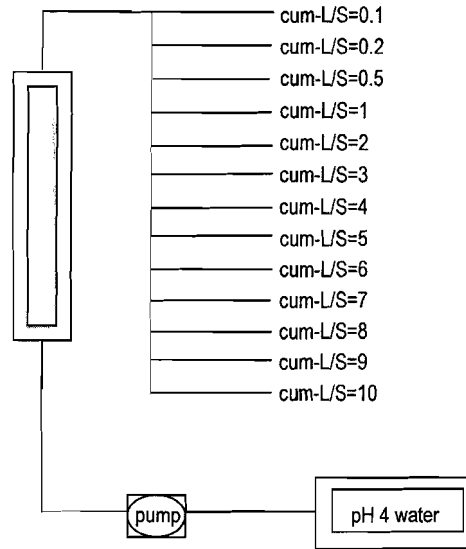


Figure 4.1 Schematic representation of the setup of a column leaching test

The cumulative emissions obtained from the column leaching test are calculated with the following formula:

$$\text{cumulative emission column test} = \sum_n [M_i] * L_i / S \quad (3)$$

in which:

i = index of the fractions

n = number of fractions

$[M_i]$ = the concentration of element M in fraction i

L/S = the liquid/solid ratio (l/kg) at fraction i

The relation between the L/S ratio and the actual time-scale can be calculated by the formula:

$$\text{number of years} = \frac{L/S * h * Da}{P} \quad (4)$$

in which:

P = infiltration (m/year)

h = thickness of the layer (m)

Da = dry volume weight of the material to be investigated (kg/l)

Analytical techniques

X-ray diffraction (XRD) was used for the identification of the mineral phases in the original and zeolitized fly ash (CuK α radiation at 40 kV using a Philips PW1730 diffractometer and PW1710 control system). Quantitative mineralogical analyses for zeolite Na-P1 were carried out by standard addition methods (see chapter 5). A CamScan scanning electron microscope (SEM), equipped with energy-dispersive X-ray analysis (EDS) was used for the morphological and chemical characterization of the zeolitized CFA.

The chemical composition of liquids was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES; elements Al, B, Ba, Ca, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr, Ti, V, Zn), hydride-atomic absorption spectrometry (hydride-AAS; elements: As, Se) and Graphite Furnace-AAS with Zeeman background correction (ZGF-AAS; element: Mo). Before the analysis, liquids were acidified with concentrated HNO₃. Prior to acidification and analysis, it was found necessary to dilute the reaction liquids obtained from the zeolitization process and the leaching experiments by a factor 10 to 100 in order to prevent interference of the high alkali concentrations with the analyses and to avoid the formation of silicate precipitates upon acidification. The pH of solutions was measured with an Orion solid state sure flow pHutrode electrode (model 61-65) connected to an Orion ISE/pH meter (model 940). This pH electrode contains no glass but a silicon sensor that leads to a more stable signal when measuring highly alkaline solutions. Relative accuracy of pH proved to be ± 0.03 up to pH 14.3 when no new calibration is carried out. Comparing results from different turns of calibration, however, showed a relative precision of only ± 0.2 .

Solids were analyzed following standard procedures that included dissolution with HF/HClO₄/HNO₃ mixed acid heating in closed Teflon vessels or by the use of a lithium metaborate melt and subsequent analysis by ICP-AES, hydride-AAS and ZGF-AAS.

3 RESULTS

Zeolitization of non pretreated CFA

Table 4.2 presents a chemical analysis of the CFA before and after zeolitization, including concentrations of minor and trace elements. It shows that the CFA contains significant amounts of heavy metals, i.e. 0.5 to 50 mg/kg for As, Cd, Mo and Se, 50 to 160 mg/kg for Cr, Ni and Pb, 160 to 320 mg/kg for Cu, V and Zn and up to 2170 mg/kg for Ba. In the zeolitized CFA these concentrations appear to be largely unchanged, except for the elements that are likely to have been solubilized as anions during the zeolitization process: compared to their concentration in the original CFA, the concentrations of As, Mo, Se and V were all strongly decreased in the zeolitized CFA, while the concentrations of Co, Cu, Ni, and Zn did hardly change. An exception is Cr that, depending on the redox conditions is expected to be solubilized as either CrO₄²⁻ or Cr(OH)₄⁻.

The element concentrations measured in the original and zeolitized CFA fit well with those

observed in the reaction fluid. Figure 4.2 shows the variation of concentration of a number of elements in the reaction fluid as a function of time. In these figures two types of behavior of the elements solubilized can be distinguished. Firstly, the type shown by As, B, Mo, Se and V, i.e. the anion forming elements, is characterized by an increase in concentration as a function of time, the rate of which usually diminishes after 1 to 8 hours. Secondly, the behavior, shown by Cd, Co, Ni, Pb, Sn, Zn and Cr, consists of an increase in concentration in the first 1 to 6 hours followed by a, usually sharp, decrease. Copper, too, shows this pattern but its concentration seems to increase again during the zeolitization reaction at 150°C. Not included in figure 4.2 is Ba, the concentration of which is almost without exception below the detection limit, i.e. smaller than 0.1 mg/l.

In addition it is indicated by figure 4.2 that the concentrations of As, B, Mo, Se and V in the reaction fluids are inversely proportional to the L/S ratio at which the zeolitization is carried out. In the experiments carried out at a L/S ratio of 3.5 the concentration of these elements is about double of those in the reaction fluids of the experiments carried out at a L/S ratio of 7. Apparently the concentrations of these elements represent a maximum availability for the point of time that the concentration is measured. Concentrations of the elements Cd, Co, Cu, Pb and Zn do not show this inverse proportionality with the L/S ratio and are apparently directly controlled by the solubility of dissolving or newly formed phases.

CFA and zeolitized CFA were subjected to standard column leaching procedures to examine the influence of zeolitization on the leaching of elements from CFA and to see whether the zeolitized CFA complies with environmental regulations.

Table 4.2 Chemical composition of CFA before and after zeolitization¹⁾ at 93 and 150°C and before and after correction for sodium and loss of ignition

	Composition as measured			Composition after correction for sodium and loss of ignition		
	CFA	zeolitized CFA		CFA	zeolitized CFA	
Zeolitization T (°C)		150	93		150	93
Correction factor	-	-	-	1.03	1.28	1.20
Oxides (wt. %)						
Al ₂ O ₃	24.9	22.4	21.8	25.7	28.7	26.3
CaO	6.9	6.3	6.1	7.1	8.1	7.3
Fe ₂ O ₃	8.8	9.2	7.7	9.1	11.8	9.3
K ₂ O	2.1	1.2	1.3	2.2	1.5	1.6
MgO	3.8	3.5	3.5	3.9	4.5	4.2
MnO	0.1	0.1	0.1	0.1	0.2	0.1
Na ₂ O	1.2	5.9	6.5	-	-	-
P ₂ O ₅	0.7	0.8	0.4	0.7	1.0	0.4
SO ₃	1.0	0.0	0.1	1.0	0.0	0.1
SiO ₂	46.9	38.3	39.1	48.5	49.0	46.9
TiO ₂	0.9	1.2	0.9	1.0	1.5	1.1
LOI (wt. %)	2.1	16.0	10.3	-	-	-
Total (wt. %)	99.4	105.0	97.8	99.4	106.4	97.4
Minor elements (mg/kg)						
As	28	8	n.a.	29	10	n.a.
B	310	n.a.	n.a.	320	n.a.	n.a.
Ba	2170	2090	1950	2240	2680	2340
Cd	1	n.a.	n.a.	1	n.a.	n.a.
Ce	195	155	140	205	195	165
Co	66	53	59	68	67	71
Cr	155	145	145	160	185	175
Cu	215	180	185	220	230	225
Li	165	155	155	170	200	190
Mo	9	3	n.a.	10	4	n.a.
Ni	140	150	135	145	190	160
Pb	125	n.a.	n.a.	130	n.a.	n.a.
Se	16	<6	<6	17	<8	<8
Sn	6	n.a.	n.a.	6	n.a.	n.a.
Sr	1390	1290	1070	1435	1650	1280
V	320	90	95	330	115	115
Zn	215	185	180	225	240	215

1) Zeolitization took place by treatment with a 2 M NaOH solution at 150°C, a L/S ratio of 3.5 and 3.75 rpm or 93°C, a L/S ratio of 2.5 and 240 rpm. n.a. = not analyzed

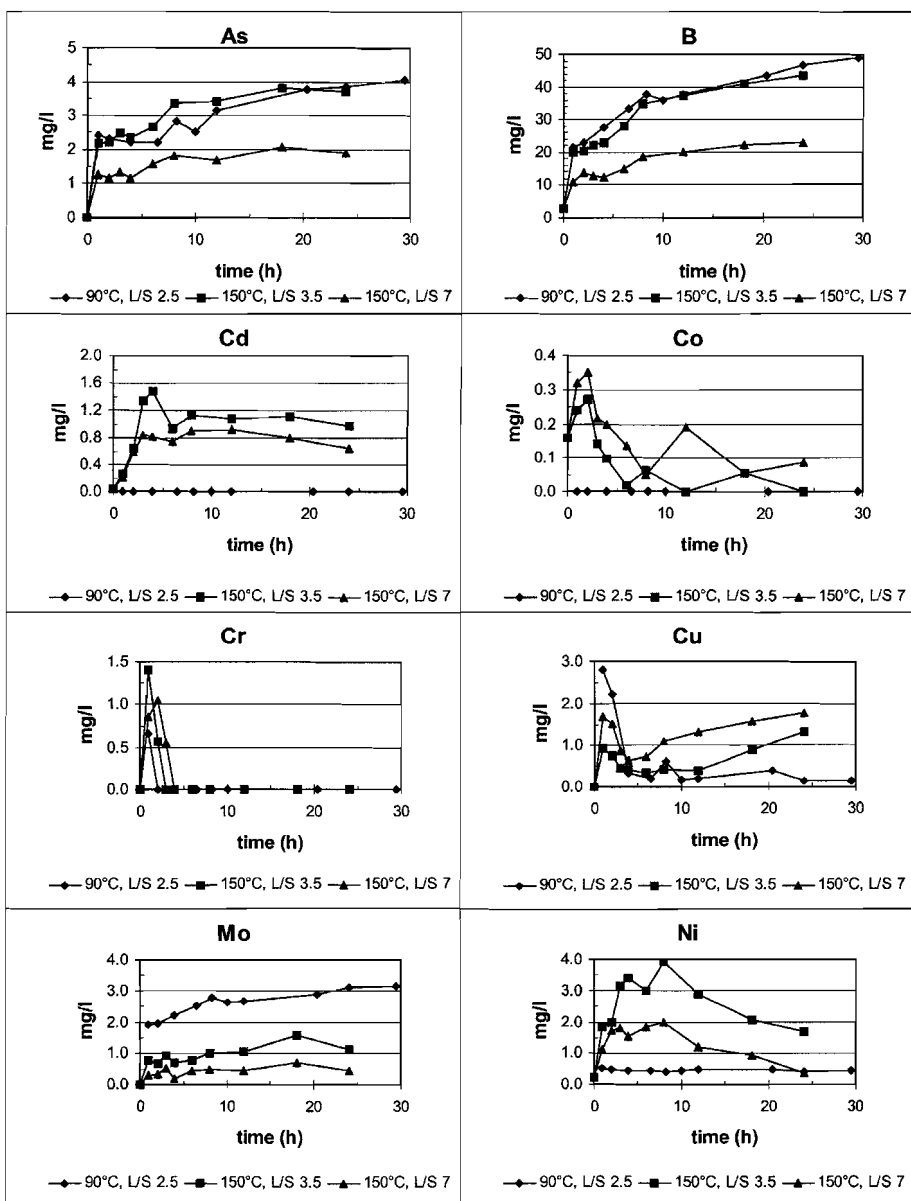


Figure 4.2 Concentration of elements as a function of reaction time in reaction fluids obtained from the zeolitization of CFA with a 2 M NaOH solution at 93 and 150°C and different L/S ratios (values below the detection limit are plotted as 0)
 --continued

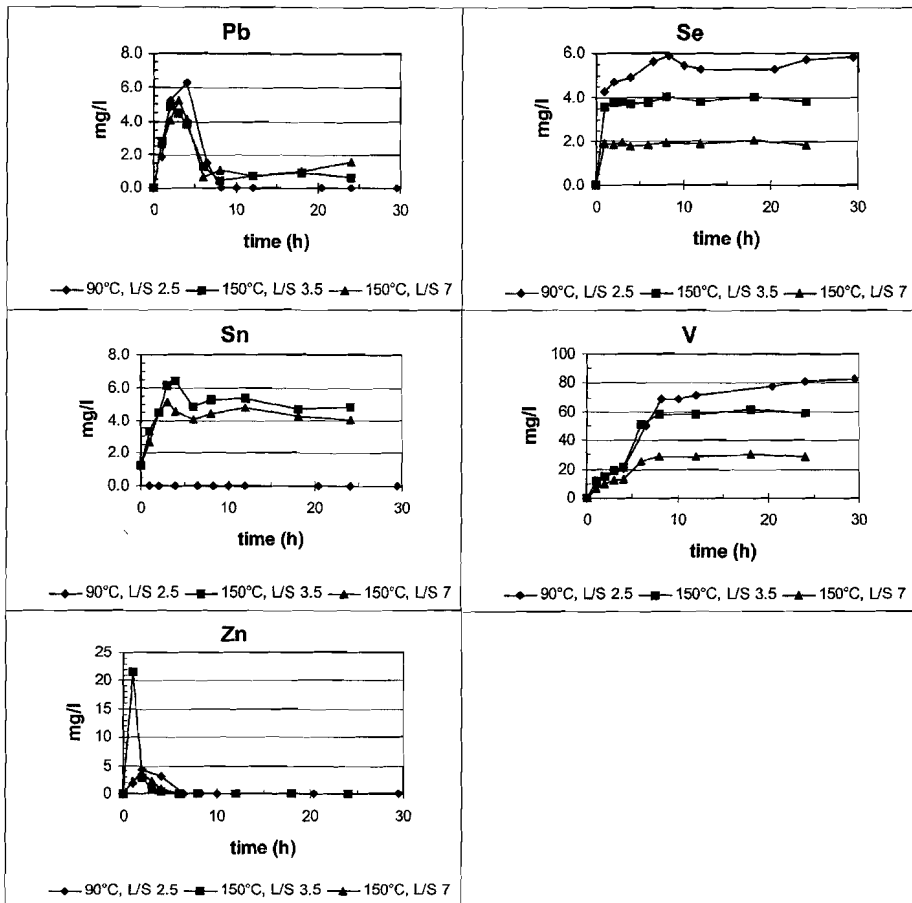


Figure 4.2 Continuation

Results column leaching experiments CFA and zeolitized CFA

Table 4.3 lists the chemical composition of CFA and zeolitized CFA, the cumulative leaching that was observed for these materials in the column leaching test and the amounts of leaching allowed by the Dutch Decree on Building Materials as calculated by the formulas (1) and (2) in the introduction. Figure 4.3 presents for a number of elements plots of their concentration in the leachate received from the column as a function of L/S ratio.

Table 4.3 Column leaching experiments: composition of CFA, zeolitized CFA, cumulative leaching from CFA and ZFA and the leaching allowed by the Dutch Decree on Building Materials (category 1 and 2) for a layer of 1 meter thickness

Element	Composition before test (mg/kg)		Cumulative leaching at L/S 10 (mg/kg)		Limit DDBM at L/S 10 at 1 m layer thickness (mg/kg)	
	CFA	ZFA	CFA	ZFA	Cat 1	Cat 2
Al	132000	116000	27	<1.5	--	--
As	28	n.a.	<0.02	0.65	0.87	7.0
B	310	n.a.	4.0	16	--	--
Ba	2170	1950		<0.2	4.2	57
Ca	49000	43400	5950	0.46	--	--
Cd	1	1	<0.02	<0.02	0.029	0.065
Co	66	59	0.60	<0.3	0.35	2.4
Cr	155	145	4.1	1.3	0.92	12
Cu	215	185	<0.5	<0.5	0.58	3.4
Fe	61700	54100	0.33	0.67	--	--
K	17400	11000	195	1060	--	--
Mg	22900	20900	2.1	<0.5	--	--
Mn	1030	920	<0.3	<0.3	--	--
Mo	9	3		0.25	0.24	0.89
Na	9100	48000	145	16500	--	--
Ni	140	135	0.35	<0.3	0.95	3.6
P	2890	1600	0.05	71	--	--
Pb	125	n.a.	<0.25	0.28	1.6	8.5
S	4120	370	1230	160	1122	22021
Se	16	<6	<0.02		0.039	0.10
Si	219000	182000	9.3	7490	--	--
Sr	1390	1070	105	<0.5	--	--
Ti	5580	5570	0.1	<0.1	--	--
V	320	95	0.02	12	1.4	32
Zn	215	180	6.6	<1.0	3.3	14

 = Leaching exceeds the category 1 limit of the DDBM;
  = Leaching exceeds the category 2 limit of the DDBM
 -- = No limit specified; n.a. = not analyzed

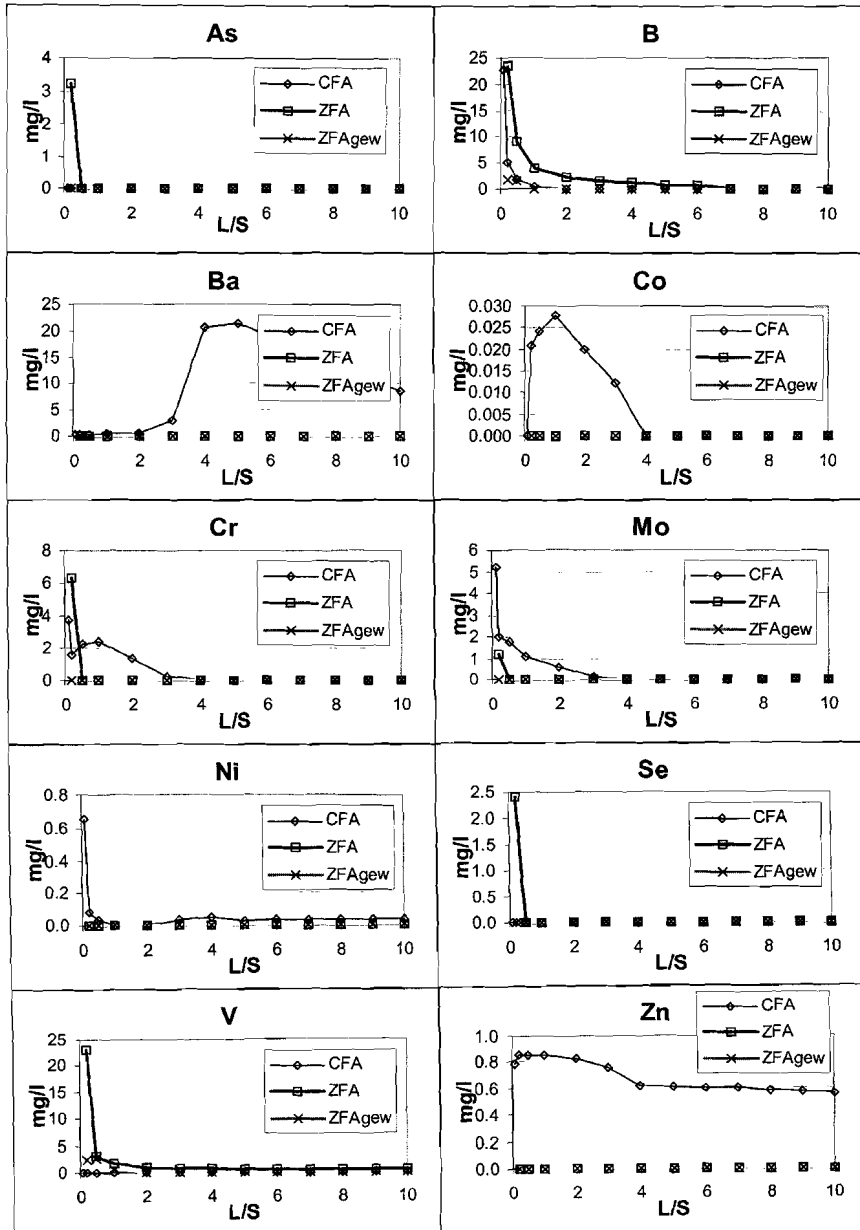


Figure 4.3 Concentration of elements in the leachate as a function of the amount of leachate passed through a column filled with fly ash (CFA), zeolitized fly ash (ZFA) or zeolitized pretreated fly ash (ZFAgew). Values below the detection limit are plotted as 0

From table 4.3 and figure 4.3 it is clear that compared to zeolitized CFA, the leaching of most elements from CFA is much higher. However, exceptions to this do exist. In particular the amounts leached of Na, K, Si, P, B, As, Se and V are higher for the zeolitized CFA. Of these only the latter three are of importance for the DDBM and only for Se (leaching exceeds category 1) and V (leaching exceeds category 2) does the zeolitized CFA not comply with the specified environmental regulations. For CFA this is the case for the elements Cu, Cr and Zn (all exceeding category 1) and the elements Ba and Mo (exceeding cat. 2). Thus, on the whole, the leaching of potentially hazardous elements from the CFA after zeolitization has decreased considerably.

Zeolitization of pretreated CFA

To examine if the leaching of elements from the zeolitized CFA could be further decreased, to a level that it doesn't exceed the regulations, CFA was washed prior to zeolitization to remove part of its heavy metal content. Suitable extractants should on the one hand remove as much as possible of the elements considered potentially hazardous but should on the other hand not affect the quantities of Si and Al from which the zeolite is synthesized. Several solutions of different aggressiveness and potential for the formation of complexes were tested. Table 4.4 shows amounts of a number of elements removed from CFA by the different pretreatments.

Table 4.4 Percentages extracted of a number of elements from coal fly ash by different extractants¹⁾

Element	CFA (mg/kg)	Extracted (%)					
		water	H ₄ -EDTA	oxalic acid	citric acid	NH ₄ -carbonate	HNO ₃
Al	131700	0.0	0.2	0.3	0.2	0.0	11
Si	219400	0.0	0.6	0.1	0.1	0.0	7
Ca	49000	16	39	2.4	15	0.4	82
Mg	22900	0.0	15	4.8	26	1.8	68
S	4120	40	70	80	79	111	100
As	28	<10	65	22	< 6.9	< 5.1	<25
B	310	7.0	86	49	91	45	85
Cr	155	0.8	12	11	19	16	16
Mo	9.4	13	93	76	109	103	100
Se	16	29	62-78	73-88	47-57	36-47	<50
V	320	1.0	21	9.1	19	3.9	54

¹⁾ Data on extractions with EDTA, oxalic and citric acid buffers and NH₄-carbonate provided by H. Nugteren (Technical University of Delft). These extractions were carried out in the scope of the KEMA project on washing of fly ashes (KEMA 1998, 1999).

With all extractants except HNO_3 , the removal from CFA of aluminum and silicon, the building stones for the zeolite to be synthesized, is minimal. For HNO_3 the extraction of these elements is substantial, i.e. ca 11% for Al and 7% for Si. The elements Ca, Mg and S, which do not contribute to the zeolite to be synthesized but form other secondary phases, are extracted well by the HNO_3 solution and somewhat less but still reasonably by the EDTA solution. The heavy metals listed in table 4.4 are extracted significantly by all of the extractants tested, except water. Especially EDTA performs well because it also has affinity for As and removes 65% of this element from CFA.

From the results above it follows that pretreatment of CFA with HNO_3 and organic extractants is beneficial for the removal from CFA of elements that form (hydr)oxy-anions in solution. To this group of elements also belong As, Se and V, that the column leaching test showed to be critical for the quality of zeolitized CFA. In addition, HNO_3 , and to a lesser extent EDTA as well, remove significant parts of Ca and Mg that otherwise would be present as hydroxides in the zeolitized product and dilute the zeolite synthesized. Compared to the zeolitization of non pretreated CFA, that of CFA washed with organic extractants results in reaction fluids in which the concentrations of elements that solubilize as anions are 20 to 80% lower. Table 4.5 presents chemical compositions of reaction fluids. Semi-quantitative analysis by X-ray diffraction shows in these cases no clear influence of the pretreatment on the final content of zeolite Na-P1.

Treatment of CFA with a 1 M HNO_3 solution differs from that with the organic extractants discussed in that it is far more aggressive and dissolves also substantial parts of the Si and Al present in the CFA. The data in table 4.4 show this clearly. The effect of this is also noticeable in the analysis of the reaction fluids obtained from the zeolitization of the pretreated CFA. In this case (see table 4.5) concentrations in solution are 40 to 97% lower for most elements that form (hydr)oxy-anionic species upon dissolution. In addition, although significant amounts of Si and Al have been removed by the pretreatment with HNO_3 , the final zeolite content was increased to ca. 45 wt. % as compared to 40 wt. % in non-pretreated CFA. Because, however, 20 wt % of CFA had been removed by the acid treatment the overall degree of conversion of CFA into zeolite is lower than that after pretreatment with organic extractants, i.e. 32 wt. % instead of 37 wt. %. A remarkable side-effect of treatment with HNO_3 are the high Si concentrations, up to 17000 mg/l measured in the reaction fluids obtained from the zeolitization of HNO_3 pretreated CFA. These suggest that a relative shortage of Al have been created by the acid extraction.

Table 4.5 Concentrations of elements (mg/l) in reaction fluids obtained from the zeolitization of pretreated and non-pretreated coal fly ash¹⁾

pretreat- ment	zeolitization at 93°C					zeolitization at 150°C	
	None	EDTA	oxalic acid/ oxalate	citric acid/ citrate	carbonate	none	HNO ₃
pH	13.8	14.0	14.0	13.9	13.8	13.7	13.6
Al	17	17	16	18	13	< 11	22.3
As	5.0	1.5	1.7	1.7	3.9	n.a.	n.a.
B	63	26	39	22	40	48	9.6
Ba	< 0.1	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.3
Ca	< 0.3	32	< 0.6	3.8	< 0.6	2.4	4.8
Cd	< 0.1	< 0.6	< 0.6	< 0.6	< 0.6	1.8	6.8
Co	< 0.2	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
Cr	< 0.3	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	2.8
Cu	< 0.1	0.5	0.4	0.7	0.4	1.5	0.8
Fe	0.4	4.4	1.1	2.2	0.7	16	31
K	1960	2340	2820	2680	2560	1630	1580
Li	< 0.1	< 0.3	< 0.3	< 0.3	< 0.3	0.03	0.11
Mg	< 0.2	< 0.3	21	< 0.3	< 0.3	1.6	2.4
Mn	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.1	0.2
Mo	3.7	1.5	1.6	1.3	1.2	2.1	1.1
Na	Sat	24320	28310	26450	25030	26615	29560
Ni	0.4	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
P	610	430	270	400	455	380	170
Pb	< 1	1.1	1.2	1.2	1.0	< 1	5
S	1890	655	375	455	240	1135	33
Se	6.9	3.0	2.3	1.5	3.9	n.a.	n.a.
Si	7140	13470	9490	9980	7170	5370	17570
Sn	< 0.5	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
Sr	n.a.	1.8	< 0.3	0.9	< 0.3	0.04	0.21
Ti	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	1.8	8.3
V	97	68	55	63	77	62	36
Zn	< 0.2	< 0.3	< 0.3	< 0.3	< 0.3	9.3	13.3

¹⁾ Conditions of synthesis: T=150°C: reaction fluid 2 M NaOH, t= 24 h, L/S = 3.5, 3.75 rpm; T=93°C: reaction fluid 2 M NaOH, t=30 h, L/S 2.5, 250 rpm; See table 4.1 for a description of the conditions of pretreatment. All analyses by ICP-AES.

Results column leaching experiments pretreated zeolitized CFA

Table 4.6 lists the cumulative leaching that was observed for the pretreated zeolitized CFA's and the amounts of leaching allowed by the Dutch Decree on Building Materials as calculated by formulas (1) and (2) in the introduction. In figure 4.3 the concentration in the leachate of a number of elements is plotted as a function of L/S ratio for the column experiments carried out with zeolitized CFA that was pretreated with EDTA.

Table 4.6 Column leaching experiments: leaching from zeolitized pretreated CFA and the limits allowed posed by the Dutch Decree on Building Materials (DDBM)

Element	Cumulative leaching cumulative at L/S 10 (mg/kg)				limits DDMD at L/S 10 at layer thickness 1 m (mg/kg)	
	EDTA	citrate	oxalate	carbonate	cat. 1	cat. 2
Al	<1.5	1.7	<1.5	<1.5	--	--
As	<0.02	<0.02	<0.02	<0.02	0.87	7.0
B	0.83	0.21	0.62	0.36	--	--
Ba	<0.2	<0.2	<0.2	<0.2	4.2	57
Ca	2.4	16	3.2	2.2	--	--
Cd	<0.02	<0.02	<0.02	<0.02	0.029	0.065
Co	<0.3	<0.3	<0.3	<0.3	0.35	2.4
Cr	<0.5	<0.5	<0.5	<0.5	0.92	12
Cu	<0.5	<0.5	<0.5	<0.5	0.58	3.4
Fe	0.34	1.5	0.48	0.26	--	--
K	630	325	240	350	--	--
Mg	<0.5	<0.5	2.2	<0.5	--	--
Mn	<0.3	<0.3	<0.3	<0.3	--	--
Mo	<0.5	<0.5	<0.5	<0.5	0.24	0.89
Na	9910	6520	5140	7100	--	--
Ni	<0.3	<0.3	<0.3	<0.3	0.95	3.6
P	5.9	1.5	1.9	2.3	--	--
Pb	<0.25	<0.25	<0.25	<0.25	1.6	8.5
S	12	<0.25	<0.25	14.3	1122	22021
Se	0.02	0.03	<0.02	0.03	0.04	0.10
Si	5470	4440	3070	4660	--	--
Sr	<0.5	<0.5	<0.5	<0.5	--	--
Ti	<0.1	0.39	<0.1	<0.1	--	--
V	1.5	0.90	1.5	3.6	1.4	32
Zn	<1.0	<1.0	<1.0	<1.0	3.3	15



Leaching exceeds the category 1 limit of the DDBM



Leaching exceeds the category 2 limit of the DDBM

-- No limit specified

From table 4.6 it can be seen that the zeolitized CFA that is pretreated with the EDTA, citrate or oxalate solution, entirely meets the regulations from the Dutch Decree on Building Materials when applied at 1 m thickness. Pretreatment of CFA with carbonate still results in too high concentrations after zeolitization of Se and V in the leachate. Altogether it can be concluded from these results that the quality of the zeolitized CFA improves when it is synthesized from CFA pretreated with the organic extractants tested in this study, compared to when it is synthesized from untreated CFA.

4 DISCUSSION

Because of the partitioning of heavy metals in CFA, described in the introduction, submitting CFA to mild extractants like EDTA or oxalic or citric acid buffers, that form chelates with heavy metals, can be useful. These extractants affect the CFA particles on the surface only and remove those surface enriched elements that are prone to form complexes with the extractant chosen. The heavy metals solubilized during the subsequent zeolitization of CFA originate then mainly from the glass matrix or from any of the other phases present that are dissolved in this process. These elements may then dissolve, form precipitates, e.g. with hydroxide or with each other, or become adsorbed on the zeolite synthesized. However, decisive for whether zeolitized CFA complies with the norms stated by the Dutch Decree on Building Materials is not the amount of heavy metals it contains but the amount of specific elements that will be released to the environment, i.e. their leachability. From the column leaching tests it follows that with respect to the environmental regulations, the elements Ba, Co, Cr, Mo and Zn are decisive, while after zeolitization it are the elements Se and V. From the plots in figure 4.3 it can be observed that the elements Ba, Co, Ni, and Zn are only released by CFA and not by the zeolitized product. This decrease in leachability of Ba, Co, Ni, and Zn, elements that are present in solution as cations, is attributed to their adsorption by the zeolite synthesized. Though those have not been detected, precipitates of these elements, e.g. hydroxides may be involved as well, but in that case they are likely to be adsorbed as the hydroxides dissolved during the column test.

Even though they are supposed to be predominantly present at the surface of CFA particles, the elements As and Se are not released by the CFA during the column leaching test, but are by the zeolitized CFA. The same holds for V, the predominance of which at the surface of CFA particles is less clear as stated in the introduction. The concentration of these elements in successive fractions of leachate obtained from the column with zeolitized CFA, decrease steeply and resembles the pattern observed in this case for Cr and Mo. Both Cr and Mo are, however, leaching in higher amounts from CFA than from zeolitized CFA. The leachate from the zeolitized CFA contains detectable amounts of Cr and Mo only in the L/S fractions up to 3.

Apparently the leaching of As, Se and V, depends on the changes CFA goes through during the zeolitization process, while the leaching of Mo does not. All four elements, i.e. As, Se, V and Mo, are thought to be present as soluble oxides in the CFA (EPRI, 1987) and are expected to form oxy-anions (arsenate, arsenite, selenate, selenite, vanadate, molybdate) upon dissolution under the alkaline conditions that prevail during the zeolitization of CFA and during the column leaching tests with CFA and zeolitized CFA. Given the high pH, above

11.6, that prevails in the column leaching tests, it is unlikely that the concentrations of these elements in the leachate are controlled by adsorption/desorption reactions, though according to Van der Hoek (1995) portlandite, even at a pH of 12.4, may still adsorb a significant amount of arsenite. Nevertheless it can be assumed that under these conditions (co)precipitation/dissolution reactions are more important in controlling the mobility of these elements. According to EPRI (1987) and Eary et al. (1990) especially precipitates with Ca and Fe but also with heavy metals like e.g. Zn and Pb are likely candidates for being the solubility controlling solids for As, Se, Mo and V. The differences in leaching of these four elements from CFA and zeolitized CFA originate then from the following:

1. The high amount of reaction fluid that stays behind in the filtrated zeolitized CFA (ca. 50 % of the weight before drying). This implies that significant amounts of already dissolved elements remain in the zeolitized CFA. Upon washing of the zeolitized CFA with water (at a L/S ratio of 10), the residual reaction fluid is gradually but not completely replaced with water. The dissolved elements thus inherited will precipitate on the surface of particles when the zeolitized CFA is dried and will be solubilized again and leached during the column leaching test. Leaching patterns of As, Se and V resemble in fact the leaching patterns of these elements observed when the zeolitized CFA was washed with water (chapter 2 of this thesis). This also holds for Mo, but this element was already almost completely removed during the zeolitization process.
2. Removal of metallic cations by adsorption on zeolite and precipitation with (residual) hydroxide. This will restrict the precipitation of oxy-anions as they will have to compete for the available metallic cations.
3. Extensive dissolution of phases in CFA (especially glass) during its zeolitization. This will liberate the heavy metals they contain. The oxy-anions that are part of this will further contribute to the processes under 1. This may especially be of importance for V whose predominance at the surface of CFA particles is less clear.

Other elements of importance for the DDBM are Cr and Sb. The leaching behavior of Cr depends heavily on the redox conditions, for which no data are available. Chromium is mainly present in CFA as Cr_2O_3 on the surface of particles and in association with iron oxides (EPRI, 1987). In the presence of Fe^{II} containing minerals, like magnetite in CFA, Cr in solution is expected to be dominantly present as Cr^{III} and not Cr^{VI} (EPRI, 1987; Eary et al., 1990). The dominant species in solution is then $\text{Cr}(\text{OH})_4^-$ and the solubility controlling solid $\text{Cr}(\text{OH})_3$, which explains the low solubility of Cr during and after zeolitization when hydroxide concentrations in solution are very high.

No data are available for Sb. However, it is expected that the behavior of this element is similar to that of Cr. The leaching of Sb too, depends heavily on the prevailing redox conditions (EPRI, 1987). Disregarding sulfides, the dominant aqueous species of Sb at a pH above 12 are $\text{Sb}(\text{OH})_4^-$ and $\text{Sb}(\text{OH})_6^-$ and their solubility is probably controlled by Sb_2O_3 and/or $\text{Sb}(\text{OH})_3$ (EPRI, 1987).

The leaching from zeolitized CFA's washed with EDTA, citrate and oxalate remained well below the norms for any element. In the leachate from these zeolitized pretreated CFA's, the concentrations of As and Se remained below the detection limit, while V was only detected in the first fractions (23 mg/l in L/S fraction 0.2, 3 mg/l in fraction 0.5). Subjecting CFA to a

treatment with organic extractants, prior to zeolitization, thus removes large parts of the As, Se and V present and appears to solve the exceeding of the norms by the zeolitized CFA. Pretreatment of CFA with extractants may indeed be beneficial for improving the quality of the zeolitized CFA with regard to the threat it could pose to the environment.

Unlike the treatment with the organic extractants, a treatment with a strong acid like a 1 M HNO_3 solution leads to the solubilization and removal of a major part of the CFA, i.e. circa 20%. Not only the upper surface layer of the CFA particles is affected by this treatment but significant parts of the glass fraction and iron oxides are solubilized as well, including the heavy metals they contain. The removal of significant parts of the Fe, Ca, Mg, P and S present leads to a conversion product in which the zeolite is less diluted by other secondary phases. If the extracted quantities of these elements were assigned to hydroxides, sulfates and phosphates they would make up 9% of the conversion product. In addition, because the removed elements can not interfere with the crystallization of zeolite, it is likely that their synthesis is easier. However, this pretreatment was not further examined because it was thought to be unrealistic from practical and financial points of view and the zeolite products obtained in this way have not been submitted to the column leaching tests. The high Si concentrations measured in the reaction fluid obtained from the zeolitization process may make it, however, interesting to consider a combination of the pretreatment with strong acid and the synthesis of pure zeolite through a two-step process as presented in chapter 3.

5 CONCLUSIONS

- The elements Ba, Co, Cu, Ni, Pb and Zn, i.e. metallic cations, are immobile during the zeolitization of CFA, their concentration in CFA does hardly change. The elements As, B, Se, Mo and V, i.e. elements that form oxy-anions upon dissolution under the prevailing alkaline conditions, are mobile during the zeolitization of CFA and are for significant parts extracted from the CFA (up to ca. 50%);
- The results of the column leaching tests with CFA and zeolitized CFA show that the general leaching of potentially hazardous elements from the CFA is reduced by zeolitization. The emission of the elements As, Se and V increases, however, by the zeolitization process. The causes of this are the inheritance of these elements from residual reaction fluid in the zeolitized CFA (further promoted by the mobilization of elements by the extensive dissolution of phases in CFA) and the competition for metallic cations that are now adsorbed by the zeolite or precipitate as hydroxides;
- Treatment of the CFA prior to zeolitization, with organic extractants like EDTA and citric or oxalic acid, removes significant parts (30-80%) of those heavy metals that are critical for the Dutch Decree on Building Materials. A similar effect is noticed when CFA is pretreated with a 1 M HNO_3 solution. In this case, however, 20% of the CFA is dissolved and significant parts of the Al (11%) and Si (7%) content of CFA are extracted;
- Pretreatment of CFA with organic extractants has no clear influence on the zeolite content reached that is in both cases ca. 40 wt. %. Treatment of CFA with a 1 M HNO_3 solution results in a higher zeolite content, i.e. 45 wt. %. However, after correction for the amount

of CFA removed, the degree of conversion proves to be lower, i.e. 32 wt. % instead of 37 wt. %;

- Pretreatment of CFA with a 1 M HNO_3 solution results in high concentration of Si in the reaction fluid, indicating that possibly a shortage of Al has been created;
- The results of the column leaching tests with zeolitized pretreated CFA show that the leaching of potentially hazardous elements is further reduced by the treatment of the CFA with organic extractants before zeolitization. When the CFA was washed with an EDTA, citrate or oxalate solution, the emission did no longer exceed the norms of the Dutch Decree on Building Materials when considering a layer of application of 1 m. In case the CFA was treated with a carbonate solution before zeolitization, the norms for Se and V were still exceeded, just as in the case of zeolitized non pretreated CFA. However, the leaching of other elements was much lower;
- The column leaching tests show that the use of extractants is beneficial for improving the quality of the zeolitized CFA with regard to the protection of the environment.

Acknowledgements

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Chapter 5

Quantitative mineralogical analysis of zeolitized coal fly ash using standard addition and Rietveld X-ray diffraction techniques

ABSTRACT

Presented are the results of quantitative X-ray diffraction analysis, carried out on untreated and zeolitized coal fly ash. Applied were the standard addition and the Rietveld method. Both methods rendered fairly consistent weight fraction of mullite (16 wt. % in the coal fly ash) and zeolite Na-P1 (ca. 33 wt. %). Determinations of the weight fraction of quartz in coal fly ash by both methods are less in agreement with each other and varied from 4 wt. % for the standard addition method to ca. 11 wt. % for the Rietveld method. The standard addition values, however, are associated with large standard deviations. This is ascribed to problems with homogeneity and possibly preferential orientation. The glass content of the coal fly ash is calculated by difference to decrease from ca. 70 wt. % to 30 wt. % in the zeolitization process. Comparing the two methods, the Rietveld method is much less laborious and lacks much of the problems of the standard addition method, especially when dealing with fully crystalline samples. However, the outcome of the refinement heavily depends on the appropriateness of the available structural data for the crystalline compounds in the starting model. In the present study the available structural data of zeolite K-G were found to be inadequate for the analysis of zeolite K-G formed from coal fly ash.

Keywords: fly ash, zeolite, X-ray diffraction, standard addition, Rietveld, quantitative analysis

1 INTRODUCTION

Development of new ways for the utilization of waste materials is one of the fields of research of geochemical engineering. Examples of this are the preparation of silica by neutralization of waste acid with olivine (Lieftink 1997; Jonckbloedt, 1998), the treatment by autoclave of jarosite (Hage, 1999) and the use of coal fly ash for the synthesis of zeolites (this thesis; Steenbruggen, 1999). More examples can be found in the overview on geochemical engineering by Vriend and Zijlstra (1998). One of the analytical techniques that is of special interest to this field is quantitative X-ray powder diffraction (QXRD), because it offers the possibility to assess the degree of success of a conversion process involving crystalline phases, i.e. how much of the waste has been converted and/or how much of the product aimed at has indeed been formed.

Conventional methods of QXRD analysis relate the intensities of diffraction peaks of crystalline phases, expressed as either peak heights or peak areas, to absolute quantities by comparing them to the intensities of diffraction peaks of an external or internal standard. The use of external standards involves the preparation of an artificial sample in which all the phases of the material to be analyzed are present in known quantities. This method has been used e.g. by Behr-Andres et al. (1993) for quantifying the amount of mullite, quartz and hematite in boiler and fluidized-bed combustion ash. In the internal standard methods, the intensity of diffraction peaks of phases present in unknown amounts is measured relative to the intensity of diffraction peaks of a standard added in known amounts. Weight fractions of the mineral phases can then be determined by comparing the measured intensities to those measured in external standards or measured in a series of samples with known additions (Standard Addition Method). For example, the American Society for Testing and Materials has issued a test method (ASTM, 1991) by which the content of zeolite Na-Y in a sample is measured by comparing the sum of a number of zeolite peak intensities to the sum obtained for a reference sample of zeolite Na-Y.

Starting in the late sixties (Rietveld, 1967 and 1969), a new technique for the structural and mineralogical analysis of crystalline materials was developed that is now widely known as the Rietveld method. This method comprises the calculation of the diffraction pattern from the instrumental and crystallographic structural parameters and fitting this pattern to the observed diffraction pattern by means of a least-squares refinement. This requires that beforehand is known which mineral phases are present in the samples. The necessary crystallographic structural data can then in most cases be extracted from literature. The Rietveld method is thus not used for the identification of mineral phases, but for the structural analysis of mineral phases and the quantification of their relative contribution to the diffraction pattern.

The Rietveld method has a number of advantages on traditional QXRD techniques like the standard addition method. First of all it is much less laborious as no series of samples have to be analyzed. Secondly peak overlap is no problem as the whole diffraction pattern is fitted by refinement of structural parameters. In addition the Rietveld method has the intrinsic

capacity to correct for changes in the diffraction pattern caused by preferred orientation and deviations in the crystalline structure. This latter aspect is especially of value when one wants to quantify the amount of zeolites in a sample. Zeolites can have a very variable composition. Their Si/Al ratio, the quantity and type of cations adsorbed and the quantity of water they contain, can vary significantly and influence the zeolite structure and diffraction pattern. Where QXRD techniques, like the standard addition method, strongly depend on the quality of the standards used, i.e. their being identical to the mineral phases to be quantified, the Rietveld method includes this kind of deviation in the refinement. Thus, in potential, the Rietveld method is much more useful than the standard addition method. Much, however, depends on the availability of appropriate structural data, i.e. the quality of the starting model.

In this study both the conventional standard addition method and the Rietveld method were used to quantify the mineral phases in original and zeolitized coal fly ash (CFA), and in particular the amount of zeolite synthesized from CFA. The aim of this study was to compare the applicability of both methods. After a short theoretical background on both methods, analytical results for unaltered and zeolitized coal fly ash obtained with both methods are presented and discussed.

2 THEORETICAL BACKGROUND

Analysis by X-ray diffraction makes use of the interaction that occurs between an X-ray beam and the electrons of the irradiated solid material, resulting in a scattering of the incoming X-ray beam in various directions. If the material exposed has an ordered structure, as is the case in crystalline materials, this will lead to a scattering pattern for the diffracted X-rays, that consists of several minima and maxima in intensity. This pattern is characteristic for the irradiated solids and can be interpreted in terms of their crystalline structure. In addition, the intensities measured can be used to quantify the amount of the various crystalline materials present in a sample of already known mineralogy. It is this latter aspect that is applied in this study.

A complete description of the X-ray analytical techniques used falls outside the scope of this thesis. Given here are short theoretical introductions on the internal standard methods in general and the standard addition method in particular, and on the Rietveld Method. Good overviews for the conventional and Rietveld methods have been published by a number of authors. The following is mainly based on Brindley (1980) and Snyder and Bish (1989) who gave an review of conventional methods, and on the International Union of Crystallography (IUCr) Monographs on Crystallography (1993) and Post and Bish (1989) who did the same for the Rietveld method.

Internal standard methods

Conventional quantitative X-ray diffraction techniques are based on the equation:

$$I_p = \frac{K_p(W_p/\rho_p)}{\mu} \quad (1)$$

where

- I_p is the intensity of a specific reflection of phase P
- W_p is the weight fraction of phase P in the sample
- K_p is a constant dependant on the nature of the sample, the reflection considered and the experimental arrangement
- ρ_p is the density of phase P
- μ is the average mass attenuation coefficient of the sample which depends on the chemical composition of the sample and on the type of radiation used.

For two phases P and Q in the same sample is then valid:

$$\frac{I_p}{I_q} = K \frac{W_p}{W_q} \quad (2)$$

where K is a constant composed of K_p , K_q , ρ_p and ρ_q

The weight fraction of a phase P in an unknown sample can then be calculated by measuring the intensities of its reflections relative to those of a standard S added in a known amount, and compare these to the intensity ratios I_p/I_s measured for mixtures of known composition which are composed of the phases in the unknown sample and the standard. The internal standard used should have a low mass attenuation coefficient and preferably only a few reflections of which at least 1 is very strong, so that small amounts of standard suffice and interference with the reflections of the phases in the unknown sample is minimized. A variation of this method is the standard addition method (SAM), used e.g. by Parker (1978) to quantify the amount of analcime in pumice. In the SAM different amounts of the phase to be quantified are added to the unknown mixture. From the changed peak intensities the amount of that phase in the original mixture can then be calculated from:

$$\frac{I_2}{I_1} = \frac{(W_1(1-W_s) + W_s)\mu_1}{W_1\mu_2} \quad (3)$$

where

- I_1 , I_2 are the intensities for a specific reflection before and after addition
- W_s is the weight fraction of standard in the sample analyzed
- W_1 is the weight fraction of the phase to be measured before addition
- μ_1 , μ_2 represent the average mass attenuation coefficients of the mixture before and after addition.

Provided that W_s is sufficiently small, the ratio of μ_2/μ_1 is approximately 1 and may be neglected in the calculation of W_1 . By analyzing samples with different additions of standard, the new intensities can be plotted as a function of the amount of standard in the sample and a linear regression line can be calculated. The concentration of phase P in the original mixture, W_1 is then given by:

$$\frac{W_1}{(1-W_1)} = -(\text{intercept of the } x\text{-axis}) \quad (4)$$

Alternatively W_1 can be calculated by dividing the intercept of the y-axis of the regression line by the sum of this intercept and the slope of the regression line. Compared to other conventional methods the standard addition method has the advantage that errors by matrix effects are minimized. Statistically it has the disadvantage that it is an extrapolation instead of an interpolation method.

Rietveld Method

As stated before, the Rietveld method compares the observed diffraction pattern to a calculated diffraction pattern, for which it tries to find the least-squares difference. The calculated pattern is based on structural crystallographic data and instrumental parameters, and is presented by the equation:

$$y_{ci} = s \sum_K L_K F_K^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bi} \quad (5)$$

where

y_{ci} is the calculated intensity at the i th step

y_{bi} is the background intensity at the i th step

s is the scale factor

K presents the Miller indices, h, k, l for a Bragg reflection

L_K contains the Lorentz, polarization and multiplicity factors

F_K is the structure factor for the K th Bragg reflection

$\phi(2\theta_i - 2\theta_K)$ is the reflection profile function with θ as the angle of diffraction

P_K is the preferred orientation function, and

A is an absorption factor

As these parameters are themselves also described by equations, the final mathematics are fairly complicated and their treatise is beyond the scope of this paper. Further details can be found in the IUCr Monographs on Crystallography (1993). It is important to note, however, that both sample specific crystal parameters and instrumental parameters are included in the calculations. This also means that reasonably good structural data on the constituent phases should be available for an adequate analysis.

Because the entire diffraction pattern is fitted in the Rietveld method, addition of a standard

is not necessary, provided that all phases present in the sample are crystalline and identified. In that case the relative weight fraction W_p of a phase P is calculated from:

$$W_p = \frac{s_p(ZMV)_p}{\sum_{i=1}^n s_i(ZMV)_i} \quad (6)$$

where

n is the number of phases in the mixture analyzed

s is the scale factor

Z is the number of formula units per unit cell

M is the mass of the formula unit and

V is the unit cell volume.

Amorphous phases can not be included in the Rietveld analysis and their quantification requires the addition of a known amount of crystalline standard. This makes it possible to scale the weight fractions calculated in the refinement to the known amount of standard, and thus to quantify by difference the amount of amorphous material present.

The Rietveld method searches the best least-squares fit to all of the thousands of measurement point simultaneously. Minimized in the least-squares refinement is the residual R_y , that is defined as:

$$R_y = \sum_i w_i (y_{oi} - y_{ci})^2 \quad (7)$$

where

w_i is the weight assigned to each step intensity and equals $1/y_{oi}$

y_{oi} is the observed intensity at the i th step, and

y_{ci} is the calculated intensity at the i th step

Criteria-of-fit

To test whether a fit is reasonable a number of criteria-of-fit have been developed. The most important of these are the weighted residual error (R_{wp}), the R-Bragg factor (R_B) and the Goodness-of-Fit indicator (GOF), each of which will be shortly explained below.

The weighted residual error (or R-weighted pattern) is defined as:

$$R_{wp} = \sqrt{\frac{\sum w_i (y_{oi} - y_{ci})^2}{\sum w_i y_{oi}^2}} \quad (8)$$

Mathematically R_{wp} is the most meaningful of the criteria-of-fit because its numerator is the residual (R_y) that is actually being minimized by the Rietveld method. It thus also is the best

indicator for the progress of the refinement. A perfect match of observed and calculated intensities would mean a R_{wp} of zero. Due to statistical noise, however, the error can at best be minimized. Typical results will render a value of 10-20% (Howard and Preston, 1989).

Based on counting statistics an estimate can be made of the R_{wp} one would expect if all observations are totally independent and correctly weighted. This estimate is called the expected error (R_e) and is defined as:

$$R_e = \sqrt{\frac{N-P-C}{\sum w_j y_{jo}^2}} \quad (9)$$

where

N is the number of observations (or steps)

P is the number of parameters varied in the refinement

C is the number of constraints in the refinement.

The Goodness-of-Fit compares the R_{wp} to the R_e and is a measure for how well the fitted model accounts for the data. It is defined as:

$$GOF = \left(\frac{R_{wp}}{R_e} \right)^2 = \frac{\sum w_j (y_{jo} - y_{ic})^2}{N-P+C} \quad (10)$$

For a perfect refinement with correctly weighted data R_{wp} would be equal to R_e and consequently the GOF would have a value of 1.0.

Finally, the R-Bragg factor is a measure of the agreement between the observed and calculated reflections and is defined as:

$$R_B = \frac{\sum |I_{Kc} - I_{Ko}|}{\sum I_{Ko}} \quad (11)$$

where I_{ko} and I_{kc} stand for the intensities respectively assigned to the observed and calculated K th Bragg reflection. The R_B is of value because it depends more heavily on the fit of the structure parameters and less on the nonstructural contribution than the other indices. It is however biased to the calculation model used since the I_{ko} values are obtained with the help of the model. A good fit would render values for R_B of less than 10% (Howard and Preston, 1989). Larger values would signify structural inaccuracies and/or systematic errors.

3 MATERIALS AND METHODS

CFA and zeolitized CFA

Analyses were carried out on CFA obtained from the Dutch "Amercentrale" and on samples of zeolitized CFA. See chapter 2 for an elaborate description of the characteristics of the

CFA and the zeolitization procedures applied. The zeolitized CFA used in this study was produced by treatment with 2 molar hydroxide solutions (NaOH and/or KOH) at a temperature of 93°C or 150°C. Table 5.1 presents an overview of the materials analyzed by QXRD that are discussed here.

Table 5.1 Overview of the materials synthesized and of the methods applied for their quantitative mineralogical analysis

Type of material ¹⁾	Conditions of zeolite synthesis	CEC ²⁾ meq/100g	XRD method ³⁾	Exp. code
CFA	-	1.3	SAM+RM	-
zeolite Na-P1	93°C, 24 h, 2 M NaOH, L/S 2.5	230	RM	960528
zeolite Na-P1	150°C, 6-24 h, 2 M NaOH, L/S 2.5	240	SAM	9.1-15.4
zeolite K-G	93°C, 96 h, 2 M KOH, L/S 2.5	200	RM	KG
zeolite ZK19	93°C, 168 h, 1.33 M NaOH, 0.67 M KOH, L/S 3	210	RM	71.1

¹⁾ zeolites contain residual CFA

²⁾ Cation exchange capacity, determined by ISRIC (Wageningen) as described in chapter 2

³⁾ SAM = Standard Addition Method, RM = Rietveld Method

Standards used in the quantitative XRD analyses

For the standard addition method standards of quartz, mullite and zeolite Na-P1 were used. Standards of quartz and mullite were respectively obtained from MERCK (Darmstadt, Germany) and from Gouda Vuurvast (Gouda, the Netherlands). Reference material of zeolite Na-P1 was synthesized following the prescript by Milton (1961) as described in appendix A. For the Rietveld method corundum was used as an internal standard. For this purpose a pure crystal, originating from Naxos (Greece) was pulverized in a tungsten carbide mill.

Standard addition method

X-ray powder diffraction in combination with standard addition was used to quantify the amount of quartz and mullite in CFA and the amount of zeolite Na-P1 in zeolitized CFA. For this purpose CFA or zeolitized CFA were mixed with the appropriate standard material to obtain samples containing 10, 20 and 25 or 30 wt. % of standard material. Standards and (zeolitized) CFA were ground separately by hand in an agate mortar after which they were manually mixed, in each case for 5 minutes. The samples with added standards were then analyzed by XRD and the integrated intensities (i.e. peak surface), corrected for background, measured of specific diffraction peaks. Table 5.2 gives an overview of the diffraction peaks of the different phases that were used for this purpose. The content of quartz was determined on the basis of the integrated intensity of one diffraction peak while for mullite and zeolite Na-P1 the average of the integrated intensities of respectively two and five diffraction peaks was used. The choice of peaks was based on their intensity and the

absence of overlap with other peaks. Measurement of the integrated peak intensities was carried out by the Wasserman ADM software package.

Table 5.2 Diffraction peaks of phases used for their quantification. In case of more than 1 diffraction peak, the mean value of their integrated intensities was used

Mineral phase	Diffraction peak			
	$^{\circ}2\theta$ range	d	Relative intensity	hkl
Quartz	20.60-21.15	4.25	27	100
Mullite	16.00-16.70	5.39	50	110
	40.50-41.30	2.21	60	121
Zeolite Na-P1	11.60-13.20	7.10	92	101
	17.00-18.50	5.02	61	200
	21.10-22.30	4.10	66	112
	27.10-29.10	3.18	100	301
	32.50-34.50	2.68	45	312

For analysis the samples were mounted on aluminum holders of constant dimensions, assuring that the same quantity of sample is irradiated in different runs. Analyses were carried out at room temperature on a Philips PW1730 diffractometer coupled to a PW1710 control system. Used was $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) at 40 kV and 30 mA, and a step scan rate of $0.02^{\circ}/\text{s}$ while spinning the sample.

Rietveld method

X-ray diffraction data for the Rietveld analysis were collected at room temperature on a Nonius PDS 120 Powder diffractometer equipped with a curved quartz monochromator ($d(101)=3.342 \text{ \AA}$) and position sensitive detector with an angular range of $120^{\circ} 2\theta$. Used was $\text{CuK}\alpha_1$ radiation ($\lambda = 1.540440 \text{ \AA}$) at 30 kV and 30 mA. Prior to analysis, samples were mixed with 10 wt. % corundum in order to be able to quantify the amount of amorphous material present in the samples. For the analysis the samples were mounted on a perspex sample holder. All analyses were carried out on duplicate samples, i.e. for each sample a duplicate was prepared separately and analyzed.

Rietveld analyses of the diffraction patterns were carried out with the *PC-Rietveld plus* package (Fischer et al., 1993), with a kernel program based on the Rietveld method (Rietveld, 1969) written by Wiles and Young (1981) and modified by Hill and Howard (1986). Included in the refinements were the minerals quartz, mullite, hematite, magnetite, corundum and the zeolites Na-P1, K-G and ZK19. Crystal lattice parameters and atomic coordinates of these phases were taken from Levien et al. (1980), Angel and Prewitt (1986), Blake et al. (1966), Wechsler et al. (1984), Ishizawa et al. (1980), Baerlocher and Meier

(1972), Calligaris et al. (1983) and Rinaldi et al. (1974). Appendix B at the end of this chapter presents an overview of these data. Refinements were carried out using the pseudo-Voigt function for the simulation of peak shape, attributing the intensities within 4 times a peak's full width at half maximum (FWHM) to that peak. For refinement the following general strategy was applied. First the background was subtracted. The *PC-Rietveld plus* package used permits this to be carried out either by refinement of a 6th order polynomial function or by inserting background levels by hand and linear interpolation between these inserted points. Background correction was subsequently followed by refinement of the scale factors, the zero-point, the crystal lattice parameters (a , b , c , α , β , γ) and the parameters of the peak shape function. Refinement of corrections for asymmetry, preferred orientation, occupation of crystallographic sites and x,y,z coordinates was only carried out when thought they could lead to significant improvements of the fit.

Concentrations for corundum obtained by the Rietveld analysis were scaled to the percentage added (ca. 10 wt. % of total sample) after which the weight percentages of the other mineral phases were adjusted. The amount of glass present was estimated by subtracting the sum of the weight percentages of the mineral phases and of the loss on ignition from 100%.

4 RESULTS AND DISCUSSION

Standard addition method

Quartz and mullite

The figures 5.1 and 5.2 present plots of the integrated peak intensities of quartz and the mean integrated peak intensities of mullite as a function of the fraction of standard in the sample. Statistical significant tests indicated that regression lines for individual analyses of each mineral were not significantly different within the 95% confidence interval and a regression line was calculated from the joint data of the duplicate samples analyzed. Table 5.3 presents the resulting concentrations and appropriate statistics of the data. From this it is calculated that CFA contains $4.1(\pm 1.6)$ wt. % quartz and $15.9(\pm 2.0)$ wt. % mullite.

The weight fractions and parameters of the obtained regression lines are characterized by large standard deviations, especially in the case of quartz. The cause of these variations lies in the problems associated with sample preparation, such as imperfect homogeneity after mixing of the standard and insufficient grinding of particles. Another error source associated with sample preparation is preferred orientation. However, analysis of quartz by XRD is relatively insensitive to this, though it may be of importance for the analysis of mullite (and zeolite Na-P1, discussed below). Using the average intensity of more than one diffraction peak corrects at least part of the error introduced by preferred orientation. Improvements of the analyses discussed here are expected by two changes: 1) increasing the number of analysis series, and 2) by improving the homogeneity of the sample to be analyzed, i.e. improving the mixing of standard and sample. However, this latter aspect is not that simple as each pretreatment may introduce new errors. For example, extensive mechanical mixing will cause abrasion of some crystallites, while sieving may cause new inhomogeneities. In

the present case results could probably have been improved by grinding and mixing of the standards and samples while being dispersed in an organic solute, like acetone or alcohol (Brindley, 1980).

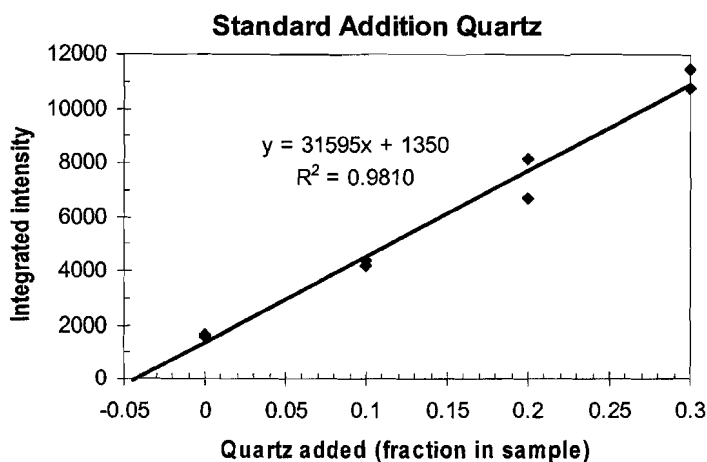


Figure 5.1 Integrated intensities of diffraction peak of quartz (hkl 100) versus the fraction of quartz standard in a sample of CFA, and resulting regression line

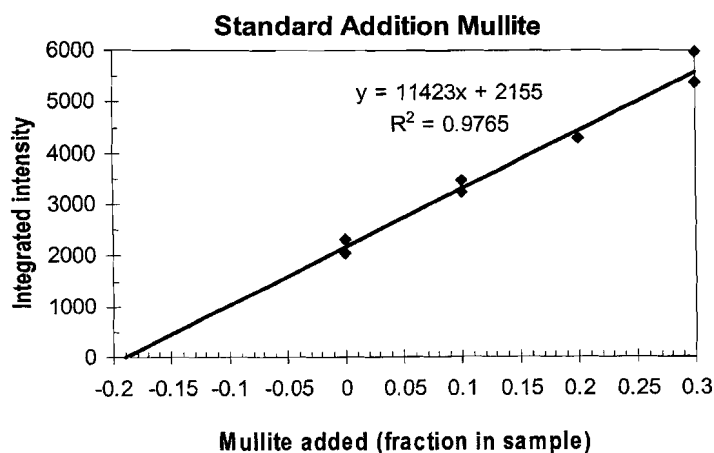


Figure 5.2 Mean integrated intensities of selected diffraction peaks of mullite (hkl 110 and 121), versus the fraction of mullite standard in a sample of CFA, and resulting regression line

Table 5.3 Concentrations of quartz and mullite in CFA, obtained by XRD standard addition method and results of the regression analysis

Mineral		Contents (wt. %)	Regression line ¹⁾		
			R ²	slope	intercept y-axis
quartz	average ²⁾ (N=2)	4.1	0.9810	31595	1350
	standard deviation	1.6		1794	336
mullite	average ²⁾ (N=2)	15.9	0.9765	11423	2155
	standard deviation	2.0		723	96

¹⁾ calculated using fractions instead of percentages

²⁾ Based on the number of analyses N

Zeolite Na-P1

For zeolite Na-P1 a number of standard addition analyses was carried out. Figure 5.3 gives an example of the regression plots obtained. The values of R² of the regression lines varied from 0.9874 to 0.9981. Resultant zeolite percentages varied from 20 to 43 wt. % and are listed in table 5.4 together with the appropriate statistics.

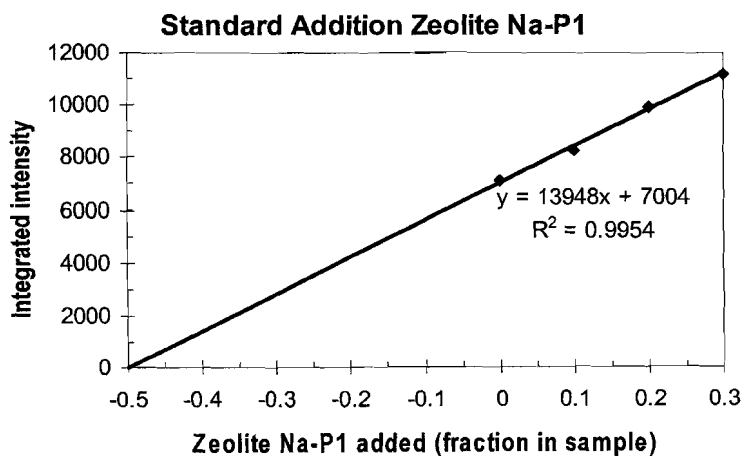


Figure 5.3 Mean integrated intensity of selected diffraction peaks of zeolite Na-P1 (*hkl* 101, 200, 112, 301 and 312) versus the fraction of zeolite standard in a sample of zeolitized CFA (conversion took place at 150°C with a 2 M NaOH solution, L/S 3.5 and a reaction time of 24 h)

The standard addition method presents a relatively laborious method for quantifying mineral phases. To obtain a less laborious, faster way for quantifying the amount of zeolite Na-P1 in converted CFA, the combined percentages of zeolite obtained by the standard addition method were used to calculate a calibration line. This line was used to estimate the content of zeolite Na-P1 in samples without carrying out additional standard additions, by plotting the averaged measured integrated intensities of the 5 appropriate peaks. This of course is only permitted on the condition that types of samples are examined similar to the ones used for the standard addition, and on the condition that instrumental parameters do not change. A plot of the calibration line, presented in figure 5.4, shows that the latter was not the case. The result of the last standard addition carried out, clearly deviates from the previous ones. The cause of this was found to be the deterioration of the X-ray tube used, which resulted in loss of intensity and which was soon afterwards replaced.

Table 5.4 Yield of zeolite Na-P1 in a number of syntheses, determined by a 4-point standard addition

Conditions of CFA treatment/zeolite synthesis: 150°C, 2 M NaOH		Yield of zeolite Na-P1 (wt. %)	Regression line ¹⁾		
			R ²	slope	intercept y-axis
18 h, L/S 4, CFA fraction >20 µm	analysis ²⁾ (N=1)	42.8	0.9885	9220	6905
	standard deviation	6.6		704	47
24 h, L/S 3.5	analysis (N=5)	38.0	0.9894	13746	6928
	standard deviation	2.8		558	47
12 h, L/S 3.5	analysis (N=1)	34.6	0.9968	13242	6992
	standard deviation	2.7		531	44
12 h, L/S 3.5, washed with acid	analysis (N=1)	29.7	0.9960	13897	5883
	standard deviation	2.6		626	52
6 h, L/S 3.5	analysis (N=2)	20.4	0.9822	16707	4283
	standard deviation	3.3		1364	114

¹⁾ Calculated using fractions instead of percentages

²⁾ Based on the number of analyses N

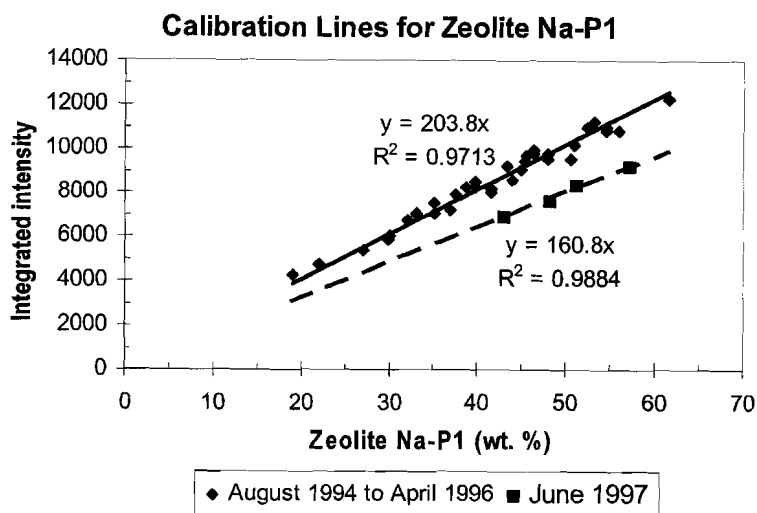


Figure 5.4 Calibration lines for the determination of the content of zeolite Na-P1 in zeolitized CFA, derived from the cumulative results of the standard addition analyses

The calibration line valid for the period August 1994 to April 1996 was used to plot the integrated intensity measured for the zeolitized CFA used for Rietveld analysis discussed further below. The average integrated peak intensity (over 5 peaks) was 5530 counts which indicates a zeolite Na-P1 content of 35 wt. %.

Magnetite and hematite

In the present study no quantitative analysis by means of standard addition was carried out for hematite and magnetite, because of the overlap of the diffraction peaks of these two mineral phases with each other and with those of quartz and mullite. As a result no reliable concentrations are available for hematite and magnetite. This is unfortunate, because the glass content is calculated by subtracting the concentrations of the major mineral phases from 100%. However, from the chemical analysis of CFA (chapter 2) it is known that the maximum iron content in CFA is 61700 mg/kg Fe corresponding to ca. 8.5 wt. % iron oxide. Because part of this iron will also be present in phases other than magnetite and hematite, this percentage represents an upper limit of the possible iron oxide content. In addition, it is estimated from magnetic separations that the magnetite content of CFA is 4 wt. % while peak intensities in the diffraction patterns indicate that the magnetite content of CFA is larger than that of hematite. Taking this into account it is estimated that the total content of iron oxide mineral phases amounts to 6 wt. %. Compared to results by Pietersen (1993) this

estimate seems still high. Pietersen (1993) quantified magnetite and hematite in a number of CFA samples by means of a combination of saturation magnetization analysis and QXRD and reported magnetite contents varying from 1.1 to 3.3 wt. % and hematite contents between 0 and 1.3 wt. % for Dutch CFA.

Glass

Though the glass content can not be measured directly by XRD it can be calculated by subtracting the concentrations of the other phases and the loss on ignition (LOI) from 100%. As stated in chapter 2, the LOI of CFA represents mainly unburnt coal and is ca. 3 wt. %. Combination of this percentage with the ones listed above for quartz, mullite and the iron mineral phases, gives an estimate of the glass content in CFA of 71 wt. %.

By assuming that quartz and mullite remain inert during the zeolitization process, an estimate can also be made for the glass content of zeolitized CFA. Because of the hydration and uptake of sodium that takes place during zeolitization and the subsequent increase in weight of ca. 10 wt. % (see chapter 2), concentrations of quartz and mullite in zeolitized CFA are estimated to be respectively 3.6 and 14.4 wt. %. For a content of zeolite Na-P1 of 35 wt. %, this then means that the amorphous fraction is ca. 40 wt. %. However, residual carbon and other amorphous phases are also included in this percentage. The most predominant of these latter are Ca- and Mg-hydroxides which, based on chemical analyses of zeolitized CFA (chapter 2), are estimated to make up ca. 10 wt. % of the zeolitized CFA. The glass¹ content of zeolitized CFA is thus ca. 30 wt. %.

Rietveld Method

Figures 5.5 to 5.8 show observed diffraction patterns for CFA and zeolitized CFA, and the calculated patterns and difference plots obtained by Rietveld analysis. Because analyses of the duplicate samples lead to similar results only one of the patterns of duplicate sample analyses is presented. All samples analyzed contain significant amounts of amorphous material which results in increased backgrounds between 10 and 50 degrees 2θ that could not be fitted by refinement of the polynomial function. Because of this, all backgrounds were fitted by hand, though this method is best suited for relatively simple patterns with well spaced intervals between the diffraction peaks. Generally, for complex patterns, like the ones in this study, better results are obtained by including the background in the refinement (Post and Bish, 1989). Fixation of the background by interpolation in these cases may result in differences between the observed and calculated patterns, especially at the base of peaks, causing relatively high R_b values. In the present study, fitting of the background by hand resulted in better weighted profile residuals (R_{wp}) and goodness-of-fit (GOF) values but also lead to much higher R-Bragg (R_b) factors which increased from values around 5 to generally values around 30.

¹ The term glass is used here in a loose definition, meaning amorphous aluminum silicates

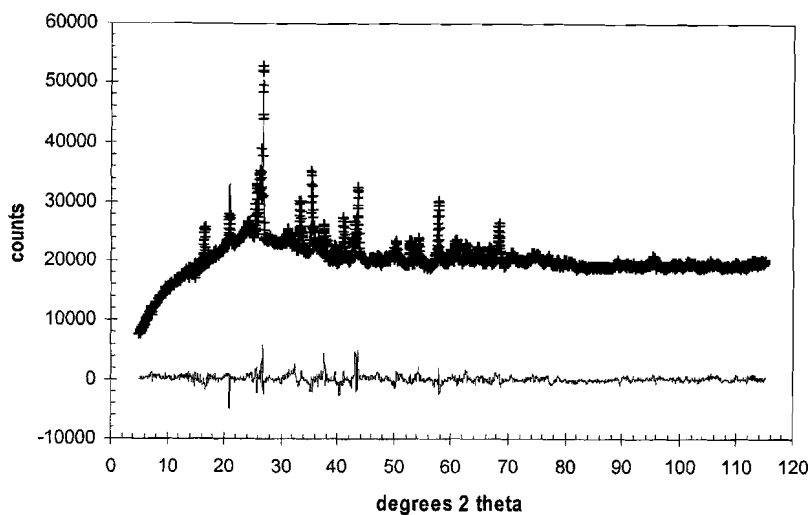


Figure 5.5 Rietveld analysis of CFA: observed (crosses) and calculated (continuous line) pattern and difference curve (bottom)

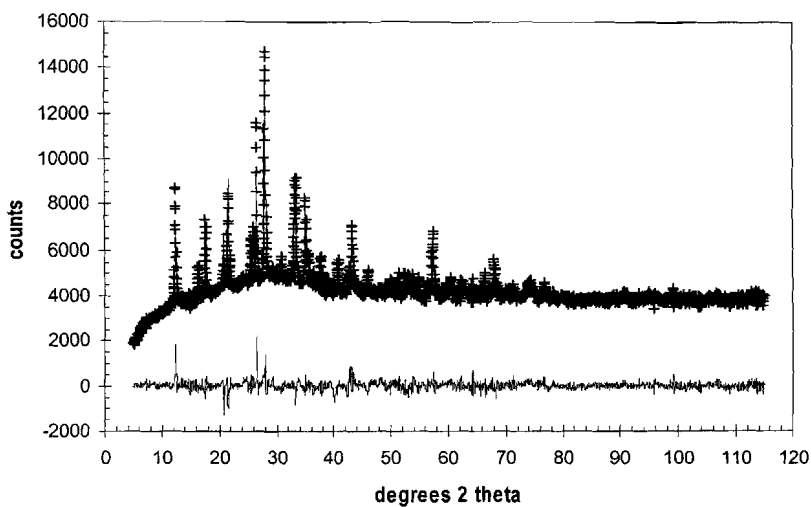


Figure 5.6 Rietveld analysis of CFA converted to zeolite Na-P1: observed (crosses) and calculated (continuous line) pattern and difference curve (bottom)

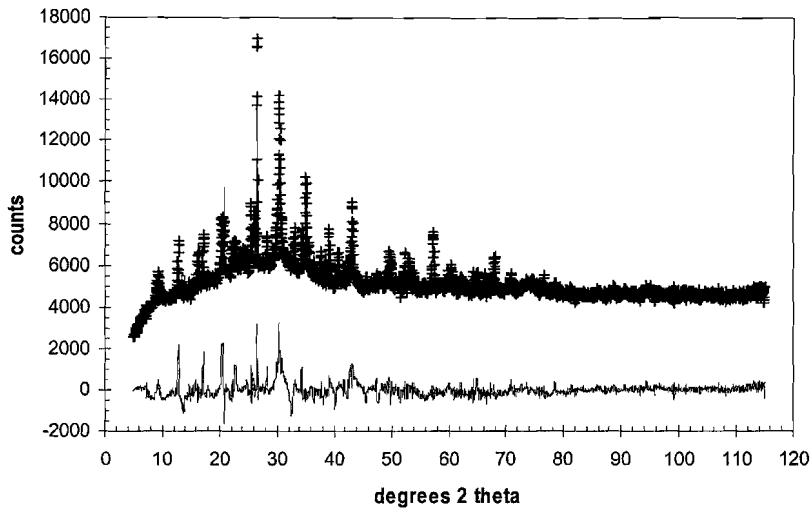


Figure 5.7 Rietveld analysis of CFA converted to zeolite K-G: observed (crosses) and calculated (continuous line) pattern and difference curve (bottom)

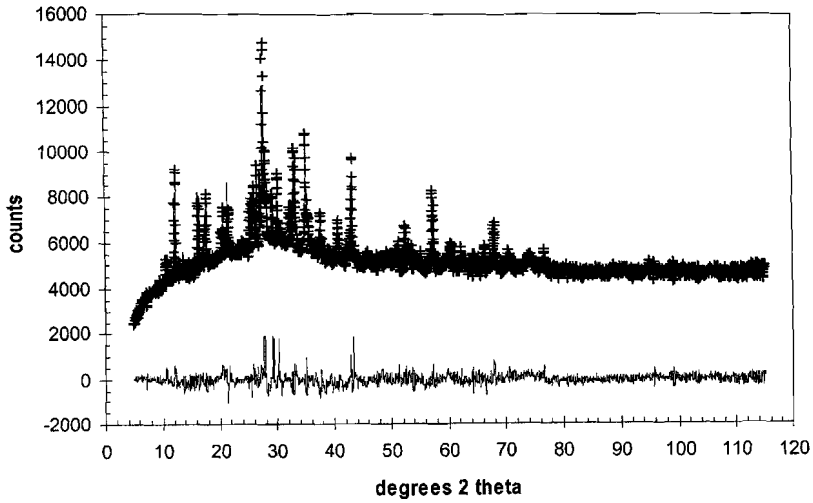


Figure 5.8 Rietveld analysis of CFA converted to zeolite ZK19: observed (crosses) and calculated (continuous line) pattern and difference curve (bottom)

Table 5.5 presents the concentrations of minerals as determined by Rietveld analysis and includes the values for R_{wp} , GOF and R_b . Table 5.6 presents the final corrected concentrations, i.e. calculated by scaling of the concentrations to the known amount of corundum added, followed by subtracting corundum from the total and normalization to 100%.

In the case of fully crystalline samples quantitative analysis by the Rietveld method has the advantage that no addition of a standard is necessary and thus no inhomogeneity can be introduced by the mixing step. However, in the present study a standard was needed, i.e. corundum, to be able to quantify the amorphous fraction, and, though in general results for duplicate samples are fairly consistent, incomplete mixing may very well be the source of the encountered differences.

The amorphous fraction in table 5.6 is estimated by difference with 100%. In case of CFA this fraction, after subtraction of the loss on ignition (3 wt. %), serves as an estimate of the glass content of CFA. For zeolitized CFA the glass content is estimated by subtraction from the difference with 100 % the loss on ignition (excluding zeolitic water and hydroxide water) and a further 10 wt.% for precipitated hydroxides, as already explained above for the standard addition method. Appendix C gives an overview of the loss on ignition values and the correction factors calculated to estimate the glass content.

Table 5.5 Results of Rietveld analyses: concentration of minerals (wt. %) in CFA and zeolitized CFA and the accompanying weighed residuals (R_{wp}) and goodness-of-fit (GOF). The R-Bragg factor (R_b) is given in brackets for each phase refined

Sample ¹⁾	Corundum ²⁾	Quartz	Mullite	Magnetite	Hematite	Zeolite	R_{wp} (%)	GOF
CFA	26.4 (20.8)	28.0 (23.7)	40.4 (35.6)	3.4 (27.5)	1.8 (40.9)	-	3.7	26.2
	30.4 (25.5)	24.9 (28.6)	36.6 (24.8)	2.0 (39.3)	6.1 (24.8)	-	2.9	20.4
Zeolite Na-P1	18.1 (20.7)	10.9 (25.1)	20.9 (22.8)	2.0 (37.8)	3.5 (24.5)	44.6 (21.5)	4.6	12.4
	20.3 (16.6)	12.3 (35.9)	18.5 (21.5)	2.2 (28.0)	2.4 (25.1)	44.3 (16.2)	3.8	6.8
Zeolite K-G	19.0 (43.9)	19.5 (67.3)	18.1 (77.0)	4.2 (64.3)	0.8 (55.8)	38.4 (72.3)	5.8	17.6
	26.7 (32.2)	16.5 (83.8)	23.3 (72.0)	3.3 (51.6)	1.6 (49.8)	28.5 (121.8)	6.0	22.7
Zeolite ZK19	23.4 (18.9)	3.7 (59.1)	17.4 (26.2)	3.2 (32.8)	0.8 (42.0)	51.6 (36.9)	3.5	14.4
	20.5 (15.2)	6.1 (48.9)	13.0 (68.6)	4.3 (31.6)	1.1 (32.6)	55.0 (40.5)	3.9	8.6

¹⁾ Presented are the results of duplicate analyses

²⁾ Corundum is added as an internal standard

Coal fly ash

Rietveld analysis leads to a reasonable fit of the diffraction pattern of CFA. Except for hematite and magnetite final calculated concentrations are similar for duplicate samples and show the CFA to contain ca. 10 wt. % of quartz, 16 wt. % of mullite and 70 wt. % of glass. Individual values for magnetite and hematite are not consistent. However, the sum of their concentrations is ca. 2.7 wt. %.

In the present refinement, structural data of 2:1 mullite, i.e. $2 \text{ Al}_2\text{O}_3 \cdot 1 \text{ SiO}_2$, presented by Angel and Prewitt (1986) were used. However, in reality the alumina content of mullite can vary considerably, according to Fischer et al. (1994) from 57-74 mol %. Composition data obtained by chemical analysis by SEM/EDS of polished sections (chapter 2) indicate the presence in zeolitized CFA of a residual phase with a Si/Al ratio of circa 0.5, possibly related to mullite. It was therefore tested if refinement of the Al and Si occupation factors of mullite improved the fit of the CFA diffraction patterns. Occupation factors changed however only slightly and no significant improvements in the outcome of the refinement was noticed.

Table 5.6 Results Rietveld analysis: weighted concentration of corundum in the samples analyzed (wt. %) and content of minerals and glass (wt. %) in CFA and zeolitized CFA calculated by correction for this amount of corundum

Sample	Corundum added (wt. %)	Content (wt. %) corrected for corundum added						
		Quartz	Mullite	Magnetite	Hematite	Zeolite	Amorphous fraction ¹⁾	Glass
CFA	10.13	12.0	17.3	1.5	0.8	-	68.6	65.6
	10.37	9.5	13.9	0.8	2.3	-	73.5	70.5
	mean	10.7	15.6	1.1	1.5	-	71.0	68.0
Zeolite Na-P1	10.15	7.1	13.6	1.3	2.3	29.1	46.5	33.8
	11.94	9.5	14.3	1.7	1.8	34.1	38.6	26.7
	mean	8.3	13.9	1.5	2.1	31.6	42.6	30.3
Zeolite K-G	10.06	15.6	14.5	3.4	0.6	30.7	35.3	19.2
	10.75	13.2	18.6	2.6	1.3	22.7	41.6	24.4
	mean	14.4	16.5	3.0	1.0	26.7	38.4	21.8
Zeolite ZK19	11.83	2.1	10.0	1.8	0.5	29.6	56.0	39.5
	11.06	3.7	7.9	2.6	0.7	33.4	51.8	36.0
	mean	2.9	8.9	2.2	0.6	31.5	53.9	37.8

¹⁾ Including LOI

Coal fly ash converted to zeolite Na-P1

Judging by the GOF values, Rietveld analysis of CFA converted to zeolite Na-P1 gave the best fit while values of R_{wp} and R_b were similar to those in other refinements. Analyses of duplicate samples were consistent with each other and indicated a zeolite and glass content of respectively ca. 32 and 30%. As expected, concentrations of quartz and mullite (respectively ca. 8 and 14 wt. %) are slightly lower than those calculated for CFA. This is in agreement with the dilution effect that occurs as a result of hydration and sodium uptake

during the zeolitization process. The sum of hematite and magnetite amounts to ca. 3.5 wt. %.

Further improvements of R_{wp} criteria-of-fit listed in table 5.5 could be obtained by refining the occupation sites of water in the zeolite. However, no convergence of the calculations could be obtained and this was not included in the results presented here.

Coal fly ash converted to zeolite K-G

Though values of R_{wp} and GOF were reasonable for the CFA converted to zeolite K-G, those of R_b were very high. Visual inspection of the observed and calculated patterns (figure 5.7) show that these are poorly fitted, mainly because the calculated patterns contain a number of diffraction peaks of zeolite K-G that are absent in the patterns actually observed.

Extensive refinement, including the site occupation factors, did not improve the fit which suggests that the structural starting model for zeolite K-G is at fault. Further structural and chemical analysis of the zeolite K-G synthesized from CFA is necessary to solve this and no final conclusions were obtained from the Rietveld analysis.

Coal fly ash converted to zeolite ZK19

Results for the CFA converted to zeolite ZK19 show a similar zeolite content as calculated for zeolite Na-P1 while the calculated concentrations of quartz and mullite are relatively low and glass content is relatively high. However, some of the R_b values are relatively high (above 40) and results for the criteria-of-fit are not completely consistent for duplicate samples, making conclusive interpretation of these results difficult.

Consistency of the results by standard addition and Rietveld method

The usefulness of quantitative analyses as discussed in this chapter, lies in the fact that they offer a measure for the quality of the zeolite product obtained, expressed by the zeolite content, and, directly related to this, a measure for the degree of conversion and thus for how much room there is for improvement. For these aims it is important to use a QXRD method which reflects the concentrations of zeolite and other major mineral phases correctly.

In the present study, both methods of QXRD used, agree fairly on the content of zeolite Na-P1 and mullite. Analysis of zeolitized CFA rendered in both cases a content of zeolite Na-P1 of ca. 33 wt. %. The weight fraction of mullite in the original CFA was determined by both methods to be ca. 16 wt. % which agrees with the ca. 14 wt. % of mullite in CFA converted to zeolite Na-P1, that is calculated by the Rietveld method, assuming that mullite remains inert during the zeolitization process.

Contrary to the concentrations of mullite and zeolite Na-P1, those calculated for quartz by both methods are significantly different. Concentrations of quartz obtained by the Rietveld method for CFA and CFA converted to zeolite Na-P1, are substantially higher than those obtained by the standard addition method for CFA, though still within the 95% confidence interval. As quartz concentrations calculated by the Rietveld method for CFA (11 wt. %) and CFA converted to zeolite Na-P1 (8 wt. %) are consistent with each other, these results suggest that the quartz content of 4 wt. % obtained by the standard addition method is too

low. Quartz values obtained from the analysis of the CFA converted to zeolite ZK19, on the other hand are more in line with those obtained by standard addition for CFA, but are characterized by relatively large R_b values and less reliable.

The concentrations of iron oxides (magnetite and hematite) obtained by the Rietveld method are in general lower than the 6 wt. % estimated in this study for the standard addition method, and more in line with the concentrations reported by Pietersen (1993), i.e. between 2 and 4 wt. %. In the present study the Rietveld method seemed to have some difficulties distinguishing between hematite and magnetite. Possibly better results would have been obtained for these iron mineral phases if cobalt instead of copper radiation had been used since that combination is less sensitive to the effects of microabsorption (Bish and Howard, 1988). A separate Rietveld analysis of the magnetic fraction from CFA ($R_{wp} = 5.4$, $GOF = 9.8$, $R_b = 12.3$) showed the magnetite to hematite ratio in that fraction to be 2.

It is hard to decide which of the two methods, standard addition or Rietveld method, gives the best estimate of the quartz content. A mass balance including the composition of the glass phase in CFA might solve this, but unfortunately accurate data for this are not available and indeed, difficult to get. The glass phase in CFA is too inhomogeneous in composition and structure to obtain such data by analytical techniques like SEM/EDS. Compositional data obtained by sequential extractions do exist, but these prove to be not specific enough for the various phases to extract reliable glass compositions from (Hollman et al, 1992, 1993; Pietersen, 1993).

In theory, zeolite concentrations can also be calculated on the basis of CEC values measured for the converted CFA's (table 5.1) and their ratio to the theoretical CEC's of the zeolites involved when pure. In the present study, using the CEC's listed in table 5.1, the zeolite concentrations obtained by the Rietveld method and zeolite compositions listed in appendix B, it can be calculated in this way that the conversion products with zeolite Na-P1, zeolite K-G and zeolite ZK19 have zeolite contents of 48 to 52 wt. %. However, this method passes over the possibility that other phases present may contribute to the CEC. Therefore, the zeolite contents calculated in this way are considered only as a check on the maximum content measured by QXRD methods.

Overall it can be stated that the differences between the standard addition method and the Rietveld method are minimal, except for the quartz concentrations. Taking into account the extensiveness of Rietveld and the fact that for both methods the aims in the beginning of this paragraph are achievable, it is concluded that the Rietveld method is a valuable tool that is much less laborious and far more versatile than traditional QXRD techniques like the standard addition method. Moreover, for purely crystalline samples, for which no addition of a standard is necessary, the Rietveld method has none of the problems associated with mixing. Much depends, however, on the correctness of the structural data in the starting model. In the present study the starting model of zeolite K-G was found to be inadequate. Composition and structure of mineral phases involved in the Rietveld refinement should be well characterized, otherwise at best an indication of the quantities present is obtained.

5 CONCLUSIONS

- Analysis of CFA and zeolitized CFA by standard addition and Rietveld analysis methods gave fairly consistent weight fractions for zeolite Na-P1 and mullite. Determined weight fraction of quartz by both methods are less in agreement with each other;
- For mullite a content of ca. 16 wt. % was measured in CFA and slightly less, in accordance with weight increase, in zeolitized CFA;
- Quartz content of CFA was about 4 wt. % according to the standard addition method and about 10 wt. % according to Rietveld method. The latter method gave again slightly lower concentrations for CFA converted to zeolite Na-P1;
- Both standard addition and Rietveld methods indicated a percentage of 30 to 35 wt. % of zeolite Na-P1 in a sample converted at 93°C with a 2 M NaOH solution;
- Results from the Rietveld analysis of zeolite K-G converted CFA were thought to be inadequate, probably because the structural starting model used is inadequate. Further analyses of the zeolite synthesized are needed to improve this;
- Results for zeolite ZK19 converted CFA by Rietveld analysis indicated relatively low concentrations of quartz and mullite. Criteria-of-fit, however, are not conclusive. The high R-Bragg factors obtained in this case indicate that a further improvement of the refinement is necessary;
- The calculated glass content of CFA is approximately halved by zeolitization and decreases from ca. 70 to 30 wt. %;
- Results by the standard addition method are characterized by relatively wide standard deviations, especially the data obtained for quartz. The cause for this is sought in lack of homogeneity (imperfect mixing);
- Compared to the standard addition method, the Rietveld method is much less laborious, requiring much less laboratory work. For fully crystalline samples many of the problems that are of importance for the standard addition method will play no role when using the Rietveld method. However, the outcome of the refinement heavily depends on the quality of the starting model. In the present study the starting model of zeolite K-G was found to be inadequate. In addition, the failure in the present study to describe the high background by a polynomial function had some adverse effects on the criteria-of-fit, especially the R-Bragg factors. This hampered the interpretation of the refinement of zeolite ZK19.

ACKNOWLEDGMENTS

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Appendix A Synthesis of standard zeolite Na-P1 (Milton, 1961)

A sodium aluminate and a sodium silicate solution were prepared separately by dissolving 3.4 g aluminum band (99.99% Al p.a. MERCK) and 16.3 g silica (containing 7.1% water), each in 25 ml 5 M NaOH solution after which the volume of each suspension was brought to 50 ml with distilled water. These two suspensions were mixed together while stirring. Stirring was continued until a homogeneous mixture had been obtained which was then put into an oven at 100°C for 24 hours. At the end of this period the zeolite synthesized was removed by filtration and its purity checked by X-ray diffraction and scanning electron microscope (SEM).

Appendix B Input structural data for Rietveld analyses. Listed Wyckoff positions and site symmetries were generated by the Altwyk Program of the National Research Council of Canada (<http://yjp.icpet.nrc.ca/altwyk>) and are based on the International Tables of Crystallography A (1983)

Mineral phase: quartz				Space group: P 3 ₂ 2 1			
Lattice constants	a	b	c	α	β	γ	
	4.916	4.916	5.405	90	90	120	
Positional parameters, isotropic thermal parameters and occupancies							
Atom-site	x	y	z	B (Å ²)	site symmetry	Wyckoff position	no. of atoms per unit cell
Si	0.4697	0	0	0.62	1	6c	3
O	0.4235	0.2669	0.1191	1.05	1	6c	6
Literature source: Levien et al. (1980)							

Mineral phase: mullite			Space group: P b a m				
Lattice constants	a	b	c	α	β	γ	
	7.578	7.682	2.886	90	90	90	
Positional parameters, isotropic thermal parameters and occupancies							
Atom-site	x	y	z	B (Å²)	site symmetry	Wyckoff position	no. of atoms per unit cell
Al	0	0	0	0.63	..2/m	0.0833	2
T1-Al	0.14901	0.34026	0.5	0.68	..m	4h	2.24
T1-Si	0.14901	0.34026	0.5	0.68	..m	4h	0.96
T2-Al	0.26647	0.20529	0.5	0.63	..m	4h	0.56
T2-Si	0.26647	0.20529	0.5	0.63	..m	4h	0.24
O-1	0.359	0.4218	0.5	1.06	..m	4h	4
O-2	0.5	0	0.5	1.56	..2/m	2d	0.8
O-3	0.4498	0.0505	0.5	0.93	..m	4h	0.8
O-4	0.1273	0.2186	0	1.1	..m	4g	4
Literature source: Angel and Prewitt (1986)							

Mineral phase: magnetite			Space group: F d 3 m				
Lattice constants	a	b	c	α	β	γ	
	8.396	8.396	8.396	90	90	90	
Positional parameters, isotropic thermal parameters and occupancies							
Atom-site	x	y	z	B (Å²)	site symmetry	Wyckoff position	no. of atoms per unit cell
Fe ^{II}	0.125	0.125	0.125	0.37	-43m	0.33333	8
Fe ^{III}	0.5	0.5	0.5	0.47	.-3m	16d	16
O	0.2547	0.2547	0.2547	0.64	.3m	32	32
Literature source: Wechsler et al. (1984)							

Mineral phase: hematite			Space group: R $\bar{3}$ c				
Lattice constants	a	b	c	α	β	γ	
	5.038	5.038	13.772	90	90	120	
Positional parameters, isotropic thermal parameters and occupancies							
Atom-site	x	y	z	B (\AA^2)	site symmetry	Wyckoff position	no. of atoms per unit cell
Fe	0	0	0.3553	0.5	3	12c	12
O	0.3059	0	0.25	0.7	0.2	18	18
Literature source: Blake et al. (1966)							

Mineral phase: corundum			Space group: $R\bar{3}c$				
Lattice constants	a	b	c	α	β	γ	
	4.754	4.754	12.99	90	90	120	
Positional parameters, isotropic thermal parameters and occupancies							
Atom	x	y	z	B (\AA^2)	site symmetry	Wyckoff position	no. of atoms per unit cell
Al	0	0	0.3523	0.32	3	12c	12
O	0.3064	0	0.25	0.33	0.2	18	18
Literature source: Ishizawa et al. (1980)							

Mineral phase: zeolite Na-P1			Space group: $I\bar{4}$				
Lattice constants	a	b	c	α	β	γ	
	10.043	10.043	10.043	90	90	90	
Positional parameters, isotropic thermal parameters and occupancies							
Atom-site	x	y	z	B (\AA^2)	site symmetry	Wyckoff position	no. of atoms per unit cell
Na-1	0.014	0.1895	0.494	4.4	1	8g	2.64
Na-2	0.359	0.0825	0.221	4	1	8g	3.44
T1-Si	0.1438	0.1692	-0.02	1.1	1	8g	4.96
T1-Al	0.1438	0.1692	-0.02	1.1	1	8g	3.04
T2-Si	0.1683	0.3579	0.2329	0.9	1	8g	4.96
T2-Al	0.1683	0.3579	0.2329	0.9	1	8g	3.04
O-1	0.189	0.0215	0.041	0.5	1	8g	8
O-2	0.1885	0.2895	0.088	1.3	1	8g	8
O-3	0.009	0.346	0.2985	2.5	1	8g	8
O-4	0.283	0.2845	0.33	2.8	1	8g	8
H ₂ O-1	0	0	0.325	5.9	2..	4	1.68
H ₂ O-2	0.2195	0.024	0.3515	2.6	1	8g	5.6
H ₂ O-3	0.293	0.002	0.352	4	1	8g	4
Literature source: Baerlocher and Meier (1972)							

Mineral phase: zeolite K-G			Space group: R $\bar{3}$ m ¹)				
Lattice constants	a	b	c	α	β	γ	
hexagonal	13.858	13.858	15.136	90	90	120	
Positional parameters, isotropic thermal parameters and occupancies							
Atom-site	x	y	z	B (Å ²)	site symmetry	Wyckoff position	no. of atoms per unit cell
K-1	0	0	0.2222	0.529	3m	6c	5.82
K-2	0.1035	0.207	0.4576	2.277	m	18h	2.46
K-3	0.1397	0.2794	0.3858	2.5	m	18h	3.72
T-Si	-0.3336	-0.4374	0.4369	0.223	1	36i	24
T-Al	-0.3336	-0.4374	0.4369	0.223	1	36i	12
O-1	0.0888	0.1777	0.1777	0.579	m	18h	18
O-2	-0.1165	-0.2329	0.2671	0.52	m	18h	18
O-3	-0.2142	-0.4285	0.4645	0.559	m	18h	18
O-4	-0.1	-0.1993	0.12	0.406	m	18h	18
H ₂ O-1	-0.3333	-0.1667	0.3333	3.2	2/m	9	5.49
H ₂ O-2	0.0868	0.1735	0.6519	2	m	18h	13.86
H ₂ O-3	0.0736	0.1473	0.3733	3.2	m	18h	2.34
Literature source: Calligaris et al. (1983)							

¹⁾ Given are the parameters in hexagonal setting that were obtained by conversion of the parameters by Calligaris et al. (1983) for rhombohedral setting: $a_{\text{hex}} = 2Aa_{\text{rhom}} \sin(\alpha_{\text{rhom}}/2)$, $c_{\text{hex}} = (9Aa_{\text{rhom}}^2 - 3Aa_{\text{hex}}^2)^{0.5}$
 conversion matrix for the x,y,z parameters:

$$\begin{pmatrix} 2/3 & 1/3 & 1/3 \\ 1/3 & 1/3 & 1/3 \\ -1/3 & -2/3 & 1/3 \end{pmatrix}$$

Mineral phase: zeolite ZK19			Space group: P 2 ₁ /m				
Lattice constants	a	b	c	α	β	γ	
	9.865	14.3	8.668	90	124.2	90	
Positional parameters, isotropic thermal parameters and occupancies							
Atom	x	y	z	B (Å ²)	site symmetry	Wyckoff position	no. of atoms per unit cell
K	0.848	0.25	0.2076	2.4	.m.	2	1.6
Na-1	0.848	0.25	0.2076	2.4	.m.	2	0.4
Na-2	0.608	0.6262	0.4401	2.14	1	4f	3.3
T1-Si	0.7362	0.0248	0.2805	1.08	1	4f	2.676
T1-Al	0.7362	0.0248	0.2805	1.08	1	4f	1.325
T2-Si	0.4206	0.1409	0.002	1.06	1	4f	2.676
T2-Al	0.4206	0.1409	0.002	1.06	1	4f	1.325
T3-Si	0.0604	0.008	0.2844	1.11	1	4f	2.676
T3-Al	0.0604	0.008	0.2844	1.11	1	4f	1.325
T4-Si	0.1204	0.1396	0.0421	1.14	1	4f	2.676
T4-Al	0.1204	0.1396	0.0421	1.14	1	4f	1.325
O-1	0.1335	0.0976	0.2289	2.04	1	4f	4
O-2	0.6445	0.5766	0.1878	1.94	1	4f	4
O-3	0.61	0.113	0.1728	1.89	1	4f	4
O-4	0.0254	0.9154	0.1494	1.85	1	4f	4
O-5	0.8957	0.044	0.2713	2.06	1	4f	4
O-6	0.3022	0.3738	0.0783	2.32	1	4f	4
O-7	0.7872	0.4795	0.4982	1.9	1	4f	4
O-8	0.5814	0.75	0.0616	1.94	.m.	2	2
O-9	0.0665	0.25	0.0196	2.12	.m.	2	2
H ₂ O-1	0.7551	0.75	0.4733	7.8	.m.	2	2
H ₂ O-2	0.1552	0.75	0.4382	7.3	.m.	2	2
H ₂ O-3	0.3208	0.8525	0.174	8.8	1	4f	4
H ₂ O-4	0.5085	0.25	0.4384	18.7	.m.	2	2
H ₂ O-5	0.5	0.5	0.5	16.6	-1	2d	2
Literature source: Rinaldi et al. (1974)							

Appendix C.1 Measured water loss from CFA and zeolitized CFA samples at 110°C and 975°C (LOI)

	Weight loss (wt. %)		
	110°C	975°C	Difference
CFA	0.2	3	2.8
zeolite Na-P	2.5	10.3	7.8
zeolite K-G	3.7	13.1	6.9
zeolite ZK19	7.3	14.3	7

Appendix C.2 Correction factors to calculate the glass content of the zeolitized CFA samples used for Rietveld analysis

Zeolite type	Zeolite ¹⁾ (wt. %)	Zeolitic water ²⁾ (wt. %)	LOI (wt. %)	LOI - zeolitic water -water in hydroxides + Ca,Mg-hydroxides ³⁾ (wt. %)	Amorphous fraction ¹⁾ (wt. %)	Glass ⁴⁾ (wt. %)
zeolite Na-P	29.1	4.6	10.3	12.7	46.5	33.8
	34.1	5.4	10.3	11.9	38.6	26.7
	31.6	5	10.3	12.3	42.6	30.3
zeolite K-G	30.7	4	13.1	16.1	35.3	19.2
	22.7	2.9	13.1	17.2	41.6	24.4
	26.7	3.5	13.1	16.6	38.4	21.8
zeolite ZK19	29.6	4.8	14.3	16.5	56	39.5
	33.4	5.5	14.3	15.8	51.8	36
	31.5	5.2	14.3	16.1	53.9	37.8

¹⁾ As calculated by the Rietveld method and presented in table 5.6

²⁾ Calculated from the zeolite content in the previous column and the compositions in appendix B

³⁾ Water loss associated with Ca- and Mg-hydroxides is in all cases estimated to be 3 wt.%, estimating the total Ca- and Mg- hydroxide content on 10 wt. % in a ratio of 10 to 7

⁴⁾ Note that the term glass is used here in a loose definition. It still includes amorphous phases other than Ca- and Mg-hydroxides

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Curriculum Vitae

Guido Hollman is op 1 maart 1965 geboren te Roermond. In juni 1983 behaalde hij zijn diploma Gymnasium-B aan de St. Ursula Scholengemeenschap in Horn. In september van datzelfde jaar startte hij met de studie Geologie aan de Faculteit Aardwetenschappen van de Universiteit Utrecht. Hij studeerde af in de Exogene Geochemie in mei 1989. Na 4 maanden voor de KEMA in Arnhem te hebben gewerkt trad hij in februari 1990 in dienst als toegevoegd onderzoeker bij de faculteit waar hij afstudeerde. Hier bleef hij tot januari 1998 aan verbonden gedurende welke tijd hij op 2 projecten werkte waarin hij onderzoek deed naar de invloed van vertering op vliegias en de mogelijkheden om uit vliegias zeolieten te synthetiseren. Beide projecten werden in samenwerking met de KEMA in Arnhem uitgevoerd. In 1998 en een deel van 1999 werd dit proefschrift geschreven. In mei 1999 begon Guido een opleiding tot Oracle systeemontwikkelaar welke eind november wordt afgerond.

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