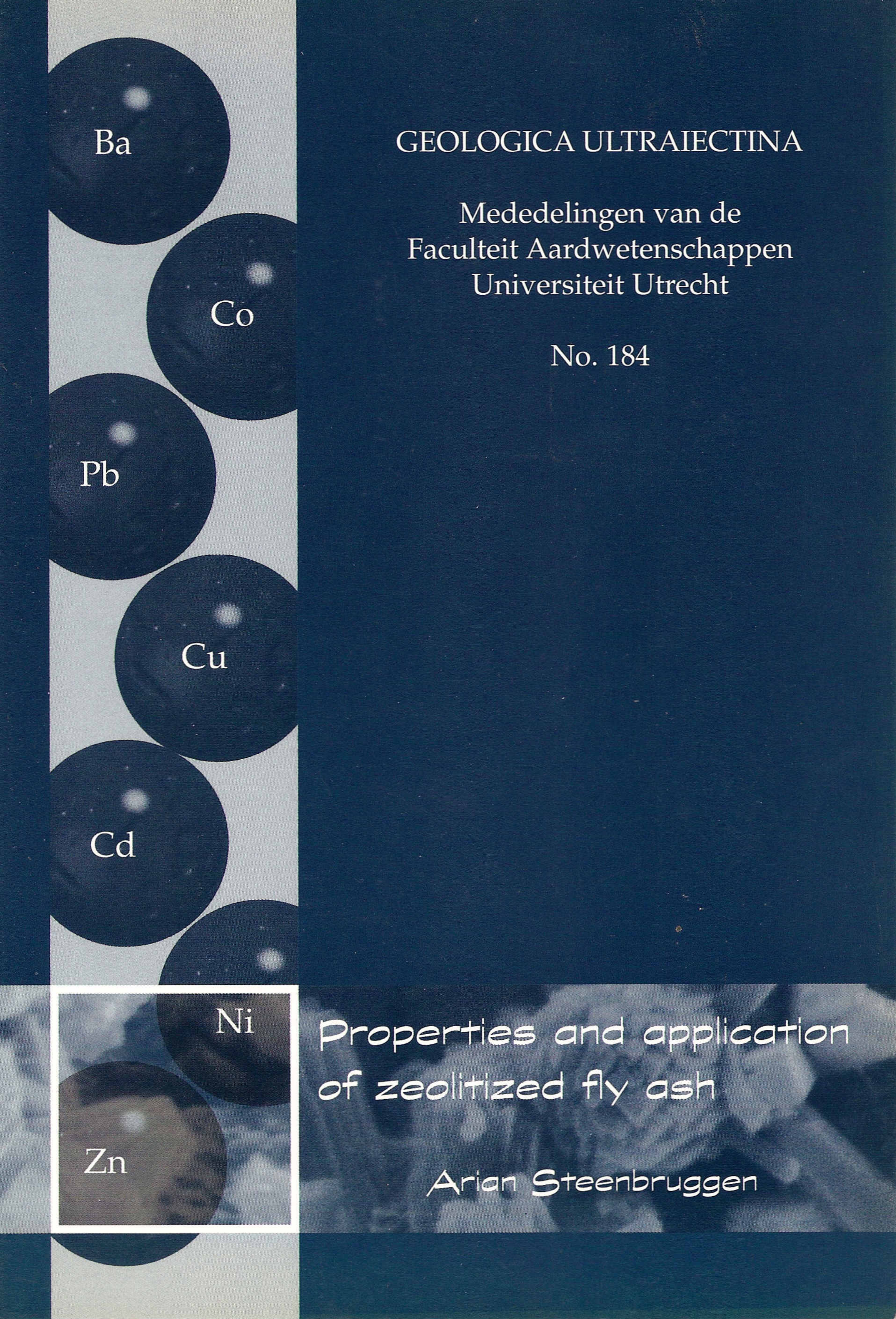

GEOLOGICA ULTRAIECTINA

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No. 184

Properties and application of zeolitized fly ash

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Properties and application of zeolitized fly ash

Eigenschappen en toepassing van gezeolitiseerd vliegas

(met een samenvatting in het nederlands)

PROEFSCHRIFT TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE UNIVERSITEIT UTRECHT
OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. H.O. VOORMA,
INGEVOLGE HET BESLUIT VAN HET COLLEGE VOOR PROMOTIES
IN HET OPENBAAR TE VERDEDIGEN OP MAANDAG 8 NOVEMBER 1999
DES MIDDAGS OM 12:00 UUR

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Gerritdina (Arian) Steenbruggen
Geboren op 20 januari 1969 te Deventer

PROMOTOR: PROF. DR. R.D. SCHUILING

CO-PROMOTOR: DR. S. P. VRIEND

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And why have eyes that see and arms
That reach
Unless you're meant to know there's
Something more?
If not to hunger for the meaning
Of it all,
Then tell me what a soul is for?
Why have the wings unless you're
Meant to fly?
And tell me please, why have a mind,
If not to question why?

Isaac Bashevis Singer
The Yeshiva Boy

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Contents

SUMMARY

The combustion of coal produces large quantities of fly ash. This waste product is at present used for the production of building materials. This use may be reduced for a number of reasons, such as: stricter environmental regulations, changes in combustion techniques and competition with other residual materials. To avoid a future surplus, there is a growing interest in new applications of coal fly ash (CFA). This thesis is the result of a research project carried out to investigate the possibility of using CFA for the synthesis of zeolites.

Chapter 1 is an introduction to this research project and contains background information on the origin and characteristics of fly ash and zeolites. **Chapter 2** describes the (orientation) experiments conducted on the adsorption properties of zeolitized fly ash (ZFA). For this purpose batch-experiments with a number of heavy metals (Ba, Co, Ni and Zn) and ammonium were carried out. In addition, stability experiments were carried out. Adsorption curves of zeolite Na-P1 suggest that the entire Cation Exchange Capacity (CEC) of this product is available for the exchange with heavy metals, if there is an excess of cations in solutions relative to the exchange sites present. In case of an excess of exchange sites relative to cations in solution, the ZFA is capable of removing the heavy metals entirely. The stability experiments show that the ZFA is stable in solution with a pH of 3 or higher.

The results if these experiments show that ZFA is a good adsorbent and has a great potential for the immobilization of pollutants such as heavy metals. In **Chapter 3** the selectivity series for 3 types of ZFA which can be synthesized from fly ash were determined. Knowledge of the selectivity series of the zeolite is important for its application. Batch-experiments with these ZFA's were carried out to study the simultaneous adsorption of Ba, Co, Ni, Zn, Cd and Cu, as representatives for the heavy metals.
The results show the following selectivity series:

for zeolite Na-P1	Ba > Cu > Cd ≈ Zn > Co > Ni
for phillipsite	Cu > Ba > Cd > Zn > Co > Ni
for zeolite K-G	Cu > Ba > Cd > Zn > Co ≈ Ni

These series are similar to the series for the natural zeolite clinoptilolite reported in the literature. As the quantity of adsorbed elements equals the quantity of Na and K released to the solution, the adsorption of the elements is attributed to ion exchange processes.

In Chapter 3 the importance of knowing the selectivity series of ZFA was pointed out when considering possible applications for the ZFA, e.g. to be able to forecast the ecotoxicological risks in using the ZFA as an immobilizer for heavy metals. This selectivity was investigated in batch-experiments. In **Chapter 4** column breakthrough experiments are described in which the ZFA was percolated with an artificially polluted solution, containing Ba, Co, Ni, Zn, Cd, Pb, and Cu. After an initial period, during which these elements were removed from solution, they appeared in the percolate in the reverse order of the selectivity series (thus in accordance

with these series) established by batch experiments earlier. The ZFA uses its complete CEC for the adsorption of the metals (2 meq/g). It is also established that the ZFA, loaded with heavy metals after the column experiments, can be regenerated with a NaCl solution.

For applicability, ZFA has to comply with the environmental regulations. In **Chapter 5** the behavior of heavy metals during the zeolitization process is examined. The leaching behavior of the ZFA was tested by standard column leaching experiments. The release of heavy metals from the coal fly ash is reduced by zeolitization; this reduction is even greater when the CFA is treated with organic extractants prior to zeolitization. In the latter case, the leaching of elements did not exceed the Dutch norms.

Following the research on the properties of the zeolitized fly ash, a number of pilot studies on the application of the product were carried out. **Chapter 6** describes a selection of these studies. These investigations were all carried out with pure zeolite Na-P1, the product of the two-step-zeolitization of fly ash.
Batch-experiments were carried out with wastewater contaminated with color pigments (yellow, red and blue) and reject water from a waste water treatment plant containing a high concentration of ammonium (about 600 mg per liter). It appeared that if the color pigments are not bound to big particles (colloidals) in the solution or organic molecules, the zeolite is able to reduce the pigments in the wastewater to below the current standards. The reject water was purified from ammonium for about 80%, but could possibly be increased to 100% by doing the treatment in more steps.
A column filled with 30 g pure zeolite Na-P1 was percolated with an ammonium containing effluent of a waste water treatment plant until complete breakthrough, then percolated with a regenerating solution containing NaCl. After 5 cycli, steady state was established, which indicates that the quantity of ammonium-cations during the loading of the zeolite is about equal to the quantity of ammonium cations desorbed during the regeneration.

SAMENVATTING

Jaarlijks komt in Nederland zo'n 900 000 ton vliegas vrij bij de verbranding van steenkool in elektriciteitscentrales. Heden ten dage wordt dit restproduct toegepast bij de productie van bouwstoffen (vulmiddel in beton, gedeeltelijk vervangen van cement, kunstgrind). De vraag is echter of in de toekomst deze afzetmarkt voor vliegas wel gegarandeerd blijft. Strengere milieuregels, veranderende verbrandingstechnieken en competitie met andere restproducten kunnen er toe leiden dat in de nabije toekomst een deel van de vliegas niet meer kan worden afgezet. Om een afvalprobleem te voorkomen, bestaat er een groeiende belangstelling voor nieuwe toepassingsmogelijkheden voor vliegas. Dit proefschrift is een deel van het resultaat van een onderzoeksproject dat is uitgevoerd om de mogelijkheden te onderzoeken om vliegas om te zetten in zeoliet (niet het onderwerp van dit proefschrift), en de eigenschappen van de gesynthetiseerde zeoliet te onderzoeken (beschreven in dit proefschrift).

Hoofdstuk 1 geeft een introductie in dit onderzoeksproject en achtergrond informatie over de oorsprong en karakteristieken van vliegas en zeoliet. **Hoofdstuk 2** rapporteert de (oriënterende) experimenten die zijn uitgevoerd om de adsorptie-eigenschappen van de gezeolitiseerde vliegas te bepalen. Voor dit doel zijn batch-experimenten uitgevoerd met een aantal zware metalen (Ba, Co, Ni, Zn) en met ammonium. De resulterende adsorptie-curves laten zien dat de complete uitwisselingscapaciteit (CEC) van de gezeolitiseerde vliegas beschikbaar is voor de uitwisseling met zware metalen, indien meer kationen in de oplossing aanwezig zijn dan beschikbare uitwisselingsplaatsen. Indien meer uitwisselingsplaatsen aanwezig zijn dan kationen in oplossing, dan is de gezeolitiseerde vliegas in staat de oplossing volledig te zuiveren van de zware metalen. Stabiliteitsexperimenten laten zien dat de zeoliet intact blijft in een oplossing met een pH van 3 of hoger.

De resultaten van deze experimenten laten zien dat de gezeolitiseerde vliegas een goede adsorbent is met groot potentieel om verontreinigingen zoals zware metalen vast te leggen. In **hoofdstuk 3** zijn de voorkeursreeksen van 3 types zeoliet gesynthetiseerd uit vliegas bepaald. Voor toepassing van de gezeolitiseerde vliegas in de praktijk is het van belang dat deze reeksen bekend zijn. Batch-experimenten met deze zeolieten zijn uitgevoerd om de simultane adsorptie van Ba, Co, Ni, Zn, Cd en Cu te onderzoeken, als vertegenwoordigers van de zware metalen.
De resultaten van deze experimenten laten de volgende voorkeursreeksen zien:
Voor zeoliet Na-P1 Ba > Cu > Cd ≈ Zn > Co > Ni
Voor phillipsiet Cu > Ba > Cd > Zn > Co > Ni
Voor zeoliet K-G Cu > Ba > Cd > Zn > Co ≈ Ni
Deze reeksen komen overeen met de reeksen voor natuurlijk zeoliet clinoptiloliet, zoals gerapporteerd in de literatuur. Omdat de hoeveelheid door de zeoliet geadsorbeerde elementen ongeveer gelijk is aan de hoeveelheid door de zeoliet aan de oplossing afgestane Na en K, kan de adsorptie van de zware metalen worden toegeschreven aan uitwisseling.

In hoofdstuk 3 is het belang van bekendheid met de voorkeursreeksen aangegeven, vooral om in geval van toepassing de ecotoxicologische risico's van het gebruik van de gezeolitiseerde vliegas te kunnen voorspellen. Deze selectiviteit was bepaald met batch-experimenten. In **hoofdstuk 4** zijn kolom doorbraak experimenten beschreven waarbij de zeoliet is gepercoleerd met een kunstmatig met Ba, Co, Ni, Zn, Cd, Cu, Pb en Cu verontreinigde oplossing. Na een beginperiode, gedurende welke deze elementen door de zeoliet uit de oplossing zijn verwijderd, verschijnen de elementen in het percolaat, en wel in de omgekeerde volgorde van de voorkeursreeks zoals die bij de batch-experimenten is bepaald (en dus in overeenstemming met de voorkeursreeks). De gezeolitiseerde vliegas benut zijn volledige uitwisselingscapaciteit voor de adsorptie van de zware metalen (2 meq/g). Uit regeneratie-expermenten is gebleken dat de gezeolitiseerde vliegas, beladen met zware metalen na de kolom experimenten, kan worden geregenereerd met een NaCl oplossing.

Voor de toepasbaarheid moet de gezeolitiseerde vliegas aan de gestelde milieunormen voldoen. In **hoofdstuk 5** is het gedrag van zware metalen gedurende het zeolitisatieproces onder de loep genomen. Het uitlooggedrag van de gezeolitiseerde vliegas is onderzocht met behulp van standaard kolomuitloogtesten. Hieruit is gebleken dat de uitloging van zware metalen uit vliegas sterk is gereduceerd door de zeolitisatie, en dat deze reductie nog groter is indien de vliegas voorafgaand aan de zeolitisatie is gewassen met organische extractanten. In het laatste geval overschrijdt de uitloging de Nederlandse normen niet.

Aansluitend op het onderzoek naar de eigenschappen van de gezeolitiseerde vliegas, is een aantal praktijkgerichte studies naar toepassingsmogelijkheden uitgevoerd. **Hoofdstuk 6** geeft een selectie weer van deze studies. De uitgevoerde experimenten zijn uitgevoerd met puur zeoliet Na-P1, gesynthetiseerd uit vliegas in een twee-staps proces.
Met afvalwater van de textielverf industrie (bevattend de kleurpigmenten geel, rood en blauw)en met afvalwater van een rioolwaterzuiveringsinstallatie wat ammonium bevat (600 mg/l) zijn batch-experimenten uitgevoerd. Afhankelijk van de combinatie van kleurpigmenten was het afvalwater van de textielverf industrie gedeeltelijk tot onder de norm te zuiveren. Het rioolzuiveringswater was in meerdere stappen volledig te zuiveren van ammonium.
Tenslotte werd een kolom gevuld met puur zeoliet gepercoleerd met hetzelfde afvalwater van een rioolwaterzuiveringsinstallatie (600 mg ammonium /l) tot volledige doorbraak, en vervolgens gepercoleerd met een regeneratie oplossing met NaCl. Na 5 cycli werd een evenwicht bereikt waarbij gedurende het belasten evenveel ammonium wordt geadsorbeerd door de zeoliet als gedurende het regenereren wordt afgegeven.

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) 305-309

At present, approximately 900,000 ton of fly ash is produced by coal combustion in the Netherlands each year. The coal fly ash is used mainly in the production of building materials. In 1996 (Aalbers et al., 1998) 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. The present use of coal fly ash (CFA) is mainly based on its pozzolanic properties, that 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 CFA would (preferably) have higher margins of profit than the present ones and should 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.

$$\text{glass} \rightarrow \text{zeolite} \rightarrow \text{analcime} \rightarrow \text{feldspar}$$

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 CFA (see e.g. Höller and Wirsching, 1985; Singer and Berkgaut, 1995; Amrhein et al., 1996).

To examine the possibilities of zeolite formation from Dutch CFA, a research project at the Utrecht University was started in 1994 in cooperation with and financed by KEMA (Arnhem), with additional financial support from 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 second of these two aims as subject, i.e. the properties and applicability of zeolitized fly ash. Research on the synthesis of zeolite from fly ash was carried out in the same project and 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 synthesis part of the project is the subject of a thesis by Hollman (1999).

This introductory chapter will present background information on the origin and characteristics 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 temperatures of 1300-1500°C are reached (Pietersen, 1993). Figure 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 formation of CO_2, SO_2, 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 in temperature, combustible volatiles in the coal will inflame and coke particles are formed. As combustion proceeds, an increasing amount of coke particles are oxidized and part of the alkalis evaporates (Fraay, 1990). The coarser mineral particles (partially) melt and drop to the bottom of the oven where they are collected 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 are 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%).

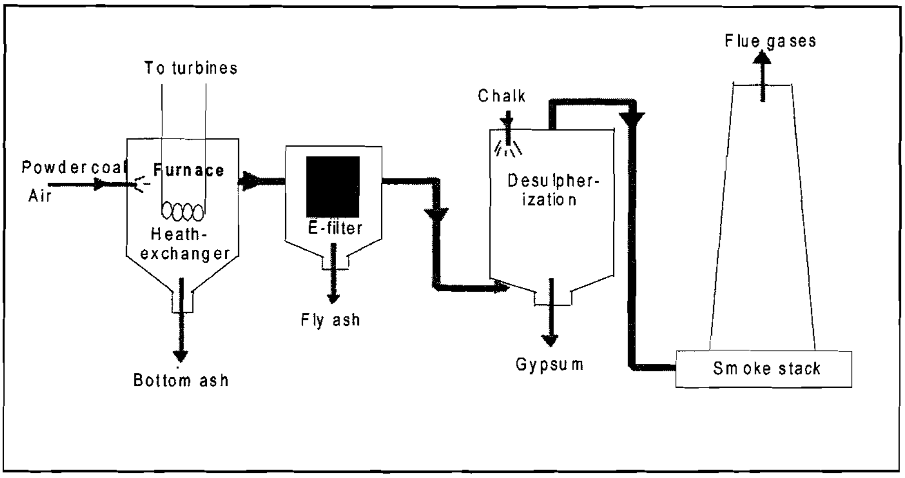


Figure 1 Flow diagram of the coal combustion process in a power station

Physical characteristics

The physical characteristics of CFA (photo 1) 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).

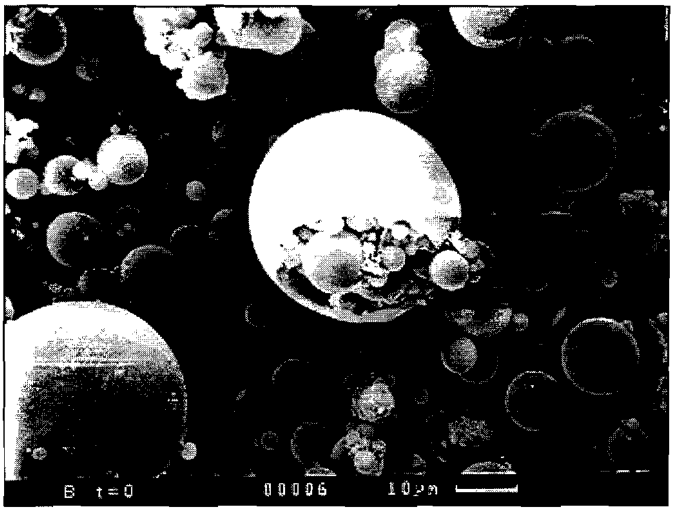


Photo 1: Coal fly ash

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 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 ^{0}C.

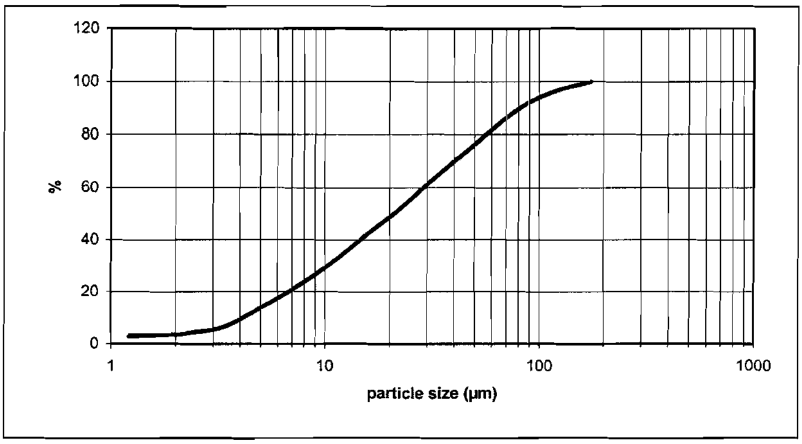


Figure 2 Particle size distribution of CFA (analyzed by Malvern 2600C analyzer)

Structural and mineralogical characteristics

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

- aluminosilicate glass;
- mullite, $Al_{4+2x}Si_{2-2x}O_{10-x}$ 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 through 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 shows 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 wherein 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 3 gives a schematic representation of this model.

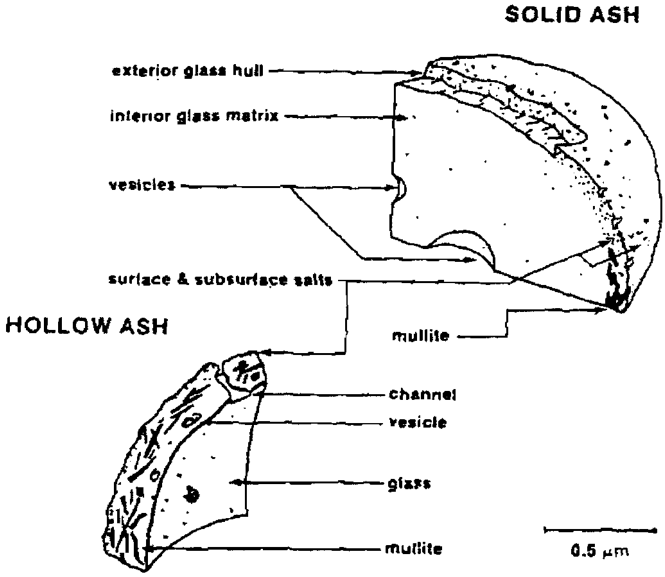


Figure 3 Structural model of CFA particles by Dudas and Warren (1987)

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 various concentrations 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 leacheability. 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.

A major 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 CFA seem only be very limited and are certainly not as large as feared in 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 CFA (VROM, 1998).

Zeolites

Zeolites (photo 2) are aluminosilicates with a skeletal structure that contains channels and cavities occupied by ions and watermolecules. These ions and watermolecules have a considerable freedom of movement and can be exchanged or reversibly dehydrated (Breck, 1974).

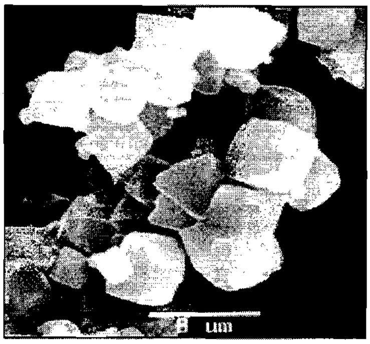
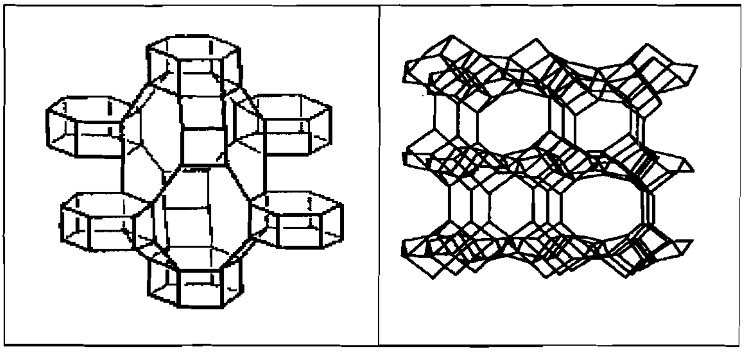


Photo 2 Zeolite X

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 (see figure 4).



A **B**

Figure 4 Examples of zeolite structures (Manly and Holmes, 1989): A) chabazite, B) mordenite

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):

$$M_{x/n}[\mathrm{Al}_x\mathrm{Si}_y\mathrm{O}_{2(x+y)}].p\mathrm{H_2O}$$

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 $\mathrm{AlO_4}$ tetrahedron cannot be directly connected to another $\mathrm{AlO_4}$ 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, natural zeolites are mined (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 with 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 several meq per gram. The magnitude and selectivity of the cation exchange capacity of a specific zeolite depends 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 does 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. Table 2 presents some properties of zeolites.

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 ion exchange materials for use 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 (photo 3) 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 feed, odor control, soil amendment (slow release of fertilizers), desiccation and waste water treatment (adsorption of heavy metals, radioactive isotopes, ammonium).

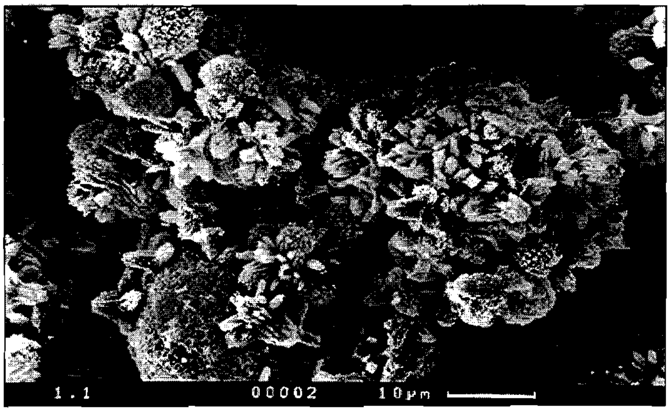


Photo 3 Synthetic zeolite Na-P1 (synthesized from fly ash)

Table 2 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 (A)		Largest molecule adsorbed	Kinetic diameter (A)
							hydrated	dehydrated		
Zeolite Na-P1	$Na_6[(AlO_2)_6(SiO_2)_{10}]\ 15H_2O$	1.1-2.5	4.4	Gismondine	2.01	0.41	3.1 x 4.4 2.8 x 4.9	2.6	H_2O	2.6
Zeolite ZK19	$(Ca,Na_2K_2)_5[(AlO_2)_{10}(SiO_2)_{22}]\ 20H_2O$	1.7-2.4	3.9	Phillipsite	2.15	0.31	4.2 x 4.4 2.8 x 4.8 3.3	?	H_2O	2.6
Zeolite K-G	$K_4[(AlO_2)_4(SiO_2)_8]\ 13H_2O$	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	$K_{42}[(AlO_2)_{42}(SiO_2)_{76}]\ 107H_2O$	?	4.0	Phillipsite	2.18	0.22	3.6	?	SO_2	3.6
Zeolite Li-ABW	$Li_4[(AlO_2)_4(SiO_2)_4]\ 4H_2O$	?	6.9	None	2.27	0.28	?	?	NH_3 (but not N_2)	2.6
Sodalite	$Na_6[(AlO_2)_6(SiO_2)_6]\ 8H_2O$	?	6.0	Sodalite	2.03	0.35	2.2	2.2	H_2O	2.6

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

? = Unknown

Ion exchange in zeolites: theoretical background

Cation exchange reactions can be expressed by the equation (Colella, 1996; Caputo 1995; Breck, 1974):

$$nM^{m+}_{s} + mN^{n+}_{z} = nM^{m+}_{z} + mN^{n+}_{s} \qquad (1)$$

where M and N represent exchanging cations with valences m and n and the subscripts s and z denote the exchanging phases, e.g. solution and zeolite.
The components that take part in equation (1) have a chemical potential μ, which can be expressed as:

$$\mu_i = \mu^{\circ}_i + RT_K \ln(a_i) \qquad (2)$$

where μ_i denotes the chemical potential of species i with activity a_i, μ°_i is the chemical potential under standard conditions, R is the gas constant and T_K is the absolute temperature. At equilibrium applies for equation (1) that the difference in the sum of the chemical potentials multiplied by the appropriate reaction coefficients is zero:

$$n\mu_{m,z} + m\mu_{n,s} - n\mu_{m,s} - m\mu_{n,z} = 0 \qquad (3)$$

The equilibrium constant K can then be expressed as:

$${}^{M}_{N}K = \frac{a^{n}_{M_z} a^{m}_{N_s}}{a^{n}_{M_s} a^{m}_{N_Z}} \qquad (4)$$

where the M and N stacked on each other before K, denote the ion couple the K applies to.

In relation to ion exchange, the equivalent fraction E of a cation is defined as the proportion of the exchange capacity of a phase that is neutralized by that cation, e.g. for M^{m+} in a zeolite:

$$E_{M_z} = \frac{mM_z}{(mM_z + nN_z)} \qquad (5)$$

When considering one cation couple, the preference a zeolite has for adsorbing one of these two, i.e. its selectivity S, can be expressed as the quotient of the equivalent fractions of the phases at equilibrium (Colella, 1996):

$$S = \frac{E_{M_z} E_{N_s}}{E_{M_s} E_{N_z}} \qquad (6)$$

The definition of the selectivity means that it can vary with the size of the actual equivalent fraction and thus with the composition of the exchanging phases. Selectivity is also of influence on the cation exchange capacity of a zeolite actually observed and will cause it to deviate from the total sum of the valences of the cations in the zeolite (which is the value it should theoretically have).

Equation (4) is often (Tsitsihvili et al., 1992) also expressed using E:

$${}^{M}_{N}K = \frac{E^{n}_{M_z} c^{m}_{N_s} \gamma^{n}_{M_z} \gamma^{m}_{N_s}}{E^{m}_{N_z} c^{n}_{M_s} \gamma^{m}_{N_z} \gamma^{n}_{M_s}} \qquad (7)$$

where c denotes the molal concentration in solution and γ denotes the activity coefficient. The

$$K_m = \frac{E^{n}_{M_z} c^{m}_{N_s}}{E^{m}_{N_z} c^{n}_{M_s}} \qquad (8)$$

first part of equation 5 is also known as the mass action coefficient K_m (Townsend, 1991):

Because K_m is defined in terms of concentration it depends on the composition of the exchanging zeolite. This is contrarily to K which is invariant in this respect because of the interactions of the exchanging cations: not the activity but the activity coefficients vary with composition of the zeolite (Townsend, 1991). This has its consequences for the prediction of ion exchange equilibrium, e.g. by geochemical modeling codes such as MINTEQA2. These are commonly based on the evaluation of the free energy, which is directly related to K and which means that the free energy of exchange is also independent of zeolite composition. Nevertheless, the free energy of exchange can be used for the prediction of ion exchange equilibrium, if the following conditions are fulfilled (Townsend, 1991):

1) adequate thermodynamic formulation;
2) accurate experimental data for one set of conditions;
3) accurate activity coefficients for the dissolved salts involved for the conditions for which one wishes to predict.

The retrieval and evaluation of these data is very complexed, especially if multicomponent systems are considered. Some mathematical methods have been developed to predict ternary equilibrium from binary data but according to Townsend (1991) and Caputo (1995) these are less accurate.

Outline of this thesis

As stated in the beginning of this chapter, the interest in new applications for CFA resulted in the research project on which this thesis is based.

In **Chapter 2** a start was made with the investigation on the adsorption properties of the zeolitized fly ash (ZFA). This was done by carrying out batch-experiments with a few heavy metals (Ba, Co, Ni and Zn) and ammonium. Stability experiments were carried out as well. All experiments were meant as a first orientation on the properties of the ZFA.

Because the results of Chapter 2 showed that ZFA is a good adsorbent and has a great potential for the immobilization of pollutants like heavy metals, in **Chapter 3** the selectivity series for 3 types of ZFA that can be synthesized from fly ash were determined. Knowledge of the selectivity series of the zeolite is important for its application. Batch-experiments with these ZFA's were carried out to study the simultaneous adsorption of Ba, Co, Ni, Zn, Cd and Cu, as representatives for the heavy metals.

In Chapter 3 the importance of the selectivity series of ZFA is pointed out when considering possible applications for the ZFA, e.g. to be able to forecast the ecotoxicological risks in using the ZFA as an immobilizer for heavy metals. This is investigated in batch-experiments, as no studies are known on the behavior of ZFA towards heavy metals under (semi) natural conditions. In **Chapter 4** column breakthrough experiments are carried out wherein the ZFA is percolated with an artificially polluted solution, containing Ba, Co, Ni, Zn, Cd, Pb, and Cu. It is also established whether the ZFA, loaded with heavy metals after the column experiments, can be regenerated with a NaCl solution.

For its applicability, ZFA has to comply with the environmental regulations. This is analyzed and discussed in **Chapter 5**. The behavior of heavy metals during the zeolitization process is examined, and the leaching behavior of the ZFA is tested by standard column leaching experiments. Investigated are whether the environmental quality of the CFA improves by zeolitization, and whether this improvement is even better if the CFA is treated with organic extractants prior zeolitization. In all case, the leaching of elements was compared to the Dutch norms.

Following the research on the properties of the zeolitized fly ash (Chapter 2-5), in **Chapter 6** a number of pilot studies on the application of the product are carried out. In this chapter a selection of these studies are described. These investigations are all carried out with pure zeolite Na-P1, the product of the two-step-zeolitization of fly ash (Hollman, 1999; Hollman et al., 1999). These pilot studies are batch experiments to orient on the possibility to remove color pigments from wastewater and a column experiment to orient on the possible use of zeolite as a filter to remove ammonium from wastewater. Both types of experiments give promising results.

Within the framework of the present research, it was not feasible to develop a geochemical model for the prediction of ion exchange equilibrium. Aim of the research carried out was to examine the adsorption properties of zeolitized fly ash, and to determine whether the product is applicable in practice. From the experiments carried out in this work, a K_m can be calculated, but not the K, which is necessary to model eventually the results obtained. After all, the K_m and selectivity vary with composition of the exchanging phases and are ill suited for the prediction of exchange equilibrium.

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2

Properties of zeolitized fly ash

Abstract

In the previous chapter the waste problems of the large quantities of fly ash, a rest product of the combustion of powdered coal, being produced yearly and the possibility of formation of zeolites out of these residues were discussed. Of great importance is the applicability of the product obtained by zeolitization. Alkaline fly ash was treated with a sodium hydroxide solution at a temperature of 150 °C. The formed zeolitized fly ash (ZFA), containing 35% zeolite Na-P1, preliminary batch-experiments with heavy metals and ammonium, and stability experiments were carried out in which the aim was to investigate the possibility to use this ZFA as an immobilizer for environmental pollutants.
Adsorption curves of ZFA, resulting from the study carried out here, suggest that the complete CEC of this product is available for the exchange with heavy metals if there is an excess of cations in solutions relative to the available exchange sites. In case there is an excess of exchange sites relative to cations in solution, the ZFA is capable to remove the complete quantity of heavy metals (present as cations) from the solution. The stability experiments show that the ZFA is stable in solution at a pH of 3 or higher. Furthermore, it appears to be important to take into account that precipitates may form, at the high pH of the solution with suspended ZFA. However, this study proves that zeolitized fly ash has an interesting potential to immobilize pollutants.

Key words: zeolitized fly ash, CEC, adsorption, heavy metals, ammonium, stability

Introduction

In the previous chapter the waste problem of the large quantities of fly ash being produced yearly and the possibility of formation of zeolites out of these residues were discussed. Of great importance is the applicability of the product obtained by zeolitization. The applicability is mainly determined by the cation exchange capacity (CEC), because this determines its capacity in adsorbing elements, and by the fact whether or not these exchange sites are available for the adsorption of the elements studied. In this chapter the first investigations into the cation exchange properties of the zeolitized product for heavy metals and ammonium are described in general terms (KEMA, 1993, 1994, 1994a, 1994b, 1995a). The main question is whether, like reported in some publications (Manly, 1989; Mondragon, 1990; Singer, 1995) the zeolitized fly ash (ZFA) is suitable for the immobilization of heavy metals. If this is the case, of course the magnitude of its adsorbing capacity is of great relevance. The experiments described in this chapter were among the first of the present research project, and are an orientation study into the properties of the ZFA (the zeolitization was the other part of this project, see Hollman, 1999), i.e. the capacity to adsorb heavy metals and NH_4, and to check the stability of ZFA at different acidities.

For this purpose, cation exchange properties were examined by carrying out batch-experiments in which the cation exchange curves for a number of heavy metals and NH_4 were determined. The stability of the ZFA was tested by batch-experiments as well.
Experiments with the heavy metals were carried out with an excess and a deficit of cation exchange sites relative to the quantity of cations in solution, in order to examine the affinity of the ZFA to adsorb heavy metals as well as to test the availability of the CEC to adsorb heavy metals. The curves of cation exchange were obtained for the cations of Ba, Co, Ni and Zn. These elements were chosen to represent the heavy metals in general. The experiments with ammonium were carried out to examine the affinity of ZFA for ammonium, an important component of for example sewage water.

Materials and Methods

All experiments were carried out with one zeolitized product consisting of 32% zeolite Na-P1. This product was formed during the treatment of fly ash (derived from the combustion of powdered coal at a temperature of 1500 °C) during 24 hours in a 2 M NaOH solution at 150 °C (Hollman, 1999). The CEC of the product was 1.6 meq per gram (determined by the International Soil Reference and Information Center (ISRIC) in Wageningen, the Netherlands, applying the ammonium acetate method (ISRIC, 1992) after samples were washed with 80% alcohol to remove excess salt).
The set up of the batch experiments is partially taken from the literature, mainly after Loizidou, 1989.

Batch-experiments with excess CEC

About five times more exchange sites of the ZFA (excess CEC) were available than there were cations in solution in these experiments. Fifty ml of a solution of 50 mg/l for one particular metal cation in the form of its nitrate salt, was added to 0.25 gram of the ZFA. Also 50 ml of a mixed solution of the metals studied previously (50 mg/l for each metal) were equilibrated with the zeolitized product. The equilibrations were performed for the time intervals of 1, 5, 10, 20, 60 minutes and 24 hours. Duplicates for each point were carried out (2 experiments for each time interval). At the appropriate time, the two phases were separated by high pressure filtration through a 0.45 μm porous membrane.

Batch-experiments with deficit CEC

In these experiments, about 10 times less exchange sites of the ZFA (deficit CEC) were available than there were cations in solution. Fifty ml of a solution of 500 mg/l for one particular metal cation originating from its nitrate salt, was added to 0.1 g of the zeolitized product. Also 50 ml of a mixed solution of the metals studied previously were equilibrated with the zeolitized product. In this case, the concentration of the solution was 500 mg/l for each metal. The equilibrations were performed for the time intervals of 1, 5, 10, 20, 60 minutes and 24 hours. Duplicates for each point were carried out. At the appropriate time, the two phases were separated by high pressure filtration through a 0.45 μm porous membrane.

Batch-experiments with ammonium

Half as many exchange sites (deficit CEC) of the ZFA were present than there were ammonium-cations in solution in these experiments. Hundred ml of a solution of 80 mg NH_4^+/l was added to 0.1 gram of the ZFA. The equilibrations were performed for the time intervals of 1, 5, 10, 20, 60 minutes and 24 hours. Duplicates for each point were carried out. At the appropriate time, the two phases were separated by high pressure filtration through a 0.45 μm porous membrane.

In table 1 an overview is given of the experimental conditions of the above mentioned experiments. In the initial solutions and the solutions after the exchange the pH was measured, and were analyzed by ICP-AES for a wide range of elements. XRD patterns from the residues after the exchange shows that the procedures have no noticeable effect on the content and structure of zeolite in the samples.

Stability experiments

To seven 0.25 g quantities of ZFA 50 ml demineralized water with pH 7, 6, 5, 4, 3, 2, and 1 was added. The suspensions were equilibrated for one hour. Afterwards, the two phases were separated by high-pressure filtration through a 0.45 μm porous membrane. The solid phase was dried, weighted, and analyzed by XRD.

Table 1: Batch-experiments: Overview of the experimental conditions of the experiments with excess CEC, deficit CEC, and with NH_4

Type experiment	Tested elements	Conc. of the elements in solution			reaction mixture			L/S	reaction time
		mg/l	meq/l	meq/g	volume (ml)	zeolite (g)	CEC present (meq/l)		(min.)
metals and excess CEC	Ba	50	0.73	0.15	50	0.25	8.0	200	1,5,10,20, 60, 1440
	Co	50	1.70	0.34					
	Ni	50	1.70	0.34					
	Zn	50	1.53	0.31					
metals and deficit CEC	Ba	500	7.30	3.65	50	0.1	3.2	500	1,5,10,20, 60,1440
	Co	500	17.0	8.50					
	Ni	500	17.0	8.50					
	Zn	500	15.3	7.65					
NH_4 and deficit CEC	NH_4	80	4.44	4.44	100	0.1	1.6	1000	1,5,10,20, 60,1440

Results and discussion

In this paragraph the results are presented and discussed per type of experiment. Results are given in percentages.

<u>Batch experiments with excess CEC</u>

The concentration of the test elements were all below detection after these experiments with excess CEC. Thus, the total quantity of test elements is adsorbed from the solution by the ZFA. Generally, after 1 minute there is more adsorbed than after 24 hours (the filtrate was analyzed, difference in concentrations 0.2%): apparently there is a little desorption during the adjustment of the equilibrium.

Besides adsorption of the test elements from the solution, elements are also released from the ZFA to the solution, e.g. S, P, Si, Ca, Na and K. Three explanations for this process can be given:

- The ZFA consists of 35% zeolite and 65% other mineral phases, dissolution of these latter will release additional elements;
- The ZFA is formed in a solution with excess sodium. After filtration and drying, the product will still contain some NaOH;
- Because of the exchange process which takes place, there will be a release of the exchangeable cations like Na, K, Ca and Mg (Breck, 1974; Gottardi, 1985).

At the prevailing concentrations it can be expected that the disappearance of elements from the solution can be ascribed to the exchange process, while about the same quantity of test elements were taken from the solution as there were exchangeable cations (Na in this case) released to the solution.

Batch-experiments with deficit CEC

These experiments were carried out in order to determine whether the complete CEC can be used for the adsorption of the elements from the solution. For this purpose, less exchange sites of the ZFA (deficit CEC) were provided than there were cations in solution.
Table 2 gives an overview of the main results of these experiments. For each tested element its adsorbed quantity is given as percentage of the CEC.

Table 2: Experiments*) with deficit CEC: Adsorption of the elements from the solution in meq/g and in percentage of the CEC

Tested element	starting solution (meq/l)	Adsorption after 24 h				Occupation of the CEC	
		Single elements		Mixed elements		single elements	mixed elements
		Meq/l	meq/g	meq/l	Meq/g	(%)	(%)
Ba	7.3	6.0	3.0	3.4	1.7	~100	Total ~100
Co	17.0	7.6	3.8	0.0	0.0	~100	
Ni	17.0	8.1	4.1	0.0	0.0	~100	
Zn	15.3	9.0	4.5	3.8	1.9	~100	

*) The pH (roughly about 8 after the reaction time) in de reaction solution was not buffered, but was controlled by the processes taking place. The CEC is 1.6 meq/g, in these experiments means this 3.2 meq/l.

In an ideal situation the decrease of the concentration of the tested elements in solution equals the increase of Na and K, while the maximal adsorption which are reached, equal the CEC. If this would be the case, then the only process that takes place is cation exchange, no precipitation takes place and the entire CEC is used for adsorption. However, this is not the case. In general, a higher concentration of elements was adsorbed from the solution than can be explained by cation exchange alone, i.e. the quantity of cations adsorbed was larger than the CEC-value (1.6 meq per gram). Figure 1 and 2 show this.
Figure 1 shows the decrease of the concentration of the elements (meq/g) in solution tested separately, as a function of time. Figure 2 shows the decrease of the concentration of the mixed elements (meq/g) in solution. Both figures show as well the increase of the concentration of potassium and sodium (meq/g) in solution as the CEC (meq/g) value of the tested product, a measure for the ion exchange process to be taken place (Assenov, 1988).

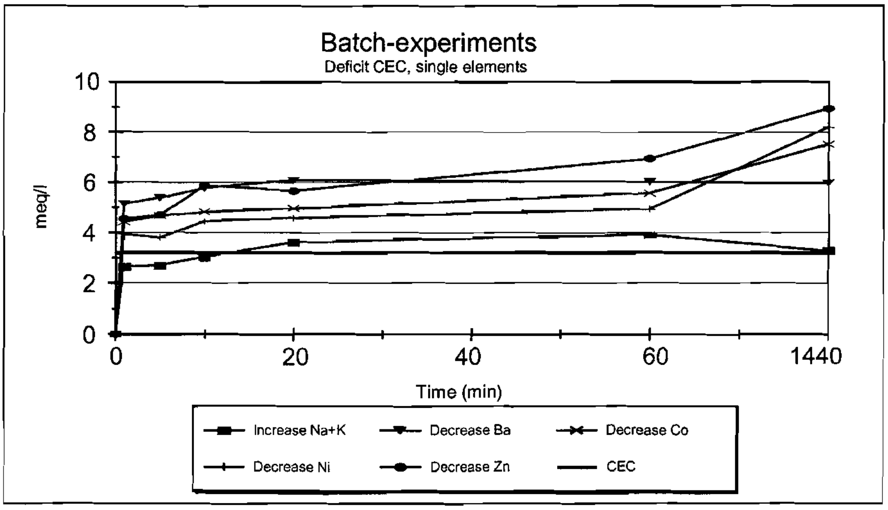

Figure 1 The decrease of the elements Ba, Co, Ni, Zn, and the increase of Na+K in solution, in case of the single tested elements

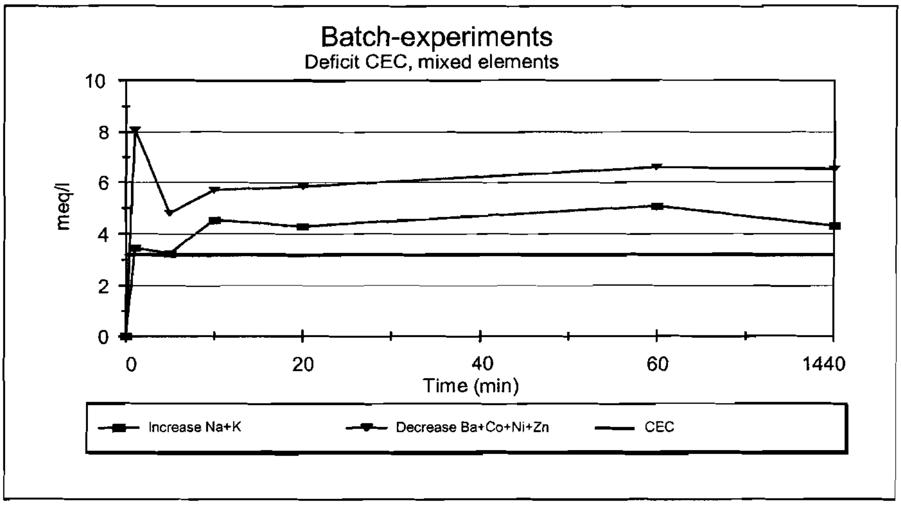

Figure 2 The increase of the sum of Na+K, and the decrease of the sum of Ba+Co+Ni+Zn in solution

As can be seen from figures 1 and 2, the decrease of the tested elements and the increase of Na and K are not equal. However, the increase of Na and K in most cases ends at the CEC-value. From this it could be concluded that cation exchange takes place (Colella, 1996; Breck, 1974) and the complete CEC is used up by the metals. Figure 3a-d show the concentration progress of the test and exchangeable elements in solution.

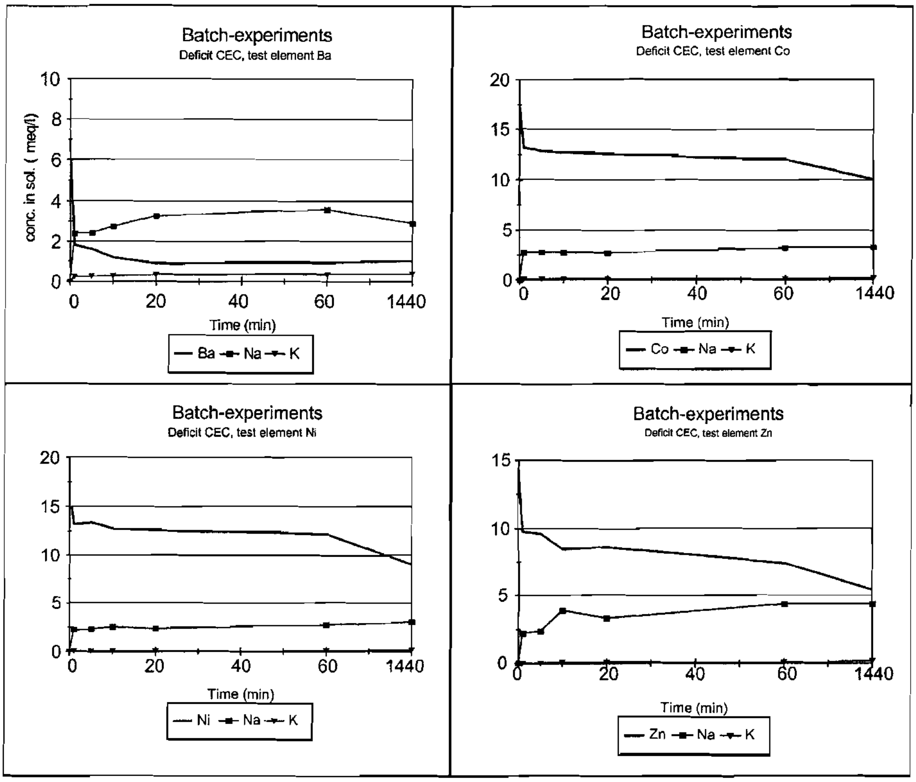

Figure 3a-d: Concentration of the test element and the exchangeable elements in solution during the batch-experiments. Remarkable is the same patterns for increase and the mirror image of the decrease of elements

From figure 3 can be seen that the patterns of concentration of the test elements and Na are very much similar, as the mirror image. This points out that it is very likely that exchange is the predominant process in the removal of elements from the solution (Colella, 1996).

From table 2, and from figures 1 and 2, it can be concluded that the removal of the tested elements is in all cases higher than could be expected from the CEC-value. From this it is clear that, besides exchange-processes, also other processes take place (KEMA, 1995a). One possibility is that the pH of the solutions after the reaction-times and the high concentrations of metals and soluble parts of the ZFA, cause precipitation of mineral phases. In order to find out what exactly causes this difference, the results of the experiments were modeled by the use of the thermodynamical equilibrium model MINTEQA2. The main results are presented in table 3. The model calculated an oversaturation in some cases which matched the 'missing' quantity of the elements. However, the precipitation reactions did not affect the exchange reactions since the total quantity of Na and K release to the solution was equal to the CEC-value.

Table 3 Experiments with deficit CEC: Calculations of the oversaturations (MINTEQA2)*)

Tested element	Oversaturated mineral phase	Calculated decrease of the tested element from the solution		
		mg/l	mmol/l	meq/l
Ba^{2+}	barite ($BaSO_4$)	1098	8	16
	witherite ($BaCO_3$)*	466	3.4	6.8
Ni^{2+}	$Ni(OH)_2$	410	7	14
	Ni_2SiO_4	998	17	34
	$Ni_4(OH)_6SO_4$	58	1	2
	$Ni_3(PO_4)_2$	147	2.5	5
Zn^{2+}	Willemite (Zn_2SiO_4)	109	1.7	3.3
	$Zn_3(PO_4)_2$	196	3	6

*) pH fixed on the pH measured after 24 hours. The CEC of the ZFA is 1.6 meq/g, this means that per liter there is 3.2 meq CEC present (suspended is 0.1 gram ZFA in 50 ml)

Batch-experiments in order to investigate the affinity of the ZFA to adsorb NH_4

Half as many exchange sites (deficit CEC) were available than there were NH_4-cations in solution, in these experiments. Table 4 shows the results of these experiments. After 5 minutes the ZFA adsorbed about 30 mg/g, comparable to 1.7 meq/g. Since the CEC of the product is 1.6 meq/g, evidently the exchange sites seems to be utilized after 5 minutes.

Table 4 Batch-experiments with NH_4: Adsorption of NH_4 by ZFA and occupation of the CEC

Adsorbed by ZFA	Reaction period (minutes)					
	1	5	10	20	60	1440
In % from starting solution	38	38	31	33	31	18
% occupation of the CEC	~100	~100	90	94	90	50

No precipitation reactions with the NH_4-cation are expected, because of the high solubility of NH_4 compounds. Thus, disappearance of NH_4 from solution is completely ascribed to exchange processes. Therefore, there are no analyses of other elements than NH_4 available from these experiments.

The results in table 4 show that during the first 5 minutes of the experiments more NH_4 is adsorbed than after a longer reaction-period, i.e. during this adjustment there is desorption as well. Within 1 hour still 90% of the CEC or more is used, but after 24 hours, this is 50%. This behavior can not be explained with these experiments, but this has to be taken into account when more experiments with NH_4 are carried out in further research. However, in practice the contact period of the zeolite with a solution will be no longer than a few minutes. By later experiments (see chapter 6) it was shown that zeolite is capable to adsorb the complete quantity from the solution, but in more than 1 step. During every step 10% of the original concentration is left.

It was beforehand expected that the CEC would not be available for the full 100%, considering the smaller charge of the NH_4-cation compared to that of most metal-cations, and the eventual difficulty for the relatively big NH_4-cation to migrate into the zeolite-apertures (Breck, 1974; Colella, 1996; Gottardi, 1985; Manly, 1989). But these tests show that there are no problems for using this ZFA as an adsorbent for ammonium, however the ideal contact time has to be determined.

Stability experiments

The stability experiments were carried out by putting some ZFA in demineralized water with different pH values. In table 5 the results of these experiments are shown.

Table 5: Batch-experiments: stability experiments with ZFA suspended in solutions of different acidity

Demineralized water pH	ZFA added (g)	weight after 1 hour equilibration (g)	Na-P1 in the solid phase after experiment*) (%)	Percentage Na-P1 left of start quantity (%)
7	0.25	0.23	35	100
6	0.25	0.22	35	100
5	0.25	0.23	35	100
4	0.25	0.21	35	100
3	0.25	0.22	35	100
2	0.25	0.19	26	74
1	0.25	0.07	0	0

*) The percentage of the zeolite Na-P1 in the untreated ZFA is 35%

From these results it can be seen that zeolite Na-P1,the zeolite phase in the ZFA, is not stable in a solution with a pH lower than 3. It has to be noted that the pH was not kept at the starting pH, so it can be expected that this ZFA is already unstable at a higher pH, when the pH is kept at a constant level. The loss of weight listed in the third column is ascribed to the dissolution of phases in the ZFA, including Na-P1.

Conclusions

From the described batch-experiments, carried out for a general insight into the properties of zeolitized fly ash, this product appears to be well suited for the immobilization of environmental pollutants like heavy metals and NH_4. The experiments described in this chapter point out:

- In case excess exchange sites are present relative to the quantity of cations in solution, heavy metals can be completely removed from the solution;
- From the experiments with deficit exchange sites it appears that the complete cation exchange capacity can be used for the exchange with heavy metals, as well as for the exchange with NH_4;
- The stability tests show that this ZFA, and probably all ZFA which is formed at high pH, must not be brought into contact with solutions with a pH value lower than ca.3.

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3

Selectivity of zeolitized fly ash in adsorbing heavy metals

Abstract

The simultaneous adsorption of Ba, Co, Ni, Zn, Cd, Cu by three types of zeolitized fly ash (ZFA: zeolite Na-P1, phillipsite, zeolite K-G) was investigated in order to derive the selectivity series for these zeolites and metals. Adsorption (batch) experiments with 10 mg ZFA in 50 ml of a solution of 3 elements (each 0.4 meq/l) out of the 6 mentioned elements were carried out. Every possible combination was tested, as well as every single element (0.4 meq/l) with the three types of zeolitized fly ash.
The results show the following selectivity series:

for zeolite Na-P1: Ba > Cu > Cd ≈ Zn > Co > Ni
for phillipsite: Cu > Ba > Cd > Zn > Co > Ni
for zeolite K-G: Cu > Ba > Cd > Zn > Co ≈ Ni

These series are similar with series found in the literature, however those tests were carried out in most cases with the natural zeolite clinoptilolite. The adsorption of the elements is attributed to ion-exchange processes, since the quantity of adsorbed elements equals the quantity of Na and K that is released to the solution.

Key words: zeolitized fly ash, adsorption, cation exchange capacity, selectivity series

Introduction

Zeolitized fly ash (ZFA) is a very good adsorbent (see Chapter 2) and has great potential for the immobilization of pollutants like the heavy metals. In case of excess exchange sites relative to the quantity of cations in solution, heavy metals are removed from the solution for over 99% and the complete cation exchange capacity (CEC) is available for the exchange with heavy metals. From literature it can be concluded that for zeolites and ZFA's the adsorption characteristics for the heavy metals vary (Amrhein, 1996; Breck, 1974; Colella, 1996, Loizidou, 1989; Singer, 1995; Zamzow, 1992). The knowledge of the selectivity series of the zeolite is of importance for the application of the product. In case all adsorption sites are used up, the zeolite will first release the elements to which it has the least affinity. These kinds of characteristics have to be taken into account in e.g. the calculation of ecotoxicological risks. In this chapter the selectivity series for the adsorption of Ba, Co, Ni, Zn, Cd, and Cu for three different types of ZFA are investigated. This is done by carrying out adsorption (batch) experiments with zeolite Na-P1, phillipsite and zeolite K-G in a solution containing 3 elements out of the 6 mentioned above. Every possible combination is tested. The results are compared with the results described in the literature.

Materials and Methods

The selectivity series are investigated for three ZFA's:

- Zeolite Na-P1, which is formed during the treatment of fly ash for 24 hours with a 2M NaOH solution at 150°C;
- Phillipsite, which is formed during the treatment of fly ash for 168 hours with a solution with 1.3 M NaOH and 0.7 M KOH at 90°C;
- Zeolite K-G , which is formed during the treatment of fly ash for 72 hours with a 2M KOH solution at 90°C.

The CEC's of the used zeolitized fly ashes are: zeolite Na-P1 2.74 meq/g, phillipsite 2.52 meq/g, and zeolite K-G 2.48 meq/g. The CEC of the products is determined by the International Soil Reference and Information Center (ISRIC) in Wageningen (Netherlands), applying the ammonium acetate method (ISRIC, 1992) after samples were washed with 80% alcohol in order to remove excess salt.

The selectivity series for the adsorption of Ba, Co, Ni, Zn, Cd, and Cu are established by the equilibration of 10 mg of the zeolite product with 50 ml of a solution containing three of the elements. Every possible combination of three elements out of six is tested (table 1).

In order to be able to compare the results of the experiments with the combination of elements to the results of the same test with only 1 element (carried out to illustrate the behavior without competition) these experiments are also carried out for the three ZFA's with the single elements, at the same concentration for each element (about 0.4 meq/l). All experiments are carried out in duplo.

Table 1 Selectivity series experiments: overview of the tested combinations of elements (every element comes up 10 times).

Ba Co Ni	Ba Ni Zn	Ba Zn Cu	Co Ni Cu	Ni Zn Cd
Ba Co Zn	Ba Ni Cd	Ba Cd Cu	Co Zn Cd	Ni Zn Cu
Ba Co Cd	Ba Ni Cu	Co Ni Zn	Co Zn Cu	Ni Cd Cu
Ba Co Cu	Ba Zn Cd	Co Ni Cd	Co Cd Cu	Zn Cd Cu

The suspensions are equilibrated for 24 hours and afterwards filtrated under high pressure through a 0.45 µm porous membrane. The resulting solutions are analyzed by ICP-AES and the pH is measured.

The concentration of each element in the starting solutions was about 0.4 meq/l (about 1.2 meq/l in total, exact concentrations are given in the results) which is based on the following considerations. The present CEC of the ZFA's in suspension is 0.5 meq/l. The concentration of each element is more than half of the CEC available per liter, but less than the total CEC per liter (0.5 meq/l). This is to derive the preference of the zeolite for the different elements. There is an excess of cations (1.2 meq/l) in solution, which insures the effect that not all cations can be adsorbed, and thus preference of the ZFA for the different elements can be studied. Table 2 gives an overview of the concentrations per element in meq/l and mg /l. A pH of 6 is chosen for the experiments because, according to calculations with the computer code MinteqA2, at this acidity and at this concentration level of cations and zeolite, all test-elements remain in solution and are present as 'free' cations. The pH was maintained at 6 by adding HNO_3.

Table 2 Selectivity series experiments: The concentrations of the tested elements

Tested element	mg/l	meq/l
Ba	27.5	0.4
Co	11.8	0.4
Ni	11.7	0.4
Zn	13.1	0.4
Cd	22.5	0.4
Cu	12.7	0.4
tested ZFA	200	0.5

Results and discussion

Appendices 3.1, 3.2, 3.3, and 3.4 give the raw analytical data (in mg/l) of these selectivity series experiments. In the tables 3, 4, 5, and 6 these data are converted to the quantities of cations adsorbed from or released to the solution. The part of the CEC utilized by the test elements during these experiments is calculated and also given in these tables. From the tables

3, 4, 5, and 6 it is evident that ZFA has a preference for the adsorption of one element above the other. Also it can be seen that in these three ZFA's, the exchangeable cations Na, K and Ca (originating from the ZFA) are released to the solution; therefore it can be stated that exchange has taken place (Colella, 1996; Breck, 1974). In the following the results of the experiments with the single elements are discussed, as well as the results with the combination of elements per type of ZFA, which will be compared to each other.

Single elements

Figure 1 shows the results of the experiments carried out with the single elements. Ba, Zn, Cd, and Cu were adsorbed from the solution for about 90%, whereas for Co this was 83% and for Ni 76%. These results, shown as well in table 3, demonstrate that every separate element will be adsorbed for more than 75% from the solution. Therefore the cause of e.g. the adsorption of only about 20% for Ni in case of testing this element at the same time with others (combination of 3 elements) is competition. Na-P1 has the lowest affinity for Ni, therefore other elements will impede the adsorption of Ni.

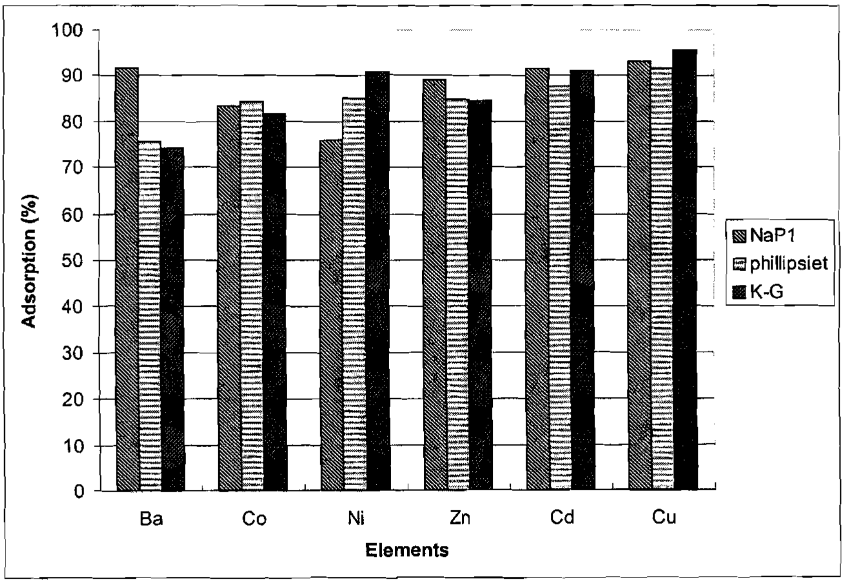

Figure 1 Adsorption of the single elements per type of ZFA

Table 3 Selectivity experiments with zeolite Na-P1, phillipsite and zeolite K-G: Experiments with the single elements
Overview of the results*)

Zeolite Tested	element tested	Ba			Co			Ni			Zn			Cd			Cu			Total adsorbed from solution meq/g	Total increase Na+K+Ca meq/g	Used exchange sites %
		conc. filtr. meq/g	adsorbed		conc. filtr. meq/g	adsorbed		conc. filtr. meq/g	Adsorbed		conc. filtr. meq/g	Adsorbed		conc. filtr. meq/g	Adsorbed		conc. filtr. meq/g	adsorbed				
			meq/g	%		meq/g	%		meq/g	%		meq/g	%		meq/g	%		meq/g	%			
NaP1	Ba	0.19	2.14	92																2.15	3.42	63
	Co				0.36	1.75	83													1.75	2.56	68
	Ni							0.51	1.60	76										1.60	2.43	66
	Zn										0.20	1.63	89							1.65	2.47	67
	Cd													0.15	1.62	92				1.60	2.50	64
	Cu																0.11	1.57	93	1.55	2.62	59
Phillipsite	Ba	0.57	1.76	76																1.75	3.47	50
	Co				0.33	1.77	84													1.75	2.54	69
	Ni							0.31	1.80	85										1.80	2.48	73
	Zn										0.28	1.56	85							1.55	2.25	69
	Cd													0.22	1.54	88				1.55	2.39	65
	Cu																0.14	1.55	92	1.55	2.63	59
K-G	Ba	0.60	1.73	74																1.75	2.80	62
	Co				0.39	1.72	82													1.70	2.30	74
	Ni							0.19	1.92	91										1.90	2.36	81
	Zn										0.28	1.55	85							1.55	2.12	73
	Cd													0.16	1.61	91				1.60	2.13	75
	Cu																0.07	1.62	96	1.60	2.37	68
Starting solution		2.35			2.10			2.10			1.85			1.75			1.70					

*) conc. filtr.= concentration in the solution after the experiment after filtrating
adsorption = adsorption of the element from the solution by the zeolite, given in meq/g and in % from the starting solution
the last three columns present respectively the sum of the adsorbed test elements, the sum of the dissolved Na+K+Ca and the percentage of the exchange sites occupied by the test elements

Zeolite Na-P1

The uptake of elements from the solution is proved always to be about equal to the release of Na, K, and Ca to the solution (see table 4). This suggests that only ion-exchange has taken place and no other reactions. In addition, the release of the exchangeable cations (and the adsorption of heavy metals) roughly equalizes in most cases the CEC value of the ZFA. The combinations of elements with Ni but without Ba do not occupy the complete CEC, probably because of the low affinity of Ni to adsorb on the ZFA whereas the other 2 elements can not occupy all present exchange sites. Figure 1 shows the uptake of test-elements by zeolite Na-P1. From this figure it can be deduced that the order of preference of adsorption for the tested elements by zeolite Na-P1 is as follows:

Ba > Cu > Cd ≈ Zn > Co > Ni

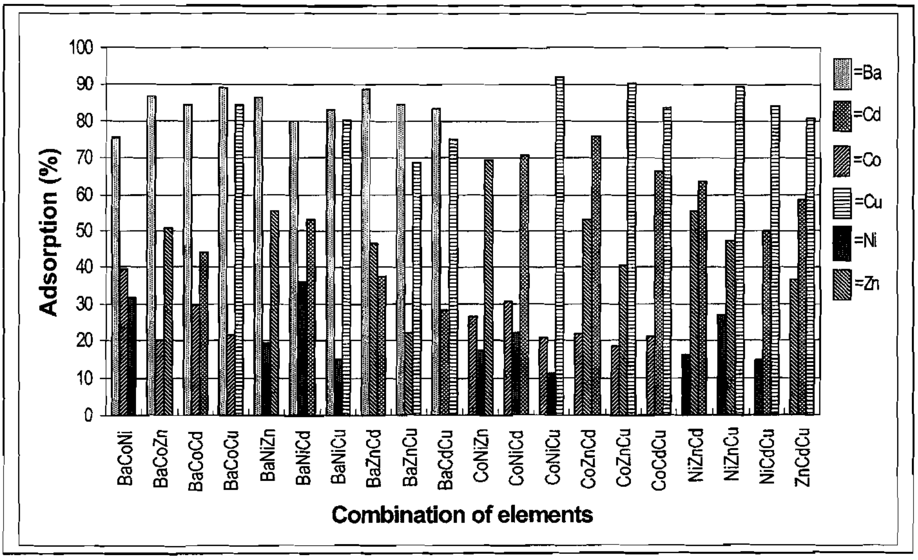

Figure 1 Adsorption of test-elements by zeolite Na-P1

Ba appeared to be taken up from the solution for 80-85%, Cu for 75-85%, Cd for 50-70%, Zn for 20-60%, Co for 20-30% and Ni for 10-25%.

Table 4 Selectivity experiments with zeolite Na-P1: Overview of the results*) compiled from the results in appendix 3.1

	Ba			Co			Ni			Zn			Cd			Cu			Total adsorbed from solution	Total increase Na+K+Ca	Used exchange sites
Element combination	Conc. filtr. meq/g	adsorbed meq/g	%	conc. filtr. meq/g	adsorbed meq/g	%	conc. filtr. meq/g	adsorbed meq/g	%	conc. filtr. meq/g	adsorbed meq/g	%	Conc. Filtr. Meq/g	adsorbed meq/g	%	conc. filtr. meq/g	adsorbed meq/g	%	meq/g	meq/g	%
BaCoNi	0.44	1.44	76	1.13	0.75	39	1.13	0.52	32										2.71	2.62	100
BaCoZn	0.23	1.64	87	1.49	0.38	20				0.79	0.81	51							2.84	2.74	100
BaCoCd	0.27	1.60	84	1.31	0.56	29							0.78	0.62	44				2.78	2.70	100
BaCoCu	0.18	1.69	89	1.47	0.41	22										0.25	1.35	84	3.45	2.63	100
BaNiZn	0.24	1.64	86				1.33	0.32	19	0.71	0.89	55							2.85	2.79	100
BaNiCd	0.35	1.52	80				1.05	0.60	36				0.66	0.74	53				2.86	2.81	100
BaNiCu	0.30	1.58	83				1.40	0.25	15							0.32	1.28	80	3.11	2.80	100
BaZnCd	0.19	1.69	89							0.85	0.75	47	0.87	0.53	38				2.96	2.80	100
BaZnCu	0.27	1.60	84							1.24	0.36	22				0.50	1.10	69	3.06	2.69	100
BaCdCu	0.29	1.59	83										1.00	0.40	28	0.40	1.20	75	3.19	2.78	100
CoNiZn				1.37	0.51	27	1.36	0.29	18	0.49	1.11	69							1.90	1.96	72
CoNiCd				1.29	0.58	31	1.29	0.36	22				0.41	0.99	71				1.93	1.85	68
CoNiCu				1.48	0.40	21	1.46	0.19	11							0.12	1.48	92	2.06	1.99	73
CoZnCd				1.46	0.41	22				0.75	0.85	53	0.34	1.06	76				2.32	2.40	88
CoZnCu				1.52	0.35	18				0.95	0.65	40				0.15	1.45	90	2.44	2.51	92
CoCdCu				1.47	0.40	21							0.47	0.93	66	0.26	1.34	84	2.67	2.63	100
NiZnCd							1.39	0.26	16	0.71	0.89	55	0.51	0.89	64				2.04	1.96	72
NiZnCu							1.21	0.44	27	0.84	0.76	47				0.17	1.43	89	2.63	2.63	100
NiCdCu							1.41	0.24	15				0.70	0.70	50	0.25	1.35	84	2.29	2.26	82
ZnCdCu										1.01	0.59	37	0.58	0.82	58	0.31	1.29	81	2.69	2.71	100
starting solution	1.88			1.90			1.65			1.60			1.40			1.60					

*) conc. filtr.= concentration in the solution after the experiment after filtrating
adsorption = adsorption of het element from the solution by zeolite Na-P1, given in meq/g and in % from the starting solution
the last three columns present respectively the sum of the adsorbed test elements, the sum of the dissolved Na+K+Ca and the percentage of the exchange sites occupied by the test elements

Phillipsite

From table 5 can be seen that the CEC of phillipsite is not completely used (average about 80%), and that adsorption is a little lower than the release. The cause of the latter is most likely the constant addition of H^+, which apparently is able to occupy a part of the exchange sites of phillipsite. The reason that not all exchange sites are occupied by the test elements can be that the sites in phillipsite are more difficult to reach for these elements, because of apertures or a lower surface charge (Colella, 1996, Breck, 1974). Therefore it is conceivable that the sites can be easily occupied by H^+. Figure 3 shows the uptake of test elements by phillipsite. From this figure it can be derived that the preference of adsorption for the test elements by phillipsite is as follows:

$Cu > Ba > Cd > Zn > Co \geq Ni$

Ba was taken up from the solution for 55-70%, Cu for 70-95%, Cd for 20-70%, Zn for 0-40%, Co for 0-55% and Ni for 0-55%. The combination Co Ni Zn is deviating from the other combinations. In this combination the affinity for Co is as high as that for Ni (which is usually higher), and the adsorption of Zn is lower than in any other combination.

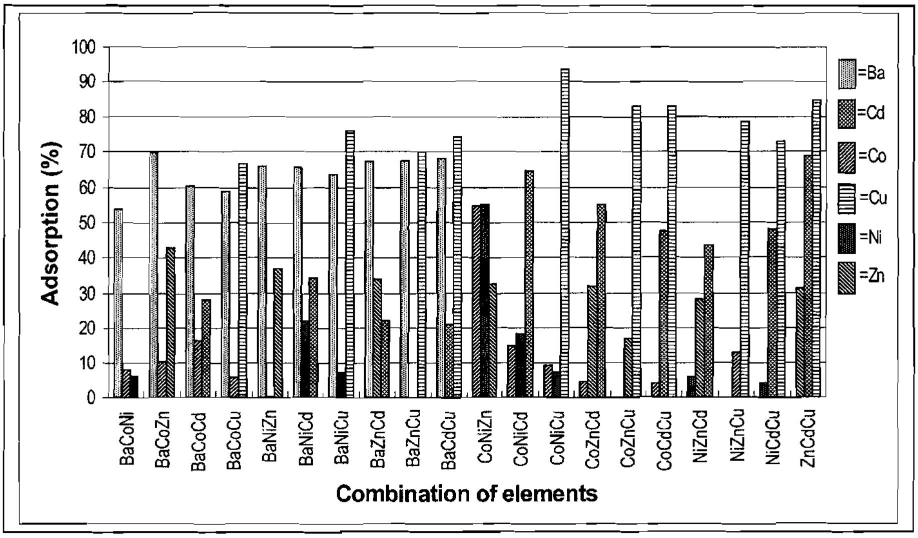

Figure 3 Adsorption of test-elements by phillipsite

Compared to the batch-experiments with single elements (in which the percentage adsorption was about 90% for both Cd and Cu, 83% for Co, Ni and Zn and 70% for Ba), the most conspicuous result is the low value for Ba in these experiments, whereas this element if it was combined with two others, has the second highest affinity for phillipsite. Probably, the partition coefficient for Ba between water and phillipsite is lower than for the metals Cd, Co, Ni and Zn, but Ba fits better in the phillipsite-structure than these mentioned metals.

Table 5 Selectivity experiments with phillipsite: overview of the results*), compiled from the results in appendix a3.2

	Ba			Co			Ni			Zn			Cd			Cu			Total adsorbed from solution	Total increase Na+K+Ca	Used exchange sites
element ombination	conc. filtr.	adsorbed		conc. filtr.	adsorbed		conc. filtr.	Adsorbed		conc. filtr.	adsorbed		Conc. Filtr.	adsorbed		conc. filtr.	adsorbed				
	meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%	Meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%
BaCoNi	1.08	1.26	54	1.95	0.16	8	1.98	0.13	6										1.55	2.54	61
BaCoZn	0.70	1.63	70	1.89	0.21	10				1.05	0.79	43							2.65	2.72	97
BaCoCd	0.93	1.40	60	1.77	0.34	16							1.26	0.50	28				2.25	2.52	89
BaCoCu	0.96	1.38	59	1.99	0.12	6										0.56	1.12	67	2.60	2.67	98
BaNiZn	0.79	1.54	66				2.10	0.01	0	1.15	0.68	37							2.25	2.53	89
BaNiCd	0.80	1.53	66				1.64	0.47	22				1.16	0.61	34				2.60	2.70	96
BaNiCu	0.85	1.49	64				1.96	0.15	7							0.41	1.28	76	2.95	2.70	109
BaZnCd	0.76	1.57	67							1.21	0.62	34	1.37	0.39	22				2.55	2.53	101
BaZnCu	0.76	1.57	67							1.84	0.00	0				0.50	1.18	70	2.75	2.77	99
BaCdCu	0.75	1.58	68										1.40	0.37	21	0.43	1.25	74	3.20	2.84	113
CoNiZn				0.96	1.15	55	0.95	1.16	55	1.24	0.60	33							2.90	2.74	106
CoNiCd				1.80	0.31	14	1.72	0.39	18				0.62	1.14	65				1.85	2.52	73
CoNiCu				1.92	0.19	9	1.96	0.15	7							0.11	1.58	93	1.95	2.48	79
CoZnCd				2.02	0.09	4				1.25	0.59	32	0.79	0.97	55				1.65	2.45	67
CoZnCu				2.11	0.00	0				1.52	0.31	17				0.29	1.40	83	1.70	2.38	72
CoCdCu				2.02	0.09	4							0.92	0.84	48	0.29	1.40	83	2.35	2.53	93
NiZnCd							1.99	0.12	6	1.32	0.52	28	0.99	0.77	44				1.35	2.44	55
NiZnCu							2.12	0.00	0	1.60	0.24	13				0.36	1.32	78	1.55	2.45	63
NiCdCu							2.02	0.09	4				0.92	0.85	48	0.46	1.23	73	2.20	2.52	87
ZnCdCu										1.26	0.58	31	0.55	1.21	69	0.26	1.43	85	3.25	2.57	126
starting solution	2.33			2.11			2.11			1.83			1.76			1.69					

*) conc. filtr.= concentration in the solution after the experiment after filtrating
adsorption = adsorption of the element from the solution by phillipsite, given in meq/g and in % from the starting solution
the last three columns present respectively the sum of the adsorbed test elements, the sum of the dissolved Na+K+Ca and the percentage of the exchange sites occupied by the test elements

Zeolite K-G

From table 5 it can be seen that the CEC of K-G, like of phillipsite, was not completely used, and that the adsorption is lower than the release of exchangeable cations. The reasons for these results may be the same as mentioned for phillipsite, namely the adding of H^+ cations. Figure 4 shows the uptake of test elements by zeolite K-G. From the results shown in this figure the preference of adsorption derived for the test elements by zeolite K-G is as follows:

$Cu > Ba > Cd > Zn > Co \approx Ni$

Ba was taken up from the solution for 55-75%, Cu for 65-90%, Cd for 40-70%, Zn for 5-55%, Co for 15-45% and Ni for 15-45%.

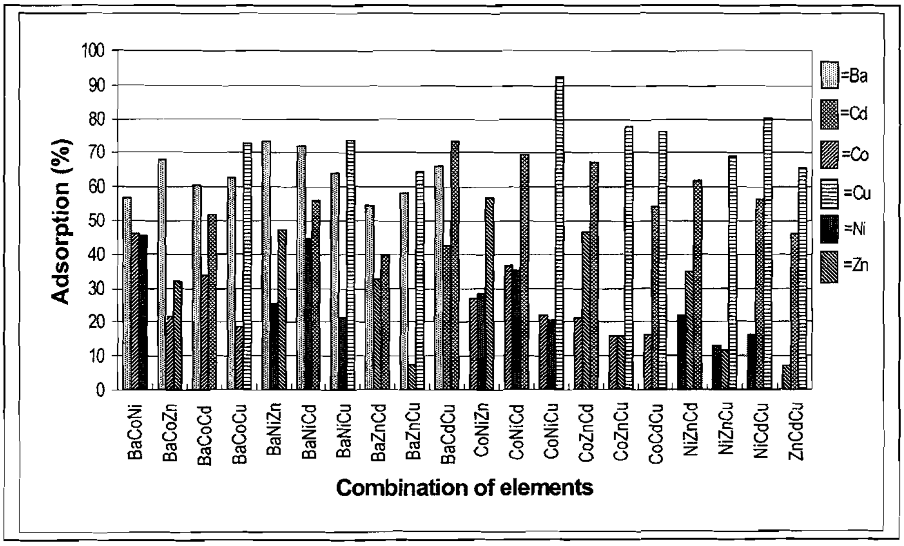

Figure 4 Adsorption of test elements by zeolite K-G

From the batch-experiments with single elements it appeared that Ni, Cd and Cu are adsorbed from the solution for about 90%, Co and Zn for 85%, and Ba for 74%. From these experiments again it can be concluded that e.g. Ni is capable of occupying exchange-sites, but that in presence of other elements it has a lower affinity.

Table 6 Selectivity experiments with zeolite K-G: overview of the results*), compiled from the results in apendix a3.3

element combination	Ba			Co			Ni			Zn			Cd			Cu			Total adsorbed from solution	Total increase Na+K+Ca	Used exchange sites
	Conc. filtr.	adsorbed		conc. filtr.	adsorbed		conc. filtr.	adsorbed		conc. filtr.	adsorbed		Conc. Filtr.	adsorbed		conc. filtr.	adsorbed				
	meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%	Meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%
BaCoNi	1.01	1.32	57	1.14	0.97	46	1.15	0.96	45										3.25	3.33	98
BaCoZn	0.75	1.58	68	1.65	0.45	22				1.25	0.59	32							2.63	3.33	79
BaCoCd	0.93	1.41	60	1.40	0.71	34							0.85	0.92	52				3.04	2.76	110
BaCoCu	0.87	1.46	63	1.72	0.39	19										0.46	1.23	73	3.08	3.24	95
BaNiZn	0.62	1.71	73				1.57	0.54	26	0.97	0.86	47							3.11	3.15	99
BaNiCd	0.66	1.68	72				1.17	0.94	44				0.77	0.99	56				3.60	3.17	114
BaNiCu	0.84	1.50	64				1.66	0.45	21							0.44	1.24	74	3.19	3.15	101
BaZnCd	1.06	1.28	55							1.24	0.60	33	1.06	0.70	40				2.57	3.08	84
BaZnCu	0.97	1.36	58							1.70	0.14	8				0.60	1.08	64	2.59	3.18	81
BaCdCu	0.79	1.54	66										1.02	0.75	42	0.45	1.24	74	3.53	3.05	116
CoNiZn				1.54	0.57	27	1.51	0.60	29	0.79	1.04	57							2.22	2.27	98
CoNiCd				1.34	0.77	37	1.37	0.74	35				0.54	1.22	69				2.74	2.38	115
CoNiCu				1.64	0.47	22	1.68	0.43	20							0.13	1.56	92	2.46	2.28	108
CoZnCd				1.66	0.45	21				0.99	0.85	46	0.58	1.19	67				2.48	2.78	89
CoZnCu				1.77	0.34	16				1.54	0.29	16				0.38	1.31	78	1.94	2.48	78
CoCdCu				1.77	0.34	16							0.81	0.96	54	0.40	1.29	76	2.58	2.96	87
NiZnCd							1.65	0.46	22	1.20	0.64	35	0.67	1.09	62				2.19	2.36	93
NiZnCu							1.84	0.27	13	1.62	0.21	12				0.52	1.17	69	1.65	2.06	80
NiCdCu							1.77	0.34	16				0.77	0.99	56	0.34	1.35	80	2.69	2.64	102
ZnCdCu										1.70	0.13	7	0.95	0.81	46	0.58	1.10	65	2.05	2.76	74
starting solution	2.33			2.11			2.11			1.83			1.76			1.69					

*)conc. filtr.= concentration in the solution after the experiment after filtrating
adsorption = adsorption of the element from the solution by zeolite K-G, given in meq/g and in % from the starting solution
the last three columns present respectively the sum of the adsorbed test elements, the sum of the dissolved Na+K+Ca and the percentage of the exchange sites occupied by the test elements

Comparison of the three ZFA's

Overall zeolite Na-P1 is the most promising ZFA, as it adsorbs and releases an quantity of cations per gram that is about equal to the CEC. The determined selectivity series for the 3 ZFA's are similar, the only difference being that for zeolite Na-P1 Ba is the element with the highest affinity and Cu is the second, whereas in case of the other 2 zeolites it is the other way round. These differences are caused by the size and shape of the apertures in the zeolite (Breck, 1974). Furthermore there are some small differences in whether the preference is higher than or equal to that of the next cation in the series. In the appendices it can be seen that there is also a difference in the release of Na, K and Ca between the ZFA's. The reason for these difference lies in the different cations that occupy the exchange position of the three zeolites. Zeolite Na-P1 is a Na-zeolite, which means that Na originally occupies the exchange sites. The small observed release of Ca and K is caused by the presence of other mineral phases in the ZFA (about 40% zeolite Na-P1, mullite, glass, hydroxides; Hollman, 1999). The concentration of Ca may be the result of the dissolution of CaOH and K may originate from residual CFA.

Phillipsite is a Na-K zeolite, which explains the described behavior of the release of cations from this product. The Ca-release is somewhat higher than from zeolite Na-P1, but this can be caused by the presence of more $Ca(OH)_2$ in this type of ZFA, or that Ca cations are better adsorbed by Na-P1 than by phillipsite.

Zeolite K-G is a K-zeolite. No Na is released, because there is no phase in the ZFA present with a significant Na content. The Ca release is even higher than from phillipsite. Zeolite K-G shows a large variability in the occupation of the exchange sites. However, by carrying out some extra experiments to check this, the same variability was observed.

Comparison with the literature

As mentioned in the introduction of this chapter, some publications give selectivity series for zeolites. Table 7 gives an overview of the published data. It is worth comparing these series with the series found in this work (table 8), amongst others for the reason of comparing the properties of natural zeolite with zeolitized fly ash.

Table 7 Overview of the selectivity series mentioned in the literature

Selectivity series	Type of zeolite	Reference
$Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$	Clinoptilolite	Assenov
$Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Fe^{2+} > Cr^{3+}$	Clinoptilolite	Loizidou
$Cu^{2+} > Cd^{2+} > Zn^{2+}$	Clinoptilolite, Phillipsite	Zamzow
$Pb^{2+} > Cu^{2+} > Cd^{2+} > Hg^{2+}$	Clinoptilolite	Kurama
$Ag^{+} > Hg^{2+} > Cd^{2+}$	Heulandite	Misaelides
$Pb^{2+} > Sr^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cs^{+}$	Zeolite Na-P1(ZFA)	Singer
$K^{+} > Li^{+} > NH_4^{+} > Sr^{2+} > Ba^{2+} > Ca^{2+} > Cs^{+} > Mg^{2+}$	Zeolite Na-P1(ZFA)	Amrhein

Table 8 Overview of the results of this work

Selectivity series	Type of zeolitized fly ash
$Ba^{2+} > Cu^{2+} > Cd^{2+} = Zn^{2+} > Co^{2+} > Ni^{2+}$	Zeolite Na-P1
$Cu^{2+} > Ba^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$	Phillipsite
$Cu^{2+} > Ba^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} = Ni^{2+}$	Zeolite K-G

The overall selectivity series from the literature for the elements and zeolites used in this research is:

Cu > Cd > Zn

which is in the same order of preference as observed in this work. Exceptions are Assenov (1988) and Loizidou (1989). However, in these experiments the concentrations of the test elements and the pH were extremely high, and it is not likely that under such circumstances only sorption processes take place. In the other publications surface-reactions were taken into account and therefore anticipated by using a pH between 4 and 7 together with low concentrations of the test-elements.

The mentioned literature does not discuss the reason for the difference in preference of the zeolite in adsorbing the different elements. The reasons must lie in the size and shape of the apertures in the zeolite, the size of the hydrolyzed cations, and therefore in the thermodynamically most favorable situation. Although some literature gives formulas for simultaneous sorption of cations theoretically derived from the ion exchange formulas, no specific research on the thermodynamics of these selectivities of cation adsorption on zeolites has been done. Further research is needed in this field.

Conclusions

Experiments were carried out to investigate the order of preference of three different types of zeolitized fly ash (ZFA), resulting in the following selectivity series:

- zeolite Na-P1: Ba > Cu > Cd ≈ Zn > Co > Ni
- phillipsite: Cu > Ba > Cd > Zn > Co > Ni
- zeolite K-G: Cu > Ba > Cd > Zn > Co ≈ Ni

These selectivity series are similar to the selectivity series found in the literature, which overall report the selectivity series as Cu > Cd > Zn. It appears that about 90% of the available exchange sites are occupied by the test elements. The tests with zeolite Na-P1 show the same quantities of adsorption of test elements from the solution as the release of exchangeable cations to the solution. As these quantities equalize the CEC-value, this ZFA turns out to be a very good and efficient exchanger. In case of phillipsite and zeolite K-G the available exchange sites were not completely occupied with test elements. However, the release of exchangeable cations (Na and K) to the solution, which does about equalize the CEC-value, suggests that the hydronium ion (H^+) plays a role in this, by occupying a part of the exchange sites. In the batch-experiments with a single test element in solution, which were carried out at the same level of concentrations as the tests with the combinations of elements, each test-element was removed from the solution for more than 75%. From this it can be concluded that each of the tested elements is adsorbed by ZFA, but that the zeolite has a preference for one element above the other.

Acknowledgments

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Appendix 3.1

Selectivity experiments with zeolite Na-P1

Concentration of the elements in solution (mg/l)

	Concentration elements in mg/l									
combination of elements	Ba	Co	Ni	Zn	Cd	Cu		Na	K	Ca
BaCoNi	6.02	6.64	6.63					10.24	1.80	0.65
BaCoZn	3.16	8.79		5.18				10.74	1.48	0.89
BaCoCd	3.72	7.74			8.78			10.58	1.85	0.67
BaCoCu	2.53	8.63				1.58		10.60	1.77	0.41
BaNiZn	3.23		7.82	4.66				10.12	1.73	1.65
BaNiCd	4.86		6.19		7.38			9.84	2.65	1.34
BaNiCu	4.12		8.23			2.01		9.55	1.83	1.99
BaZnCd	2.57			5.59	9.83			10.86	1.75	0.90
BaZnCu	3.73			8.14		3.17		10.58	1.46	0.82
BaCdCu	3.97				11.29	2.51		10.70	1.59	1.01
CoNiZn		8.07	7.99	3.21				7.54	1.81	0.36
CoNiCd		7.62	7.55		4.62			7.22	1.49	0.36
CoNiCu		8.72	8.59			0.79		7.76	1.50	0.44
CoZnCd		8.62		4.90	3.81			10.19	1.09	< b.g.
CoZnCu		8.97		6.24		0.97		11.02	0.90	< b.g.
CoCdCu		8.68			5.31	1.68		11.39	1.23	< b.g.
NiZnCd			8.15	4.68	5.70			7.68	1.65	0.32
NiZnCu			7.08	5.50		1.08		11.36	1.22	0.20
NiCdCu			8.28		7.85	1.62		7.41	1.46	0.65
ZnCdCu				6.62	6.55	1.98		11.64	1.17	< b.g.
start concentration										
Ba	25.81									
Co		11.19								
Ni			9.69							
Zn				10.46						
Cd					15.74					
Cu						10.17				

Appendix 3.2

Selectivity experiments with phillipsite

Concentration of the elements in solution (mg/l)

	Concentration elements in mg/l									
combination of elements	Ba	Co	Ni	Zn	Cd	Cu		Na	K	Ca
BaCoNi	14.81	11.46	11.69					4.18	8.21	2.32
BaCoZn	9.68	11.16		6.84				4.21	8.03	3.13
BaCoCd	12.80	10.41			14.21			4.81	7.28	2.17
BaCoCu	13.13	11.70				3.59		5.26	7.21	2.41
BaNiZn	10.85		12.39	7.54				5.52	5.70	2.41
BaNiCd	11.02		9.67		13.01			5.14	8.32	2.06
BaNiCu	11.61		11.56			2.58		4.58	7.79	2.84
BaZnCd	10.45			7.93	15.42			5.71	4.53	2.86
BaZnCu	10.46			12.03		3.20		5.54	4.93	3.74
BaCdCu	10.30				15.68	2.76		5.94	7.79	2.23
CoNiZn		5.63	5.59	8.09				5.78	7.05	2.33
CoNiCd		10.62	10.15		7.00			5.75	5.96	2.04
CoNiCu		11.30	11.54			0.71		4.88	5.74	2.73
CoZnCd		11.87		8.16	8.87			6.12	4.70	2.10
CoZnCu		12.42		9.95		1.83		4.37	6.03	2.62
CoCdCu		11.92			10.37	1.84		5.25	4.89	3.06
NiZnCd			11.72	8.61	11.16			4.55	7.44	2.01
NiZnCu			12.51	10.45		2.31		5.10	6.03	2.27
NiCdCu			11.91		10.32	2.92		5.78	5.12	2.46
ZnCdCu				8.23	6.19	1.66		6.14	4.77	2.52
start concentration										
Ba	32.04									
Co		12.42								
Ni			12.44							
Zn				12.00						
Cd					19.83					
Cu						10.73				

Appendix 3.3

Selectivity experiments with zeolite K-G

Concentration of the elements in solution (mg/l)

	Concentration elements in mg/l									
combination of elements	Ba	Co	Ni	Zn	Cd	Cu		Na	K	Ca
BaCoNi	13.88	6.70	6.76					0.00	14.12	6.10
BaCoZn	10.31	9.75		8.14				0.81	15.47	4.73
BaCoCd	12.70	8.22			9.54			0.00	13.37	4.21
BaCoCu	11.98	10.11				2.93		0.00	16.22	4.67
BaNiZn	8.57		9.21	6.37				0.00	15.17	4.87
BaNiCd	9.04		6.88		8.71			0.00	16.09	4.45
BaNiCu	11.47		9.77			2.82		0.00	15.38	4.74
BaZnCd	14.53			8.08	11.96			0.00	14.78	4.78
BaZnCu	13.32			11.09		3.83		0.00	15.86	4.64
BaCdCu	10.83				11.41	2.84		0.00	15.35	4.35
CoNiZn		9.05	8.85	5.20				0.00	12.17	2.86
CoNiCd		7.88	8.03		6.07			0.00	11.94	3.43
CoNiCu		9.68	9.86			0.81		0.00	12.34	2.80
CoZnCd		9.80		6.44	6.49			0.52	13.73	3.64
CoZnCu		10.44		10.09		2.39		0.00	12.59	3.50
CoCdCu		10.42			9.07	2.55		0.00	13.46	4.96
NiZnCd			9.69	7.82	7.54			0.00	11.65	3.49
NiZnCu			10.80	10.60		3.31		0.00	10.11	3.08
NiCdCu			10.38		8.66	2.14		0.00	13.29	3.79
ZnCdCu				11.15	10.70	3.70		0.12	13.11	4.26
start concentration										
Ba	32.04									
Co		12.42								
Ni			12.44							
Zn				12.00						
Cd					19.83					
Cu						10.73				

Appendix 3.4

Selectivity experiments with zeolite Na-P1, phillipsite and zeolite K-G:

Experiments with the single elements
Concentration of the elements in solution (mg/l)

		concentration in solution (mg/l)									
Exp. with zeolite	Exp. with element:	Ba	Co	Ni	Zn	Cd	Cu		Na	K	Ca
NaP1	Ba	2.67							9.31	2.28	4.44
	Co		2.09						8.82	1.50	1.82
	Ni			2.99					7.70	2.08	1.94
	Zn				1.31				8.88	1.46	1.42
	Cd					1.65			9.22	1.40	1.25
	Cu						0.72		9.53	1.61	1.39
phillipsite	Ba	7.85							5.77	7.41	5.07
	Co		1.97						5.51	4.05	3.29
	Ni			1.85					5.08	4.83	3.05
	Zn				1.83				4.85	4.02	2.75
	Cd					2.47			5.27	4.88	2.50
	Cu						0.89		4.73	7.56	2.56
K-G	Ba	8.27							0.00	14.66	3.71
	Co		2.29						0.00	12.57	2.76
	Ni			1.14					0.00	13.08	2.75
	Zn				1.85				0.00	12.62	2.04
	Cd					1.75			0.00	12.75	2.01
	Cu						0.45		0.00	12.78	2.93
starting solution		32.04	12.42	12.44	12.00	19.83	10.73				

4

Examining the empirically determined properties of zeolitized fly ash by column breakthrough experiments

Abstract
Column breakthrough experiments were carried out whereby zeolitized fly ash (ZFA) was percolated with an artificially polluted solution containing Ba, Co, Ni, Zn, Cd, Pb, and Cu. It is shown that after an initial period, during which these elements are removed from solution, they show up in the percolate in the reverse order of the selectivity series established earlier by batch experiments. The ZFA uses its complete CEC for the adsorption of the metals (2 meq/g). It is also established that the ZFA, loaded with heavy metals after the column experiments, can be regenerated with a NaCl solution.

Key words: zeolitized fly ash (ZFA), CEC, adsorption, selectivity series, column breakthrough experiments, heavy metals

Introduction

In the previous chapter the selectivity series for the simultaneous adsorption of Ba, Co, Ni, Zn, Cd, Pb, and Cu on zeolitized fly ash (ZFA) were determined. It was stated that the importance of this series is in the application of the ZFA, e.g. being able to forecast the ecotoxicological risks in applying the ZFA as an immobilizer of heavy metals. However, this was investigated in batch-experiments. No studies are known on the behavior of ZFA towards heavy metals under (semi) natural conditions. Therefore, column experiments were carried out whereby the ZFA was percolated with an artificially polluted solution, containing the heavy metals mentioned above.

The aim of these experiments was to determine the 'breakthrough' point, i.e. the moment at which one or more of the test elements appear in the percolate. In addition, it was investigated if the ZFA, loaded with heavy metals, after the column experiments can be regenerated. Regeneration is of importance for an economically feasible application of ZFA. Finally, the possibility will be discussed to explain the results by geochemical modeling, obtained by using the chemical equilibrium program CHARON (Delft Hydraulics, 1991).

Materials and methods

The column breakthrough experiments were carried out with one type of ZFA: zeolite Na-P1, which was formed by the treatment of fly ash during 24 hours in a 2M NaOH solution at 150°C. To prevent the formation of precipitates during the column experiments, the ZFA was washed with nitric acid (1.6 mmol H^+ per gram ZFA, L/S 2, during 1 hour) to neutralize excess hydroxide. After the treatment, the pH of this solution was 8.3. The CEC of this pretreated ZFA is 2.1 meq/g. 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 samples were washed with 80% alcohol in order to remove excess salt.

Five columns were each packed with 30 gram (washed and dried in an oven at 40°C) ZFA which were then percolated (flow rate 8.3 ±0.2 ml per hour) with a solution (hereafter called 'starting solution') containing Ba, Co, Ni, Zn, Cd, Pb and Cu. The concentration of the elements in the starting solution differed per column, in order to study the influence of concentration on the adsorption behavior. To limit the influence of Ba for which all types of zeolite Na-P1 have a strong affinity (see chapter 2 and 3), only one column was percolated with a starting solution that contained Ba. In table 1 the concentrations of the test elements in the starting solutions per column experiment are given.

Table 1 Column experiments: the concentration of the test elements in the starting solutions

Element	column 1		column 2		column 3		column 4		column 5 (blank)	
	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l	mg/l
Ba	0	0	1.5	103	0	0	0	0	0	0
Cd	1.5	84	1.5	84	1.13	63	0.75	42	0	0
Co	1.5	44	1.5	44	1.13	33	0.75	22	0	0
Cu	1.5	48	1.5	48	1.13	37	0.75	24	0	0
Ni	1.5	44	1.5	44	1.13	33	0.75	22	0	0
Pb	1.5	155	1.5	155	1.13	116	0.75	78	0	0
Zn	1.5	49	1.5	49	1.13	37	0.75	25	0	0
Total	9.0		10.5		6.8		4.5		0	

The solution exiting a column (the percolate) was collected in fractions of 1 day. Once a week the last collected fraction was analyzed by ICP-AES. In every fraction the pH was measured. If no particularities were noticed, the samples of one week were mixed and 100 ml of this mixture was acidified and stored at least for the duration of the experiments.

The regeneration experiments after the column (adsorption) experiments were carried out with the zeolites in column 1 and 2. A 10 meq Na/l solution (dissolved from its chloride salt, pH 7.2) was percolated in the same way as the starting solutions containing the heavy metals. The percolates of these experiments also were collected every day, and analyzed once a week.

The results of column 5 (blank experiment, see appendix) are used to correct for reactions or processes that occur when the ZFA is percolated with only water. Data from this blank experiment are subtracted from the data of the other column experiments.

Results

Calculations, based on the quantity and CEC of ZFA in the columns, and on the concentration of the test elements in the starting solutions, show that theoretically (thus in the most ideal situation without precipitates and other site reactions) 5 weeks after the start of these column experiments test elements are expected in the percolates of column 1 and 2. However, instead 'breakthrough' occurred only after 21 weeks. To find the reason for this retardation, the experiment in column 4 was stopped after 10 weeks and the ZFA was analyzed by XRD for mineralogical changes. This showed that the quality and the quantity of the ZFA had remained unchanged but also that $Cd(OH)_2$ and $CdPb(OH)_4$ had been formed. To shorten the time needed for breakthrough, the flow rate of the percolation of column 3 was speeded up from 8 to 25 ml/hour. However, the column lost its permeability after a few days at this high flow rate, and this experiment was aborted as well. Tables 2 and 3 and figure 1 give an overview of the progress of the concentrations of the test elements in the percolates of respectively column experiments 1 and 2 as a function of time. The raw analysis data used for these tables are given in appendix 4, table a4.1, a4.2, and a4.3.

Table 2 Column experiments: progress of the concentration of elements in the percolate of column1

Percolation time (weeks)	pH percolate	Concentration test elements (meq/l)						
		Cd	Co	Cu	Ni	Pb	Zn	Total
		Starting solution						
		1.60	1.40	1.50	1.40	1.60	1.60	9.10
		Percolate[1]						
1 - 20	10.5 - 8.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21	8.0	0.00	0.50	0.00	0.70	0.00	0.00	1.20
22	7.8	0.00	1.40	0.00	2.20	0.00	0.00	3.60
23	7.6	0.00	2.10	0.00	2.90	0.00	0.00	5.00
24	7.5	0.00	3.10	0.00	3.20	0.00	1.10	7.40
25	7.3	0.00	3.30	0.00	3.20	0.00	1.70	8.20
26	7.3	0.00	3.20	0.00	2.30	0.00	3.80	9.30
27	7.1	0.50	2.40	0.00	2.00	0.00	4.80	9.70
28	7.0	2.90	2.10	0.00	1.40	0.00	2.90	9.30
29	7.1	4.10	1.40	1.50	1.40	0.00	2.50	10.9
30	7.2	4.60	1.40	2.00	1.40	0.00	1.80	11.2
31	6.9	2.20	1.40	3.20	1.40	0.00	1.60	9.80
32	7.0	1.90	1.40	4.90	1.40	3.00	1.60	14.2
33	7.0	1.60	1.40	2.00	1.40	1.60	1.60	9.60
34	7.0	1.50	1.40	1.50	1.40	1.60	1.60	9.00
35	7.0	1.60	1.40	1.50	1.40	1.60	1.60	9.10

1) Start of breakthrough marked by gray color ▭

Table 3 Column experiments: progress of the concentration of elements in the percolate of column 2

Percolation time (weeks)	pH Percolate	Concentration test elements (meq/l)							
		Ba	Cd	Co	Cu	Ni	Pb	Zn	Total
		Starting solution							
		1.60	1.60	1.40	1.50	1.40	1.60	1.60	10.7
		Percolate[1)]							
1 - 20	10.5 – 8.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21	8.1	0.00	0.00	0.30	0.00	0.80	0.00	0.00	1.10
22	7.9	0.00	0.00	1.60	0.00	2.00	0.00	0.00	3.60
23	7.8	0.00	0.00	2.30	0.00	2.80	0.00	0.00	5.10
24	7.7	0.00	0.00	2.80	0.00	3.00	0.00	1.30	7.10
25	7.5	0.00	0.00	3.10	0.00	3.00	0.00	2.00	8.10
26	7.4	0.00	0.50	2.80	0.00	2.10	0.00	3.00	8.40
27	7.3	0.00	2.90	2.30	0.00	1.90	0.00	4.00	11.1
28	7.2	0.00	4.00	1.70	1.50	1.40	0.00	2.70	11.3
29	7.2	0.00	3.70	1.40	2.00	1.40	0.00	2.00	10.5
30	7.1	0.00	2.90	1.40	3.20	1.40	0.00	1.60	10.5
31	6.9	0.00	1.60	1.40	4.00	1.40	0.00	1.60	10.0
32	7.0	0.00	1.60	1.40	2.00	1.40	2.80	1.60	10.8
33	7.0	1.60	1.60	1.40	1.50	1.40	2.20	1.60	11.1
34	7.0	1.60	1.60	1.40	1.50	1.40	1.60	1.60	10.7
35	7.0	1.60	1.60	1.40	1.50	1.40	1.60	1.60	10.7

1) Start of breakthrough marked by grey color ▭

After 21 weeks test elements were detected in the percolates of column 1 and 2. From table 2 and 3, the order of 'breakthrough' of the elements can be derived. Ni and Co are the first elements detected, followed by Zn, Cd, Cu, Pb and finally Ba (for column 2 only). This is the reverse order of the selectivity series derived in the previous chapter.

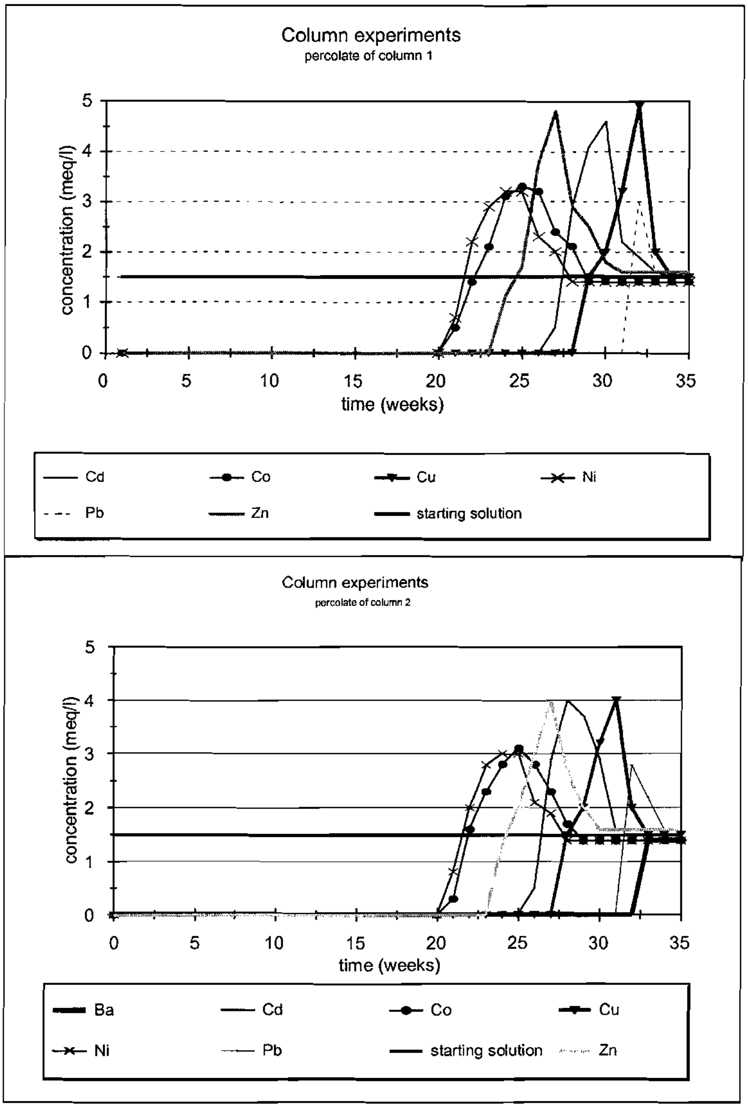

Figure 1 *Concentration of the elements in the percolates of column 1 and 2*

Remarkable in table 2, 3 and figure 1 is that the concentration of the breakthrough element is higher than the concentration of that element in the starting solution. These ‘peaks’ last about 6 weeks. This appearance will be discussed in the next paragraph.
Figure 2 shows the change in pH during these experiments.

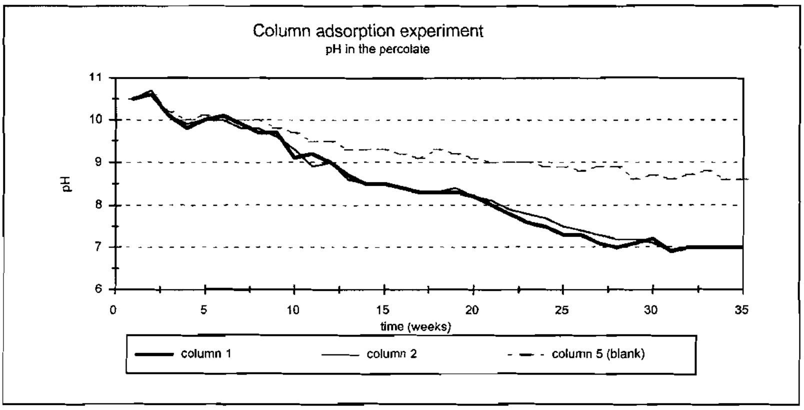

Figure 2 *pH progress in the percolates*

The release of Na and K from the ZFA to the percolating solution is an indication that ion exchange has taken place. Therefore it is important to compare the quantity of elements that are taken up and released by the ZFA. When these quantities are about equal, it can be stated that ion exchange is the only adsorption process that took place. In case more elements are taken up than Na and K are released, obviously more processes took place. Table 4 gives an overview of the quantities of elements taken up from the starting solution, release of elements to the percolating solution and the expected processes in the zeolite. This table is based on the data given in appendix 4, tables a4.6 and a4.7, presenting the raw analytical data corrected for the blank experiment, and is illustrated by figure 3.

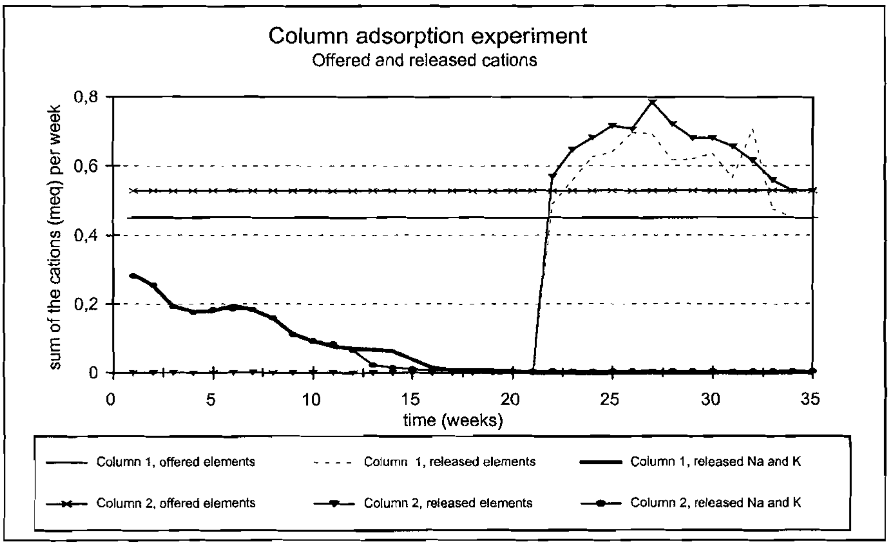

Figure 3 *Illustration of the elements offered, taken up and released by the ZFA*

Table 4 Column experiments: elements taken up and released by the ZFA and expected processes taken place

Percolation time (weeks)	pH	Column 1					Column 2				
		Sum of test elements (meq/week)		Release Na+ K (meq/week)	Estimated Processes		Sum of test elements (meq/week)		Release Na+ K (meq/week)	Estimated processes	
		uptake from start sol.	in percolate		exchange	other	uptake from start sol.	in percolate		exchange	other
1	10.5	13.65	0.00	8.55	8.55	5.10	16.05	0.00	8.43	8.43	7.62
2	10.6	13.65	0.00	7.57	7.57	6.08	16.05	0.00	7.65	7.65	8.40
3	10.1	13.65	0.00	5.83	5.83	7.82	16.05	0.00	5.82	5.82	10.23
4	9.8	13.65	0.00	5.34	5.34	8.31	16.05	0.00	5.30	5.30	10.75
5	10.0	13.65	0.00	5.37	5.37	8.28	16.05	0.00	5.50	5.50	10.55
6	10.1	13.65	0.00	5.85	5.85	7.80	16.05	0.00	5.58	5.58	10.47
7	9.9	13.65	0.00	5.50	5.50	8.15	16.05	0.00	5.53	5.53	10.52
8	9.7	13.65	0.00	4.79	4.79	8.86	16.05	0.00	4.79	4.79	11.26
9	9.7	13.65	0.00	3.38	3.38	10.27	16.05	0.00	3.34	3.34	12.71
10	9.1	13.65	0.00	2.75	2.75	10.90	16.05	0.00	2.78	2.78	13.27
11	9.2	13.65	0.00	2.36	2.36	11.29	16.05	0.00	2.54	2.54	13.51
12	9.0	13.65	0.00	2.16	2.16	11.49	16.05	0.00	2.00	2.00	14.05
13	8.7	13.65	0.00	2.03	2.03	11.62	16.05	0.00	0.72	0.72	15.33
14	8.5	13.65	0.00	1.91	1.91	11.74	16.05	0.00	0.47	0.47	15.58
15	8.5	13.65	0.00	1.23	1.23	12.42	16.05	0.00	0.35	0.35	15.70
16	8.4	13.65	0.00	0.49	0.49	13.16	16.05	0.00	0.24	0.24	15.81
17	8.3	13.65	0.00	0.30	0.30	13.35	16.05	0.00	0.23	0.23	15.82
18	8.3	13.65	0.00	0.24	0.24	13.41	16.05	0.00	0.20	0.20	15.85
19	8.3	13.65	0.00	0.19	0.19	13.46	16.05	0.00	0.16	0.16	15.89
20	8.2	13.65	0.00	0.17	0.17	13.48	16.05	0.00	0.14	0.14	15.91
21	8.0	11.85	1.80	0.10	0.10	11.75	14.40	1.65	0.14	0.14	14.26
22	7.8	8.25	5.40	0.04	0.04	8.21	10.65	5.40	0.10	0.10	10.55
23	7.6	6.15	7.50	0.05	0.05	6.10	8.40	7.65	0.14	0.14	8.26
24	7.5	2.55	11.10	0.02	0.02	2.53	5.40	10.65	0.13	0.13	5.27
25	7.3	1.35	12.30	0.01	0.01	1.34	3.90	12.15	0.12	0.12	3.78
26	7.3	-0.30	13.95	0.01	0.01	-0.31	4.20	11.85	0.10	0.10	4.10
27	7.1	-0.90	14.55	0.00	0.00	-0.90	3.00	13.05	0.00	0.00	3.00
28	7.0	-0.30	13.95	0.00	0.00	-0.30	0.75	15.30	0.00	0.00	0.75
29	7.1	-2.70	16.35	0.00	0.00	-2.70	-0.15	16.20	0.07	0.07	-0.22
30	7.2	-3.15	16.80	0.00	0.00	-3.15	-0.90	16.95	0.05	0.05	-0.95
31	6.9	-1.05	14.70	0.00	0.00	-1.05	-0.90	16.95	0.05	0.05	-0.95
32	7.0	-7.65	21.30	0.01	0.01	-7.66	-0.15	16.20	0.05	0.05	-0.20
33	7.0	-0.75	14.40	0.01	0.01	-0.76	-0.90	16.95	0.05	0.05	-0.95
34	7.0	0.15	13.50	0.00	0.00	0.15	0.15	16.05	0.10	0.10	0.05
35	7.0	0.00	13.65	0.01	0.01	-0.01	0.00	16.05	0.05	0.05	-0.05
Total after 35 weeks		286.50	191.25	66.29	66.29	220.21	368.85	193.05	62.91	62.91	305.94

Regeneration experiments

After the column experiments as described above were terminated, it was investigated whether the ZFA, loaded with heavy metals, could be regenerated again with a solution containing 10 meq Na per liter. These regeneration experiments were carried out like the breakthrough experiments, except that the starting solution with the test elements was replaced by the Na solution. The concentrations of the elements in the percolate of column 1 and 2 obtained in the regeneration experiments are given in table 5 and table 6. The pH of the regenerating solution was 7.2.

Table 5 Column regeneration experiments: concentration of the elements in the percolate of column 1*

Regeneration time (weeks)	pH percolate	Concentration elements in percolate (meq/l)						
		Cd	Co	Cu	Na	Ni	Pb	Zn
1	6.8	<0.05	<0.07	6.2	5.2	<0.12	<0.14	<0.05
2	7.0	<0.05	<0.07	<0.04	9.8	<0.12	<0.14	<0.05
3	6.9	<0.05	<0.07	<0.04	9.5	<0.12	<0.14	<0.05
4	6.9	<0.05	<0.07	<0.04	10.1	<0.12	<0.14	<0.05

* before the regeneration the exchange sites of the ZFA in column 1 are occupied with Pb and Cu

Table 6 Column regeneration experiments: concentration of the elements in the percolate of column 2*

Regeneration time (weeks)	pH percolate	Concentration elements in percolate (meq/l)							
		Ba	Cd	Co	Cu	Na	Ni	Pb	Zn
1	7.1	<0.01	<0.05	<0.07	<0.04	10.2	<0.12	<0.14	<0.05
2	7.0	<0.01	<0.05	<0.07	<0.04	9.9	<0.12	<0.14	<0.05
3	6.8	<0.01	<0.05	<0.07	<0.04	9.6	<0.12	<0.14	<0.05
4	7.1	<0.01	<0.05	<0.07	<0.04	9.9	<0.12	<0.14	<0.05

* before the regeneration the exchange sites of the ZFA in column 2 are occupied with Ba

Discussion

The breakthrough 'peaks', illustrated in figure 2, last about 6 weeks. The cause of this appearance is an effect of the ion exchange process. Just before the test elements are released to the percolate, all the exchange sites of the zeolite are occupied. This is the moment at which the elements in the starting solution with a high affinity for the ZFA replace the elements with less affinity already adsorbed on the zeolite. In this way, Ni will be released first to the solution and until all the Ni is replaced at the exchange sites, this will cause a concentration peak, because the Ni present in the starting solution exits the column as well. This process continues until all the exchange sites are occupied with the element with the highest affinity.

From then on, the concentration of the percolate equals the concentration of the starting solution.
Another indication that the ion exchange process does indeed take place is the fact that from around week 26 onwards the total concentration of the test elements in the percolate equals about the total concentration of the test elements in the starting solution.

That indeed at the end of the experiments the exchange sites are occupied by the elements with the highest affinity can be deduced from the fact that no large peak is detected for these elements just before the moment that the concentration of the starting solution equals that of the percolate. The sites that were first occupied by elements that were later replaced, will be claimed for the largest part by the element(s) with the highest affinity. Therefore, in the end of the experiment there will be about 60 meq of these element(s) in the ZFA. In case these elements would leave the column as well, a large concentration peak would appear. In appendix 4, table a4.4 and a4.5, the peaks from figure 1 are quantified. Table 7 gives a summary of these calculations.

Table 7 Column experiments: quantification of the peaks from figure 1

Column	Difference between test elements in the starting solution and the percolate (meq), between the start of the breakthrough and the moment that the concentration in the percolate equals the concentration in the starting solution							
	Ba	Cd	Co	Cu	Ni	Pb	Zn	Total
1	x	11.55	11.70	9.15	11.10	2.10	11.85	57.45
2	0.00	10.65	10.20	7.80	9.60	2.70	8.55	60.90

From this table it can be seen that, except for Ba and Pb, the peaks are about similar in meq. Ba remains in the column for 100% and Pb for about 75%, while only a few percent of Cu is irreversibly adsorbed to the ZFA in the column.

Processes different from ion exchange can only explain the delayed start of the breakthrough. The fact that at the end of the experiments 9 meq of test elements per gram ZFA is left behind in the column, whereas the CEC is only 2 meq per gram, is a strong indication that other processes take place as well. The cause of these phenomena can mainly be found in the pH. The ZFA was washed with nitric acid prior to the experiments in order to avoid pH's higher than 8 during the experiments. However, figure 3, which gives the progress of the pH in the percolate during the experiments, shows that this is not the case. The pH started at ca.10, and decreases to around 8 only after ca. 20 weeks (see figure 2). The progress of the pH in the percolate of the blank experiment differs from this in that it decreases much less and has a pH of ca. 9 after 20 weeks. This can be caused by 2 processes, both of which can play a role. The first is that during the washing of the ZFA before the experiment, a part of the exchange sites which were first occupied by Na, are replaced with H^+. During the experiment the exchange sites are occupied by the test elements. The H^+ ions are released to the solution and lower the pH. In the blank experiment, no test elements are used, so the H^+ ions on the exchange sites

will not be released and thus the pH in the percolate of the blank decreases less than that of the percolates of the other columns. The second process for the different pH development of the blank is related to the dissolution of residual glass and other amorphous aluminosilicate phases. This dissolution is a slow process that leads to the release of hydroxide and the pH increase to ca. 10, observed in the first weeks of the column experiments. The result is the formation of hydroxide precipitates as shown by the analysis of the ZFA from column 4. In case of the blank, however, no precipitates with heavy metals can be formed, and the pH will be higher. It can be expected that the hydroxide precipitates in column 1 and 2 that are formed during the high pH period will dissolve again at lower pH. However, because of the very slow acidity changes in practice, this will be a very slow process.
Other arguments which can explain partly the retardation of the breakthrough are the facts that other (site)reactions can play a role as well (e.g. adsorption on hydroxides), and that the measured CEC is a minimum value (personal communication of Mr. van Reeuwijk from ISRIC).

From the arguments above, it is obvious that the quantity of Na and K released to the solutions does not equal the quantity of test elements taken up by ZFA. In total 9 meq of test elements per gram ZFA is kept in the column, whereas only 2 meq per gram can be explained from the CEC. The other 7 meq per gram zeolite is thus via other processes than ion exchange retained by the material in the column, most likely at this pH as precipitates. However, the 2 meq Na and K released to the solution make it reasonable that the CEC of the zeolite (being 2.1 meq/g) is completely used.

Regeneration experiments

After the column experiments, before the regeneration, the exchange sites of column 1 are occupied with Pb and Cu (in total 63 meq), and the exchange sites of column 2 with Ba (as well 63 meq), furthermore both columns contain precipitates (column 1 maximal 220 meq, column 2 maximal 306 meq, see table 4). From table 5 it can be derived that during the first week of the regeneration Cu is released to the percolating solution since the Na concentration in the percolate is lower than in the starting solution. These quantities of Na and Cu are about equal. This indicates that exchange (desorption) has taken place. Table 6 shows that none of the elements that are adsorbed on the ZFA in column 2 is released during the regeneration experiment. The Na concentration in the starting solution and the percolate are about equal, indicating no exchange has taken place.

Taking into account the flow rate of percolation of 8 ml/h, equivalent to 1.4 liter per week, in table 8 (derived from the tables 5 and 6) an overview is given of the quantity of elements presented by the regenerating solution and the quantity of elements released to the percolating solution during the regeneration experiment. It can be concluded from table 8 that the ZFA in column 1 released an quantity of 8.7 meq of elements to the percolating solution. The quantity of Na taken up from the percolating solution is about equal i.e. 7.7 meq, which indicates that the release is not entirely due to the dissolution of precipitates, but a consequence of ion exchange.

Table 8 Column regeneration experiments: quantity of Na taken up from the regenerating solution and of the elements released from ZFA

Percolation time (weeks)	Column 1			Column 2		
	Na (meq/week)		Elements (excl. Na) total in percolate (meq/week)	Na (meq/week)		Elements (excl. Na) total in percolate (meq/week)
	Taken up from startsol.	In percolate		Taken up from startsol.	In percolate	
1	6.7	7.3	8.7	0.0	14.3	0.0
2	0.3	13.7	0.0	0.1	13.9	0.0
3	0.7	13.3	0.0	0.5	13.5	0.0
4	0.0	14.1	0.0	0.1	13.9	0.0
Total	7.7		8.7	0.7		0

According to Breck (1974) the adsorption of Ba and Pb by zeolite Na-P1 is an irreversible process, probably because of a change in structure from Na-P1 to Na-P2. These experiments confirm the irreversibility of adsorption of these two elements, but also indicate that the regeneration of the other elements is possible.

During the regeneration experiments there were no elements detected which were 'immobilized' during the column breakthrough experiments. This indicates that no precipitates did start to dissolve. In fact this was expected: the precipitates which were formed during the column experiments are stable at pH around 7, which is the pH of the percolate during regeneration.

Geochemical modeling

Geochemical modeling can be used to predict the behavior of a system under certain conditions. In order to be able to make predictions, a geochemical model has to be calibrated and verified with a well defined set of experiments first. A system is described by:

1. its composition (of the solid, liquid and gas phase);
2. the chemical reactions taking place.

In the experiments with the Zeolitised Fly Ash (ZFA) described in the earlier chapters, the exchange of heavy metals with the sorption complex was clearly established. Nonetheless, the experiments also showed that the exchange reaction was not the only reaction taking place:

1. the rise in pH can not be explained by the simple exchange of cations;
2. precipitation was demonstrated in column 4 of the breakthrough experiment. Moreover, precipitation is obvious when the initial mass of the columns 1 and 2 (30 g) is compared with the mass after the experiment, respectively 40 and 42 g;
3. release of Si and other elements points out that part of the solid phase dissolves.

Chemical reactions are driven by thermodynamic instability: each system strives for an equilibrium state which is the state of minimal Gibbs free energy. Obviously, equilibrium is often not reached instantaneously and kinetics play a major role. In order to examine the possibility of geochemical modeling of the present results some preliminary calculations were performed with the program CHARON. The chemical equilibrium program CHARON determines the state of minimal Gibbs free energy of a system (Delft hydraulics, 1991), based on its overall composition (chemical components presents) and the thermodynamic properties of its constituents. CHARON was used to set up a simple 1-dimensional model. The system is described in table 9. In the model only the exchange of the metals with the ZFA was included according to equations 1 and 2:

$$NaCEC + \tfrac{1}{2}\,Me^{2+} \leftrightarrow Me_{0.5}CEC + Na^{+} \qquad (1)$$

$$Me_{0.5}CEC + \tfrac{1}{2}\,Me'^{\,2+} \leftrightarrow Me'_{0.5}CEC + \tfrac{1}{2}\,Me^{2+} \qquad (2)$$

Me stands for any of the metals Ba, Cd, Co, Cu, Ni, Pb and Zn.

Table 9 System definition for CHARON simulation

	Initial condition (mole/l)	boundary condition (mmole/l)
Solution		
Ba^{2+}	1×10^{-5}	0.75
Cd^{2+}	1×10^{-5}	0.75
Cu^{2+}	1×10^{-5}	0.75
Ni^{2+}	1×10^{-5}	0.75
Zn^{2+}	1×10^{-5}	0.75
Co^{2+}	1×10^{-5}	0.75
Na^{+}	1×10^{-5}	1×10^{-5}
H_2O	55.5	55.5
ZFA		
CaCEC	0	0
HCEC	0	0
NaCEC	500	0
CdCEC	0	0
ZnCEC	0	0
CuCEC	0	0
BaCEC	0	0
CoCEC	0	0
NiCEC	0	0

The adsorption complex is assumed to be completely occupied by sodium initially. As no thermodynamic constants are available for the ZFA adsorption complex, only relative enthalpies are assumed according to the selectivity series determined in chapter 3: Ba > Cu > Cd ≈ Zn > Co > Ni. Barium has the highest affinity to the adsorption complex, nickel the least.

When a solution, containing the metals in equal concentrations of 1.5 meq/l, is percolated through a column containing an adsorption complex, the metals break through in the reverse order of the selectivity series (figure 4), as was shown in the practical breakthrough experiment (figure 1). The rise in concentration above the initial value can clearly be seen and is the result of the development of an adsorption/desorption front. The broadening of the peaks results from numerical dispersion. Eventually, all metals adopt their initial concentration of 0.75 mmole/l.

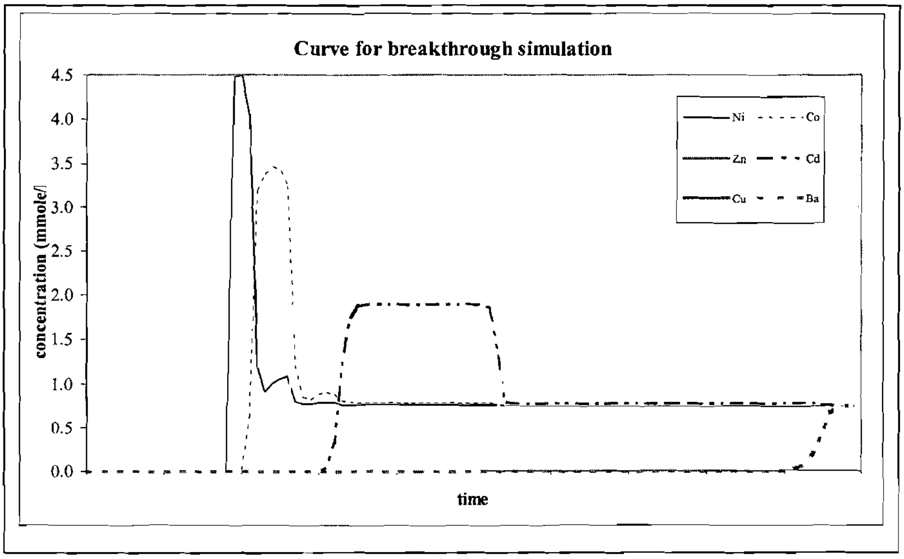

Figure 4 Breakthrough pattern as a result of geochemical modeling

Remarkably, the model simulation showed a rise in pH as well (Figure 5). The rise occurring in the simulation is the result of an exchange of protons against sodium on the adsorption sites, thus removing H^+ from solution and raising the pH. Given the large amount of adsorption sites available in a relatively small volume of water, the increase in pH is substantial.

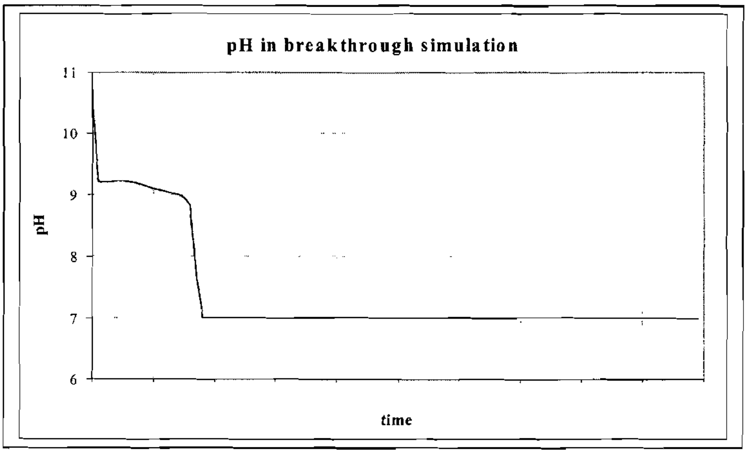

Figure 5 *pH progress according to the model simulation*

It can be concluded that the breakthrough can be modeled with CHARON. However, results are qualitative since no thermodynamic data were available for this specific ZFA adsorption complex.

Further research into the (complete set of) chemical reactions occurring when ZFA is brought into contact with a solution, is needed to set up a full predictive model. Actual thermodynamic data may be derived from the experiments, although additional experiments are most likely needed to better support these data.

Conclusions

It appeared that the ZFA in a more practical situation like the column experiment described in this chapter, behave the same as in the smaller scale batch experiments. The breakthrough of the elements, which happens when the ZFA is completely saturated with the cations and therefore can not immobilize more cations, appeared in the reverse order of the selectivity series (and thus in accordance with these series) which were investigated in chapter 3 by batch experiments and was conform expectations. The element towards which the ZFA has the least affinity (the last in the selectivity series), will be the one that is first replaced at the cation exchange sites.

The ZFA in the columns, with a CEC of 2 meq per gram, takes up 9 meq cations from the percolating solution per gram ZFA. Desorption experiments and the release of Na and K to the percolating solution during the experiments point out that the complete CEC i.e. 2 meq/g is used for the adsorption of test elements. The other 7 meq cations per gram ZFA is precipitated in the columns, due to the high pH (8-10). The precipitated test elements can be released if the pH of the percolating solution is low or decreases (the pH of the starting

solution in these experiments was about 4), but in natural circumstances this will be a very slow process, so that this will be a controlled process.
From the desorption experiments it can be concluded that it is possible to regenerate the ZFA, but that Pb and Ba are irreversibly adsorbed, which confirms results reported in literature.

Acknowledgments

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Appendix 4.1

Adsorption of elements by zeolite Na-P1 (ZFA) in column 1

concentration elements in the percolate of column 1 (mg/l)

Sample	Day	S	P	B	Si	Al	Mg	V	Ca	Sr	Na	K		Cd	Co	Cu	Ni	Pb	Zn
1c1/2	1	10.33	7.35	18.85	84.28	0.22	< d.l.	1.45	4.69	0.40	520.00	27.37		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1c4/2	4	1.93	3.49	2.84	60.41	0.32	< d.l.	0.25	1.38	0.27	299.32	21.71		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1c7/2	7	1.21	2.70	1.50	50.31	0.42	< d.l.	0.18	1.01	0.27	257.12	16.11		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C11/2	11	0.89	2.11	0.74	54.11	< d.l.	< d.l.	0.14	0.74	< d.l.	220.52	8.32		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C14/2	14	0.67	1.76	0.54	41.79	< d.l.	< d.l.	0.13	0.74	< d.l.	195.62	7.18		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C18/2	18	0.51	1.56	0.33	22.59	0.63	0.11	0.12	0.67	0.25	165.17	6.89		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C21/2	21	0.47	1.37	0.26	16.98	0.70	0.18	0.10	0.48	< d.l.	139.76	6.71		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C26/2	26	0.43	1.24	0.19	14.52	0.52	0.26	0.08	0.30	< d.l.	127.27	5.38		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C28/2	28	0.44	1.11	0.27	12.96	0.41	0.45	0.08	0.20	< d.l.	126.10	3.69		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C3/3	32	0.32	0.84	0.14	10.80	0.45	0.75	< d.l.	< d.l.	< d.l.	107.85	4.02		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C5/3	34	0.32	0.70	0.12	9.30	0.24	1.32	< d.l.	< d.l.	< d.l.	118.43	3.41		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C10/3	39	0.22	0.58	< d.l.	< d.l.	< d.l.	1.54	0.08	< d.l.	< d.l.	118.77	4.20		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C13/3	42	0.23	0.63	0.07	< d.l.	< d.l.	1.35	< d.l.	< d.l.	< d.l.	116.80	3.91		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C17/3	46	0.54	0.50	0.13	22.86	0.22	< d.l.	< d.l.	1.31	< d.l.	109.68	4.45		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C20/3	49	0.46	0.44	0.14	24.04	<b.g.	< d.l.	< d.l.	1.63	< d.l.	104.84	4.46		< d.l.	< d.l	< d.l.	< d.l.	< d.l.	< d.l.
1C24/3	53	0.38	0.25	< d.l.	21.04	< d.l.	0.48	< d.l.	1.67	< d.l.	96.91	4.09		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C27/3	56	0.46	0.21	0.12	19.72	0.20	0.71	< d.l.	2.52	< d.l.	79.54	3.80		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C31/3	60	0.52	< d.l.	< d.l.	18.81	0.18	0.89	< d.l.	2.08	< d.l.	68.03	4.09		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C3/4	63	0.61	0.24	0.11	18.20	0.15	1.11	0.01	1.85	< d.l.	58.08	3.85		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C7/4	67	0.65	< d.l.	0.09	16.54	< d.l.	1.65	< d.l.	2.26	< d.l.	52.98	3.58		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C10/4	70	0.18	< d.l.	0.06	15.43	< d.l.	1.16	< d.l.	2.05	< d.l.	50.99	2.88		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C14/4	74	0.49	< d.l.	0.07	15.74	< d.l.	1.90	< d.l.	3.79	< d.l.	46.97	4.26		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1c18/4	78	< d.l.	< d.l.	< d.l.	17.51	0.32	1.26	< d.l	2.01	< d.l.	45.49	5.00		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1C21/4	81	< d.l.	< d.l.	< d.l.	17.64	< d.l.	1.61	< d.l.	3.62	< d.l.	40.92	5.79		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1 30/4	90	0.49	< d.l.	< d.l.	16.22	< d.l	1.27	< d.l.	6.29	< d.l.	36.63	4.59		< d.l.	< d.l.	< d.l.	< d.l	< d.l.	< d.l.
1C5/5	95	0.21	< d.l.	0.08	15.03	< d.l.	0.91	< d.l.	6.69	< d.l.	35.98	4.27		< d.l.	< d.l.	< d.l.	< d.l.	< d.l	< d.l.
1C12/5	102	0.56	< d.l.	0.66	14.30	0.27	0.94	< d.l.	9.01	< d.l.	33.79	4.35		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1 21/5	109	0.26	< d.l.	< d.l.	13.92	< d.l.	1.69	0.02	9.78	< d.l.	22.80	4.63		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1 28/5	116	< d.l.	< d.l.	0.14	12.85	< d.l.	1.71	< d.l.	9.46	< d.l.	12.31	3.33		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1 4/6	123	< d.l.	< d.l.	< d.l.	13.67	< d.l	0.32	< d.l.	9.59	< d.l.	8.90	3.05		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1 11/6	130	< d.l.	< d.l.	< d.l.	13.34	< d.l.	< d.l.	< d.l.	9.91	< d.l.	7.60	2.88		< d.l.	< d.l.	< d.l.	< d.l	< d.l.	< d.l.
1 18/6	137	< d.l.	< d.l.	0.18	11.94	< d.l.	< d.l.	< d.l.	9.97	< d.l.	6.19	2.88		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1 25/6	144	< d.l.	< d.l.	< d.l.	11.22	< d.l.	1.32	< d.l.	10.11	< d.l.	5.85	2.04		< d.l.	14.73	< d.l.	20.55	< d.l.	< d.l.
1 2/7	151	< d.l.	< d.l.	< d.l.	9.69	< d.l.	1.45	< d.l.	9.55	< d.l.	4.98	2.06		< d.l.	41.23	< d.l.	64.57	< d.l.	< d.l.
1 9/7	158	< d.l.	< d.l.	< d.l.	10.05	< d.l.	1.45	< d.l.	10.03	< d.l.	4.04	2.07		< d.l.	61.85	< d.l.	85.12	< d.l.	< d.l
1 9/7	165	< d.l.	< d.l.	< d.l.	12.70	< d.l.	1.55	< d.l.	11.82	< d.l.	4.24	2.58		< d.l.	91.30	< d.l.	93.92	< d.l.	35.97
1 16/7	172	< d.l.	< d.l.	< d.l.	12.08	< d.l.	1.39	< d.l.	10.95	< d.l.	3.36	2.52		< d.l.	97.19	< d.l.	93.92	< d.l.	55.59
1 23/7	179	< d.l.	< d.l.	< d.l.	9.92	< d.l.	1.02	< d.l.	9.56	< d.l.	3.20	2.23		< d.l.	94.24	< d.l.	67.51	< d.l.	124.26
1 30/7	186	< d.l.	< d.l.	< d.l.	9.82	< d.l.	1.08	< d.l.	9.33	< d.l.	3.26	2.12		28.10	70.68	< d.l.	58.70	< d.l.	156.96
1 6/8	193	0.15	< d.l.	< d.l.	9.07	< d.l.	0.75	< d.l.	8.86	< d.l.	2.50	1.91		162.98	61.85	< d.l.	40.90	< d.l.	94.83
1 13/8	200	< d.l.	< d.l.	< d.l.	9.08	< d.l.	0.93	< d.l.	9.10	< d.l.	2.10	1.56		230.42	41.23	47.63	40.20	< d.l.	81.75
1 20/8	207	< d.l.	< d.l.	< d.l.	9.02	< d.l.	0.89	< d.l.	9.05	< d.l.	< d.l.	1.32		258.52	40.90	63.50	41.50	< d.l.	58.86
1 27/8	214	< d.l.	< d.l.	< d.l.	9.08	< d.l.	0.79	< d.l.	8.99	< d.l.	< d.l.	1.46		123.64	41.23	101.60	40.50	< d.l.	55.78
1 3/9	221	< d.l.	< d.l.	< d.l.	8.42	< d.l.	0.75	< d.l.	9.25	< d.l.	< d.l.	1.54		106.78	40.50	155.58	40.80	310.80	55.20
1 10/9	228	< d.l.	< d.l.	< d.l.	8.43	< d.l.	0.87	< d.l.	9.46	< d.l.	< d.l.	1.87		77.90	40.60	63.50	40.30	165.00	54.80
1 17/9	235	< d.l.	< d.l.	< d.l.	7.89	< d.l.	0.69	< d.l.	8.96	< d.l.	< d.l.	1.71		78.68	40.80	44.45	41.10	165.00	55.78
1 24/9	242	< d.l.	< d.l.	< d.l.	8.45	< d.l.	0.82	< d.l.	8.75	< d.l.	< d.l.	1.32		78.50	41.23	44.45	40.20	165.00	55.00
1 1/10	249	< d.l.	< d.l.	< d.l.	8.96	< d.l.	0.75	< d.l.	9.05	< d.l.	< d.l.	1.62		78.70	40.70	45.30	41.10	165.40	55.20

Appendix 4.2

Adsorption of elements by zeolite Na-P1 (ZFA) in column 2

concentration elements in the percolate of column 2 (mg/l)

Sample	Day	S	P	B	Si	Al	Mg	V	Ca	Na	K	Ba	Cd	Co	Cu	Ni	Pb	Zn
2c1/2	1	8.07	9.10	21.46	94.77	0.26	< d.l.	1.62	3.75	530.11	28.80	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2c4/2	4	2.20	3.67	2.87	65.26	0.47	< d.l.	0.27	1.47	292.28	19.04	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2c7/2	7	1.26	2.70	1.49	51.68	0.48	< d.l.	0.18	1.04	250.69	18.09	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C11/2	11	1.00	2.21	0.75	55.08	< d.l.	< d.l.	0.15	1.06	215.20	8.49	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C14/2	14	0.71	1.94	0.58	47.13	< d.l.	< d.l.	0.13	0.64	203.24	7.66	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C18/2	18	0.53	1.74	0.35	24.96	0.62	0.11	0.12	0.56	169.41	6.13	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C21/2	21	0.59	1.65	0.27	19.44	0.62	0.15	0.10	0.49	135.12	5.10	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C26/2	26	0.44	1.36	0.19	14.56	0.49	< d.l.	0.08	0.15	127.92	4.40	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C28/2	28	0.51	1.23	0.27	13.19	0.44	< d.l.	0.08	0.42	124.26	3.97	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C3/3	32	0.32	0.95	0.14	10.78	0.39	< d.l.	< d.l.	< d.l.	113.91	3.22	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C5/3	34	0.39	0.86	0.13	9.75	0.26	< d.l.	< d.l.	< d.l.	116.30	3.16	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C10/3	39	0.30	0.72	< d.l.	< d.l.	0.16	0.38	0.09	< d.l.	115.80	3.06	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C13/3	42	0.30	0.63	0.06	< d.l.	0.18	1.28	< d.l.	< d.l.	112.83	2.65	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C17/3	46	0.56	0.46	0.13	22.23	0.24	< d.l.	< d.l.	0.10	111.73	2.47	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C20/3	49	0.44	0.35	0.13	22.74	0.15	< d.l.	< d.l.	<b.g.	105.87	2.87	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C24/3	53	0.37	< d.l.	< d.l.	20.12	< d.l.	2.58	< d.l.	0.29	95.97	4.67	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C27/3	56	0.50	< d.l.	0.12	20.29	0.22	2.46	< d.l.	1.64	79.21	5.85	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C31/3	60	0.38	< d.l.	< d.l.	18.83	0.17	2.64	< d.l.	1.55	65.79	6.04	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C3/4	63	0.61	< d.l.	0.10	18.17	< d.l.	2.66	< d.l.	2.10	55.94	7.04	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C7/4	67	0.47	< d.l.	0.07	17.52	< d.l.	2.35	< d.l.	2.95	50.85	6.80	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C10/4	70	0.18	< d.l.	0.06	16.49	< d.l.	1.55	< d.l.	3.33	50.42	6.01	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C14/4	74	0.53	< d.l.	0.07	16.52	< d.l.	1.98	< d.l.	5.54	47.11	6.54	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2c18/4	78	< d.l.	< d.l.	< d.l.	16.20	< d.l.	1.78	< d.l.	5.17	48.45	6.79	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C21/4	81	< d.l.	< d.l.	< d.l.	17.10	< d.l.	1.90	< d.l.	5.20	43.38	6.85	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 30/4	90	0.51	< d.l.	< d.l.	16.09	< d.l.	1.73	< d.l.	9.48	27.98	5.77	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C5/5	95	0.33	< d.l.	0.10	16.46	< d.l.	1.35	< d.l.	10.25	14.94	5.76	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2C12/5	102	0.47	< d.l.	0.65	14.02	0.26	1.21	< d.l.	11.65	11.53	4.76	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 21/5	109	0.16	< d.l.	< d.l.	14.34	< d.l.	1.91	0.01	12.62	9.88	4.66	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 28/5	116	< d.l.	< d.l.	0.11	12.79	< d.l.	1.71	< d.l.	12.37	9.06	3.29	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 4/6	123	< d.l.	< d.l.	< d.l.	14.23	< d.l.	0.59	< d.l.	13.21	7.77	3.45	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 11/6	130	< d.l.	< d.l.	< d.l.	13.80	< d.l.	0.49	< d.l.	13.62	6.60	3.21	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 18/6	137	< d.l.	< d.l.	0.12	11.96	< d.l.	0.33	< d.l.	13.04	4.97	3.12	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2 25/6	144	< d.l.	< d.l.	< d.l.	12.92	< d.l.	2.10	< d.l.	13.76	4.76	2.44	< d.l.	< d.l.	6.80	< d.l.	23.50	< d.l.	< d.l.
2 2/7	151	< d.l.	< d.l.	< d.l.	11.84	< d.l.	2.17	< d.l.	12.96	4.40	2.41	< d.l.	< d.l.	47.10	< d.l.	58.70	< d.l.	< d.l.
2 9/7	158	< d.l.	< d.l.	< d.l.	11.52	< d.l.	2.10	< d.l.	13.43	4.04	2.30	< d.l.	< d.l.	67.70	< d.l.	82.20	< d.l.	< d.l.
2 9/7	165	< d.l.	< d.l.	< d.l.	14.22	< d.l.	2.30	< d.l.	15.36	4.60	2.73	< d.l.	< d.l.	82.50	< d.l.	88.10	< d.l.	42.50
2 16/7	172	< d.l.	< d.l.	< d.l.	13.67	< d.l.	2.14	< d.l.	15.25	4.10	2.57	< d.l.	< d.l.	91.30	< d.l.	88.10	< d.l.	65.40
2 23/7	179	< d.l.	< d.l.	< d.l.	11.88	< d.l.	1.73	< d.l.	13.83	3.85	2.28	< d.l.	28.10	82.50	< d.l.	61.60	< d.l.	98.10
2 30/7	186	< d.l.	< d.l.	0.49	11.17	< d.l.	1.62	< d.l.	13.23	3.66	2.08	< d.l.	163.00	67.70	< d.l.	55.80	< d.l.	131.00
2 6/8	193	0.17	< d.l.	< d.l.	10.90	< d.l.	1.26	< d.l.	12.74	< d.l.	1.85	< d.l.	224.80	50.10	47.60	41.10	< d.l.	88.30
2 13/8	200	< d.l.	< d.l.	< d.l.	10.96	< d.l.	1.43	< d.l.	13.36	< d.l.	1.64	< d.l.	207.90	41.20	63.50	40.00	< d.l.	65.40
2 20/8	207	< d.l.	< d.l.	< d.l.	10.95	< d.l.	1.25	< d.l.	13.25	< d.l.	1.56	< d.l.	163.00	41.10	101.60	40.60	< d.l.	52.30
2 27/8	214	< d.l.	< d.l.	< d.l.	10.88	< d.l.	1.35	< d.l.	12.99	< d.l.	1.44	< d.l.	89.90	40.50	127.00	42.00	< d.l.	51.30
1 3/9	221	< d.l.	< d.l.	< d.l.	9.20	< d.l.	1.05	< d.l.	12.55	< d.l.	1.45	< d.l.	88.80	40.80	63.50	41.50	290.00	52.00
1 10/9	228	< d.l.	< d.l.	< d.l.	8.50	< d.l.	0.87	< d.l.	11.89	< d.l.	1.57	96.10	89.50	41.50	47.60	40.80	228.00	53.00
1 17/9	235	< d.l.	< d.l.	< d.l.	8.59	< d.l.	0.81	< d.l.	12.09	< d.l.	1.52	94.90	89.80	41.90	47.00	40.90	166.00	52.90
1 24/9	242	< d.l.	< d.l.	< d.l.	10.30	< d.l.	0.92	< d.l.	13.08	< d.l.	1.93	95.70	89.00	42.00	46.50	41.00	166.00	52.10
1 1/10	249	< d.l.	< d.l.	< d.l.	9.25	< d.l.	0.79	< d.l.	12.35	< d.l.	1.45	96.20	90.20	41.30	47.20	41.20	166.00	52.50

Appendix 4.3

Adsorption of elements by zeolite Na-P1 (ZFA) in a column:
concentration elements in the percolate of the blank experiment (column 5 (mg/l))

Sample	Day	S	P	B	Si	Al	Mg	V	Ca	Na	K		Ba	Cd	Co	Cu	Ni	Zn
1/2	1	6.70	9.60	23.73	95.62	0.32	< d.l.	2.00	3.56	379.25	26.02		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
4/2	4	2.36	4.25	3.12	67.95	0.36	< d.l.	0.30	1.35	177.78	19.01		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
7/2	7	1.36	2.99	1.73	54.82	0.48	< d.l.	0.20	0.91	128.39	17.11		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
11/2	11	1.04	2.67	0.93	66.48	< d.l.	< d.l.	0.16	1.10	95.14	8.94		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
14/2	14	0.91	2.41	0.79	62.30	0.36	< d.l.	0.15	1.50	88.77	7.02		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
18/2	18	0.79	2.25	0.47	34.43	0.99	0.25	0.13	1.80	72.53	6.94		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
21/2	21	0.63	2.04	0.36	25.57	0.87	0.18	0.12	0.67	53.52	6.85		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
26/2	26	0.56	1.86	0.27	21.78	0.91	0.08	0.10	0.42	47.13	5.61		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
28/2	28	0.56	1.75	0.34	20.96	0.90	0.06	0.10	0.59	42.57	3.79		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3/3	32	0.44	1.45	0.18	16.91	0.80	< d.l.	< d.l.	0.15	32.53	4.23		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
5/3	34	0.45	1.37	0.18	16.46	0.64	< d.l.	< d.l.	0.03	29.10	3.38		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
10/3	39	2.86	1.31	< d.l.	< d.l.	0.52	< d.l.	< d.l.	0.33	34.45	3.25		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
13/3	42	0.38	1.16	0.10	< d.l.	0.60	< d.l.	< d.l.	< d.l.	23.06	2.66		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
17/3	46	0.65	1.15	0.17	41.03	0.65	< d.l.	< d.l.	0.42	25.59	2.53		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
20/3	49	0.51	1.03	0.17	41.20	0.54	< d.l.	< d.l.	0.25	22.39	2.70		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
24/3	53	0.45	0.83	0.05	37.16	0.31	< d.l.	< d.l.	< d.l.	19.08	2.21		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
27/3	56	0.53	0.72	0.14	33.64	0.52	< d.l.	< d.l.	0.94	12.99	1.62		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
31/3	60	0.44	0.52	< d.l.	30.91	0.49	< d.l.	< d.l.	< d.l.	11.79	2.36		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3/4	63	0.68	0.62	0.13	29.97	0.50	< d.l.	< d.l.	< d.l.	12.63	2.21		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
7/4	67	0.52	0.46	0.09	28.55	0.47	< d.l.	< d.l.	< d.l.	10.23	2.11		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
10/4	70	0.32	0.46	0.09	27.46	0.48	< d.l.	< d.l.	< d.l.	11.08	1.67		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
14/4	74	0.58	0.48	0.09	24.93	0.34	< d.l.	< d.l.	0.80	11.70	1.70		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
18/4	78	< d.l.	0.56	< d.l.	24.05	0.63	< d.l.	< d.l.	< d.l.	11.76	1.79		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
21/4	81	0.25	0.50	0.07	26.97	0.74	< d.l.	< d.l.	0.63	8.65	2.31		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
30/4	90	0.49	0.28	< d.l.	21.26	0.39	< d.l.	< d.l.	0.56	6.29	1.81		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
5/5	95	0.23	0.24	0 08	17.66	0.56	< d.l.	< d.l.	0.48	6.24	1.82		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
12/5	102	0.50	< d.l.	0.66	14.49	0.75	< d.l.	< d.l.	0.25	5.79	2.03		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
21/5	109	0.28	0.40	< d.l.	11.90	0.20	< d.l.	< d.l.	< d.l.	5.58	1.90		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
28/5	116	< d.l.	0.30	0.08	9.64	0.22	< d.l.	< d.l.	< d.l.	6.06	1.08		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
4/6	123	< d.l.	< d.l.	< d.l.	9.94	0.54	< d.l.	< d.l.	< d.l.	5.24	1.32		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
11/6	130	< d.l.	< d.l.	< d.l.	9.71	0.49	< d.l.	< d.l.	< d.l.	4.61	1.62		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
18/6	137	< d.l.	< d.l.	< d.l.	8.14	0.41	< d.l.	< d.l.	< d.l.	3.78	1.96		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
25/6	144	< d.l.	< d.l.	< d.l.	6.72	0.28	< d.l.	< d.l.	< d.l.	3.70	1.34		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
2/7	151	< d.l.	< d.l.	< d.l.	6.62	0.47	< d.l.	< d.l.	0.37	3.58	1.79		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
9/7	158	< d.l.	< d.l.	< d.l.	6.31	0.40	< d.l.	< d.l.	0.32	3.64	1.60		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
9/7	165	< d.l.	< d.l.	< d.l.	7.36	0.27	< d.l.	< d.l.	0.54	3.75	2.12		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
16/7	172	< d.l.	< d.l.	< d.l.	6.71	0.51	< d.l.	< d.l.	2 28	3.36	2.01		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
23/7	179	< d.l.	< d.l.	< d.l.	5.88	0.30	< d.l.	< d.l.	0.29	3.20	1.97		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
30/7	186	< d.l.	< d.l.	< d.l.	5.31	0.28	< d.l.	< d.l.	0.26	3.26	1.86		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
6/8	193	< d.l.	< d.l.	< d.l.	4.58	0.24	< d.l.	< d.l.	0.49	2.50	1.82		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
13/8	200	< d.l.	< d.l.	< d.l.	4.49	0.41	< d.l.	< d.l.	0.67	2.10	1.72		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
20/8	207	< d.l.	< d.l.	< d.l.	4.25	< d.l.	< d.l.	< d.l.	0.52	< d.l.	1.56		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
27/8	214	< d.l.	< d.l.	< d.l.	4.00	< d.l.	< d.l.	< d.l.	0.59	< d.l.	1.44		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3/9	221	< d.l.	< d.l.	< d.l.	4.02	< d.l.	< d.l.	< d.l.	0.45	< d.l.	1.45		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
10/9	228	< d.l.	< d.l.	< d.l.	3.86	< d.l.	< d.l.	< d.l.	0.25	< d.l.	1.57		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
17/9	235	< d.l.	< d.l.	< d.l.	3.99	< d.l.	< d.l.	< d.l.	0.56	< d.l.	1.52		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
24/9	242	< d.l.	< d.l.	< d.l.	3.89	< d.l.	< d.l.	< d.l.	0.52	< d.l.	1.93		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
1/10	249	< d.l.	< d.l.	< d.l.	3.65	< d.l.	< d.l.	< d.l.	0.59	< d.l.	1.45		< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.

Appendix 4.4

Uptake of elements by zeolite Na-P1 (ZFA) in column 1:

Overview breakthrough in column (total amount of testelements detected in the percolate of 1 week) and the amount supplied by the starting solution

Percolation time (weeks)	pH	Amount of elements in meq/week												
		Cd		Co		Cu		Ni		Pb		Zn		
		Starting solution:												
		2.40		2.10		2.25		2.10		2.40		2.40		
		Percolate												
		breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	
1*)	10.5	0.00		0.00		0.00		0.00		0.00		0.00		
20*)	8.2	0.00		0.00		0.00		0.00		0.00		0.00		
21	8.0	0.00		0.75	0.00	0.00		1.05	0.00	0.00		0.00		
22	7.8	0.00		2.10	0.00	0.00		3.30	1.20	0.00		0.00		
23	7.6	0.00		3.15	1.05	0.00		4.35	2.25	0.00		0.00		
24	7.5	0.00		4.65	2.55	0.00		4.80	2.70	0.00		1.65	0.00	
25	7.3	0.00		4.95	2.85	0.00		4.80	2.70	0.00		2.55	0.15	
26	7.3	0.00		4.80	2.70	0.00		3.45	1.35	0.00		5.70	3.30	
27	7.1	0.75		3.60	1.50	0.00		3.00	0.90	0.00		7.20	4.80	
28	7.0	4.35	1.95	3.15	1.05	0.00		2.10	0.00	0.00		4.35	1.95	
29	7.1	6.15	3.75	2.10	0.00	2.25	0.00	2.10	0.00	0.00		3.75	1.35	
30	7.2	6.90	4.50	2.10	0.00	3.00	0.75	2.10	0.00	0.00		2.70	0.30	
31	6.9	3.30	0.90	2.10	0.00	4.80	2.55	2.10	0.00	0.00		2.40	0.00	
32	7.0	2.85	0.45	2.10	0.00	7.35	5.10	2.10	0.00	4.50	2.10	2.40	0.00	
33	7.0	2.40	0.00	2.10	0.00	3.00	0.75	2.10	0.00	2.40	0.00	2.40	0.00	
34	7.0	2.25	0.00	2.10	0.00	2.25	0.00	2.10	0.00	2.40	0.00	2.40	0.00	
35	7.0	2.40	0.00	2.10	0.00	2.25	0.00	2.10	0.00	2.40	0.00	2.40	0.00	
Total			11.55		11.70		9.15		11.10		2.10		11.85	sum of the elements 57.45

*) The difference between breakthrough and the amount which is supplied by the starting solution
This amount is probably released by ion exchange

Appendix 4.5

Uptake of elements by zeolite Na-P1 (ZFA) in column 2:

Overview breakthrough in column (total amount of testelements detected in the percolate of 1 week) and the amount supplied by the starting solution

Percolation time (weeks)	pH	Amount of elements in meq/week														
		Ba		Cd		Co		Cu		Ni		Pb		Zn		
		Starting solution:														
		2.40		2.40		2.10		2.25		2.10		2.40		2.40		
		Percolate.														
		breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	breakthrough	difference*)	
1	10.5	0		0		0		0		0		0		0		
20	8.2	0		0		0		0		0		0		0		
21	8.1	0		0		0.45		0		1.20	0.00	0		0		
22	7.9	0		0		2.40	0.30	0		3.00	0.90	0		0		
23	7.8	0		0		3.45	1.35	0		4.20	2.10	0		0		
24	7.7	0		0		4.20	2.10	0		4.50	2.40	0		1.95	0.00	
25	7.5	0		0		4.65	2.55	0		4.50	2.40	0		3.00	0.60	
26	7.4	0		0.75	0.00	4.20	2.10	0		3.15	1.05	0		4.50	2.10	
27	7.3	0		4.35	1.95	3.45	1.35	0		2.85	0.75	0		6.00	3.60	
28	7.2	0		6.00	3.60	2.55	0.45	2.25	0.00	2.10	0.00	0		4.05	1.65	
29	7.2	0		5.55	3.15	2.10	0.00	3.00	0.75	2.10	0.00	0		3.00	0.60	
30	7.1	0		4.35	1.95	2.10	0.00	4.80	2.55	2.10	0.00	0		2.40	0.00	
31	6.9	0		2.40	0.00	2.10	0.00	6.00	3.75	2.10	0.00	0		2.40	0.00	
32	7.0	0		2.40	0.00	2.10	0.00	3.00	0.75	2.10	0.00	4.20	1.80	2.40	0.00	
33	7.0	2.40	0.00	2.40	0.00	2.10	0.00	2.25	0.00	2.10	0.00	3.30	0.90	2.40	0.00	
34	7.0	2.40	0.00	2.40	0.00	2.10	0.00	2.25	0.00	2.10	0.00	2.40	0.00	2.40	0.00	
35	7.0	2.40	0.00	2.40	0.00	2.10	0.00	2.25	0.00	2.10	0.00	2.40	0.00	2.40	0.00	
Total			0.00		10.65		10.20		7.80	8.75	9.60	2.65	2.70		8.55	sum of the elements 60.9

*) The difference between breakthrough and the amount which is supplied by the starting solution
This amount is probably released by ion exchange

Appendix 4.6

Uptake of elements by zeolite Na-P1 (ZFA) in column 1:

Overview of the amount of test elements supplied by the starting solution, the amount of test elements taken up by the ZFA in the column, and the amount detected in the percolate (meq/week)

Percolation time (weeks)	pH	Amount of elements in meq/week																				
		Cd			Co			Cu			Ni			Zn			Pb			Total of test elements		
		supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate
1 t/m 20	10.5 - 8.2	48,00	48,00	0,00	42,00	42,00	0,00	45,00	45,00	0,00	42,00	42,00	0,00	48,00	48,00	0,00	48,00	48,00	0,00	273	273	0
21	8,0	2,40	2,40	0,00	2,10	1,35	0,75	2,25	2,25	0,00	2,10	1,05	1,05	2,40	2,40	0,00	2,40	2,40	0,00	13,65	11,85	1,8
22	7,8	2,40	2,40	0,00	2,10	0,00	2,10	2,25	2,25	0,00	2,10	-1,20	3,30	2,40	2,40	0,00	2,40	2,40	0,00	13,65	8,25	5,4
23	7,6	2,40	2,40	0,00	2,10	-1,05	3,15	2,25	2,25	0,00	2,10	-2,25	4,35	2,40	2,40	0,00	2,40	2,40	0,00	13,65	6,15	7,5
24	7,5	2,40	2,40	0,00	2,10	-2,55	4,65	2,25	2,25	0,00	2,10	-2,70	4,80	2,40	0,75	1,65	2,40	2,40	0,00	13,65	2,55	11,1
25	7,3	2,40	2,40	0,00	2,10	-2,85	4,95	2,25	2,25	0,00	2,10	-2,70	4,80	2,40	-0,15	2,55	2,40	2,40	0,00	13,65	1,35	12,3
26	7,3	2,40	2,40	0,00	2,10	-2,70	4,80	2,25	2,25	0,00	2,10	-1,35	3,45	2,40	-3,30	5,70	2,40	2,40	0,00	13,65	-0,3	13,95
27	7,1	2,40	1,65	0,75	2,10	-1,50	3,60	2,25	2,25	0,00	2,10	-0,90	3,00	2,40	-4,80	7,20	2,40	2,40	0,00	13,65	-0,9	14,55
28	7,0	2,40	-1,95	4,35	2,10	-1,05	3,15	2,25	2,25	0,00	2,10	0,00	2,10	2,40	-1,95	4,35	2,40	2,40	0,00	13,65	-0,3	13,95
29	7,1	2,40	-3,75	6,15	2,10	0,00	2,10	2,25	0,00	2,25	2,10	0,00	2,10	2,40	-1,35	3,75	2,40	2,40	0,00	13,65	-2,7	16,35
30	7,2	2,40	-4,50	6,90	2,10	0,00	2,10	2,25	-0,75	3,00	2,10	0,00	2,10	2,40	-0,30	2,70	2,40	2,40	0,00	13,65	-3,15	16,8
31	6,9	2,40	-0,90	3,30	2,10	0,00	2,10	2,25	-2,55	4,80	2,10	0,00	2,10	2,40	0,00	2,40	2,40	2,40	0,00	13,65	-1,05	14,7
32	7,0	2,40	-0,45	2,85	2,10	0,00	2,10	2,25	-5,10	7,35	2,10	0,00	2,10	2,40	0,00	2,40	2,40	-2,10	4,50	13,65	-7,65	21,3
33	7,0	2,40	0,00	2,40	2,10	0,00	2,10	2,25	-0,75	3,00	2,10	0,00	2,10	2,40	0,00	2,40	2,40	0,00	2,40	13,65	-0,75	14,4
34	7,0	2,40	0,15	2,25	2,10	0,00	2,10	2,25	0,00	2,25	2,10	0,00	2,10	2,40	0,00	2,40	2,40	0,00	2,40	13,65	0,15	13,5
35	7,0	2,40	0,00	2,40	2,10	0,00	2,10	2,25	0,00	2,25	2,10	0,00	2,10	2,40	0,00	2,40	2,40	0,00	2,40	13,65	0	13,65
Total in 35 weeks		84,00	52,65	31,35	73,50	31,65	41,85	78,75	53,85	24,90	73,50	31,95	41,55	84,00	44,10	39,90	84,00	72,30	11,70	477,75	286,5	191,25

(-): release from ZFA to the percolate

Uptake of elements by zeolite Na-P1 (ZFA) in column 1:

Overview of the cumulative amount of test elements supplied, taken up, and released to the percolate

Percolation time (weeks)	pH	Cd			Co			Cu			Ni			Zn			Pb			Total of test elements		
		Amount of elements in the starting solution in meq/week																				
		2,40			2,10			2,25			2,10			2,40			2,40			9,10		
		Cumulative amount of elements in meq																				
		supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate
1 t/m 20	10.5 - 8.2	48,00	48,00	0,00	42,00	42,00	0,00	45,00	45,00	0,00	42,00	42,00	0,00	48,00	48,00	0,00	48,00	48,00	0,00	225,00	273,00	0,00
21	8,0	50,40	50,40	0,00	2,10	43,35	0,75	2,25	47,25	0,00	2,10	43,05	1,05	2,40	50,40	0,00	2,40	50,40	0,00	59,25	284,85	1,80
22	7,8	52,80	52,80	0,00	2,10	43,35	2,85	2,25	49,50	0,00	2,10	41,85	4,35	2,40	52,80	0,00	2,40	52,80	0,00	61,65	293,10	7,20
23	7,6	55,20	55,20	0,00	2,10	42,30	6,00	2,25	51,75	0,00	2,10	39,60	8,70	2,40	55,20	0,00	2,40	55,20	0,00	64,05	299,25	14,70
24	7,5	57,60	57,60	0,00	2,10	39,75	10,65	2,25	54,00	0,00	2,10	36,90	13,50	2,40	55,95	1,65	2,40	57,60	0,00	68,10	301,80	25,80
25	7,3	60,00	60,00	0,00	2,10	36,90	15,60	2,25	56,25	0,00	2,10	34,20	18,30	2,40	55,80	4,20	2,40	60,00	0,00	73,05	303,15	38,10
26	7,3	62,40	62,40	0,00	2,10	34,20	20,40	2,25	58,50	0,00	2,10	32,85	21,75	2,40	52,50	9,90	2,40	62,40	0,00	81,15	302,85	52,05
27	7,1	64,80	64,05	0,00	2,10	32,70	24,00	2,25	60,75	0,00	2,10	31,95	24,75	2,40	47,70	17,10	2,40	64,80	0,00	90,75	301,95	65,85
28	7,0	67,20	62,10	5,10	2,10	31,65	27,15	2,25	63,00	0,00	2,10	31,95	26,85	2,40	45,75	21,45	2,40	67,20	0,00	97,50	301,65	80,55
29	7,1	69,60	58,35	11,25	2,10	31,65	29,25	2,25	63,00	2,25	2,10	31,95	28,95	2,40	44,40	25,20	2,40	69,60	0,00	103,65	298,95	96,90
30	7,2	72,00	53,85	18,15	2,10	31,65	31,35	2,25	62,25	5,25	2,10	31,95	31,05	2,40	44,10	27,90	2,40	72,00	0,00	108,75	295,80	113,70
31	6,9	74,40	52,95	21,45	2,10	31,65	33,45	2,25	59,70	10,05	2,10	31,95	33,15	2,40	44,10	30,30	2,40	74,40	0,00	113,55	294,75	128,40
32	7,0	76,80	52,50	24,30	2,10	31,65	35,55	2,25	54,60	17,40	2,10	31,95	35,25	2,40	44,10	32,70	2,40	72,30	4,50	118,35	287,10	149,70
33	7,0	79,20	52,50	26,70	2,10	31,65	37,65	2,25	53,85	20,40	2,10	31,95	37,35	2,40	44,10	35,10	2,40	72,30	6,90	123,15	286,35	164,10
34	7,0	81,60	52,65	28,95	2,10	31,65	39,75	2,25	53,85	22,65	2,10	31,95	39,45	2,40	44,10	37,50	2,40	72,30	9,30	127,95	286,50	177,60
35	7,0	84,00	52,65	31,35	2,10	31,65	41,85	2,25	53,85	24,90	2,10	31,95	41,55	2,40	44,10	39,90	2,40	72,30	11,70	132,75	286,50	191,25

Appendix 4.7

Uptake of elements by zeolite Na-P1 (ZFA) in column 2:

Overview of the amount of test elements supplied by the starting solution, the amount of test elements taken up by the ZFA in the column, and the amount detected in the percolate (meq/week)

Percolation time (weeks)	pH	Amount of elements in meq/week																							
		Ba			Cd			Co			Cu			Ni			Zn			Pb			Total of test elements		
		supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate
1 t/m 20	10.5 - 8.2	48,00	48,00	0,00	48,00	48,00	0,00	42,00	42,00	0,00	45,00	45,00	0,00	42,00	42,00	0,00	48,00	48,00	0,00	48,00	48,00	0,00	321,00	321,00	0,00
21	8,1	2,40	2,40	0,00	2,40	2,40	0,00	2,10	1,65	0,45	2,25	2,25	0,00	2,10	0,90	1,20	2,40	2,40	0,00	2,40	2,40	0,00	16,05	14,40	1,65
22	7,9	2,40	2,40	0,00	2,40	2,40	0,00	2,10	-0,30	2,40	2,25	2,25	0,00	2,10	-0,90	3,00	2,40	2,40	0,00	2,40	2,40	0,00	16,05	10,65	5,40
23	7,8	2,40	2,40	0,00	2,40	2,40	0,00	2,10	-1,35	3,45	2,25	2,25	0,00	2,10	-2,10	4,20	2,40	2,40	0,00	2,40	2,40	0,00	16,05	8,40	7,65
24	7,7	2,40	2,40	0,00	2,40	2,40	0,00	2,10	-2,10	4,20	2,25	2,25	0,00	2,10	-2,40	4,50	2,40	0,45	1,95	2,40	2,40	0,00	16,05	5,40	10,65
25	7,5	2,40	2,40	0,00	2,40	2,40	0,00	2,10	-2,55	4,65	2,25	2,25	0,00	2,10	-2,40	4,50	2,40	-0,60	3,00	2,40	2,40	0,00	16,05	3,90	12,15
26	7,4	2,40	2,40	0,00	2,40	2,40	0,00	2,10	-2,10	4,20	2,25	2,25	0,00	2,10	-1,05	3,15	2,40	-2,10	4,50	2,40	2,40	0,00	16,05	4,20	11,85
27	7,3	2,40	2,40	0,00	2,40	1,65	0,75	2,10	-1,35	3,45	2,25	2,25	0,00	2,10	-0,75	2,85	2,40	-3,60	6,00	2,40	2,40	0,00	16,05	3,00	13,05
28	7,2	2,40	2,40	0,00	2,40	-1,95	4,35	2,10	-0,45	2,55	2,25	0,00	2,25	2,10	0,00	2,10	2,40	-1,65	4,05	2,40	2,40	0,00	16,05	0,75	15,30
29	7,2	2,40	2,40	0,00	2,40	-3,60	6,00	2,10	0,00	2,10	2,25	-0,75	3,00	2,10	0,00	2,10	2,40	-0,60	3,00	2,40	2,40	0,00	16,05	-0,15	16,20
30	7,1	2,40	2,40	0,00	2,40	-3,15	5,55	2,10	0,00	2,10	2,25	-2,55	4,80	2,10	0,00	2,10	2,40	0,00	2,40	2,40	2,40	0,00	16,05	-0,90	16,95
31	6,9	2,40	2,40	0,00	2,40	-1,95	4,35	2,10	0,00	2,10	2,25	-3,75	6,00	2,10	0,00	2,10	2,40	0,00	2,40	2,40	2,40	0,00	16,05	-0,90	16,95
32	7,0	2,40	2,40	0,00	2,40	0,00	2,40	2,10	0,00	2,10	2,25	-0,75	3,00	2,10	0,00	2,10	2,40	0,00	2,40	2,40	-1,80	4,20	16,05	-0,15	16,20
33	7,0	2,40	0,00	2,40	2,40	0,00	2,40	2,10	0,00	2,10	2,25	0,00	2,25	2,10	0,00	2,10	2,40	0,00	2,40	2,40	-0,90	3,30	16,05	-0,90	16,95
34	7,0	2,40	0,00	2,40	2,40	0,15	2,40	2,10	0,00	2,10	2,25	0,00	2,25	2,10	0,00	2,10	2,40	0,00	2,40	2,40	0,00	2,40	16,05	0,15	16,05
35	7,0	2,40	0,00	2,40	2,40	0,00	2,40	2,10	0,00	2,10	2,25	0,00	2,25	2,10	0,00	2,10	2,40	0,00	2,40	2,40	0,00	2,40	16,05	0,00	16,05
Total in 35 weeks		84,00	76,80	7,20	84,00	53,55	30,60	73,50	33,45	40,05	78,75	52,95	25,80	73,50	33,30	40,20	84,00	47,10	36,90	84,00	71,70	12,30	561,75	368,85	193,05

(-): release from ZFA to the percolate

Uptake of elements by zeolite Na-P1 (ZFA) in column 2:

Overview of the cumulative amount of test elements supplied, taken up, and released to the percolate

Percolation time (weeks)	pH	Ba			Cd			Co			Cu			Ni			Zn			Pb			Total of test elements		
		Amount of elements in the starting solution in meq/week																							
		2,40			2,40			2,10			2,25			2,10			2,40			2,40			10,70		
		Cumulative amount of elements in meq																							
		supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate	supplied	uptake	in percolate
1 t/m 20	10.5 - 8.2	48,00	48,00	0,00	48,00	48,00	0,00	42,00	42,00	0,00	45,00	45,00	0,00	42,00	42,00	0,00	48,00	48,00	0,00	48,00	48,00	0,00	321,00	321,00	0,00
21	8,1	2,40	50,40	0,00	2,40	50,40	0,00	2,10	43,65	0,45	2,25	47,25	0,00	2,10	42,90	1,20	2,40	50,40	0,00	2,40	50,40	0,00	16,05	335,40	1,65
22	7,9	2,40	52,80	0,00	2,40	52,80	0,00	2,10	43,35	2,85	2,25	49,50	0,00	2,10	42,00	4,20	2,40	52,80	0,00	2,40	52,80	0,00	16,05	346,05	7,05
23	7,8	2,40	55,20	0,00	2,40	55,20	0,00	2,10	42,00	6,30	2,25	51,75	0,00	2,10	39,90	8,40	2,40	55,20	0,00	2,40	55,20	0,00	16,05	354,45	14,70
24	7,7	2,40	57,60	0,00	2,40	57,60	0,00	2,10	39,90	10,50	2,25	54,00	0,00	2,10	37,50	12,90	2,40	55,65	1,95	2,40	57,60	0,00	16,05	359,85	25,35
25	7,5	2,40	60,00	0,00	2,40	60,00	0,00	2,10	37,35	15,15	2,25	56,25	0,00	2,10	35,10	17,40	2,40	55,05	4,95	2,40	60,00	0,00	16,05	363,75	37,50
26	7,4	2,40	62,40	0,00	2,40	62,40	0,00	2,10	35,25	19,35	2,25	58,50	0,00	2,10	34,05	20,55	2,40	52,95	9,45	2,40	62,40	0,00	16,05	367,95	49,35
27	7,3	2,40	64,80	0,00	2,40	64,05	0,75	2,10	33,90	22,80	2,25	60,75	0,00	2,10	33,30	23,40	2,40	49,35	15,45	2,40	64,80	0,00	16,05	370,95	62,40
28	7,2	2,40	67,20	0,00	2,40	62,10	5,10	2,10	33,45	25,35	2,25	60,75	2,25	2,10	33,30	25,50	2,40	47,70	19,50	2,40	67,20	0,00	16,05	371,70	77,70
29	7,2	2,40	69,60	0,00	2,40	58,50	11,10	2,10	33,45	27,45	2,25	60,00	5,25	2,10	33,30	27,60	2,40	47,10	22,50	2,40	69,60	0,00	16,05	371,55	93,90
30	7,1	2,40	72,00	0,00	2,40	55,35	16,65	2,10	33,45	29,55	2,25	57,45	10,05	2,10	33,30	29,70	2,40	47,10	24,90	2,40	72,00	0,00	16,05	370,65	110,85
31	6,9	2,40	74,40	0,00	2,40	53,40	21,00	2,10	33,45	31,65	2,25	53,70	16,05	2,10	33,30	31,80	2,40	47,10	27,30	2,40	74,40	0,00	16,05	369,75	127,80
32	7,0	2,40	76,80	0,00	2,40	53,40	23,40	2,10	33,45	33,75	2,25	52,95	19,05	2,10	33,30	33,90	2,40	47,10	29,70	2,40	72,60	4,20	16,05	369,60	144,00
33	7,0	2,40	76,80	2,40	2,40	53,40	25,80	2,10	33,45	35,85	2,25	52,95	21,30	2,10	33,30	36,00	2,40	47,10	32,10	2,40	71,70	7,50	16,05	368,70	160,95
34	7,0	2,40	76,80	4,80	2,40	53,55	28,20	2,10	33,45	37,95	2,25	52,95	23,55	2,10	33,30	38,10	2,40	47,10	34,50	2,40	71,70	9,90	16,05	368,85	177,00
35	7,0	2,40	76,80	7,20	2,40	53,55	30,60	2,10	33,45	40,05	2,25	52,95	25,80	2,10	33,30	40,20	2,40	47,10	36,90	2,40	71,70	12,30	16,05	368,85	193,05

5

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

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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 of ca. 40 wt. %.

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

Introduction

Coal fly ash (CFA) is an inhomogeneous substance consisting of particles of different composition and sizes, ranging from smaller than 0.1 mm up to circa 200 mm, which have been formed by the melting and volatilization of 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). The

Netherlands Standardization Institute (1995) has established procedures for both tests. 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/($m^2 \cdot$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:

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

In which

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

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 by Hollman (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.

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 a 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 HNO_3 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 5.1 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 5.1.

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 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_4EDTA	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 5.1 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 5.1 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-ratio's the pH is measured in the collected fraction and a representative sample is taken for analysis.

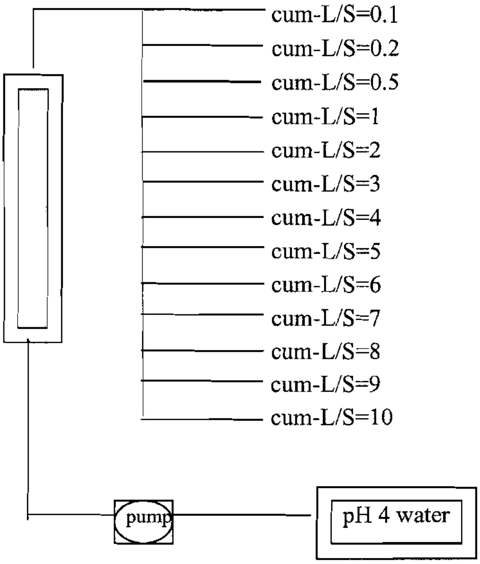

Figure 5.1 Schematic representation of the setup of a column-leaching test

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

$$\text{Cumulative emission column test} = \sum_{n} [M_i] * L_i / S \qquad \textbf{(3)}$$

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:

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

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 (CuKa 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 (Hollman, 1999). 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 HNO_3. 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 pHuture 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 $HF/HClO_4/HNO_3$ 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.

Results

Zeolitization of non pretreated CFA

Table 5.2 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 CrO_4^{2-} or $Cr(OH)_4^-$.

The element concentrations measured in the original and zeolitized CFA fit well with those observed in the reaction fluid. Figure 5.1 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 5.1 is Ba, the concentration of which is almost without conception below the detection limit, i.e. smaller than 0.1 mg/l.

In addition it is indicated by figure 5.1 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 reaction kinetics.

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 or not the zeolitized CFA complies with environmental regulations.

Table 2 Chemical composition of CFA before and after zeolitization[1] 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_2O_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_2O_3	8.8	9.2	7.7	9.1	11.8	9.3
K_2O	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_2O	1.2	5.9	6.5	-	-	-
P_2O_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

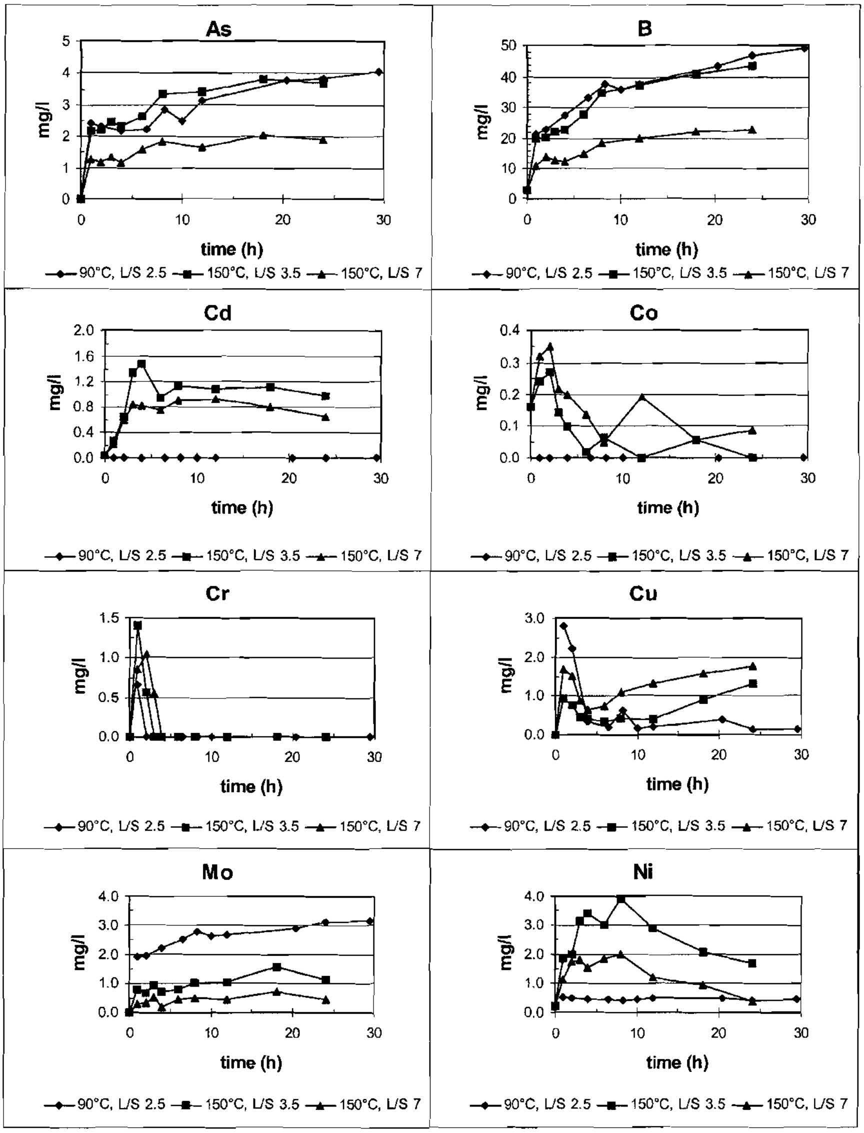

Figure 1 Concentration of elements as a function of reaction time in reaction fluids obtained from the zeolitization of CFA with a 2 M NaOH solution at 93 and 150°C and different L/S ratios (values below the detection limit are plotted as 0) -- *continued*

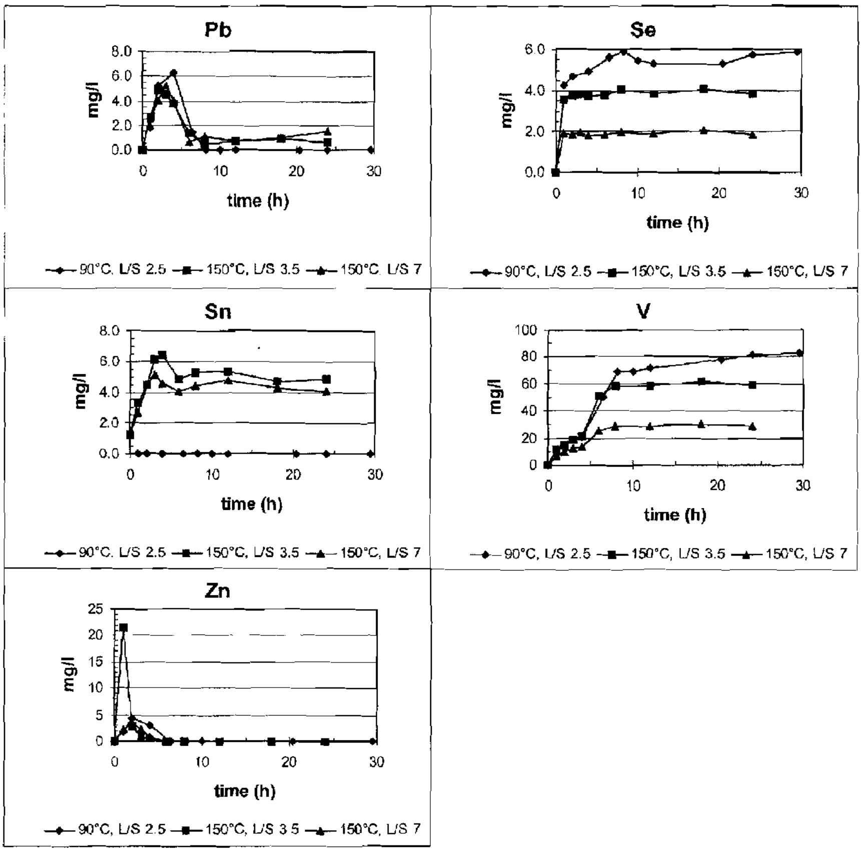

Figure 1 *Continuation*

Results column leaching experiments CFA and zeolitized CFA

Table 5.3 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 5.2 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 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		Cumulative leaching at L/S		Limit DDBM at L/S	
	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	65	<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	2.7	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	0.48	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 cat. 1 limit of the DDBM; ■ = leaching exceeds the cat. 2 limit of the DDBM

-- = No limit specified; n.a. = not analyzed

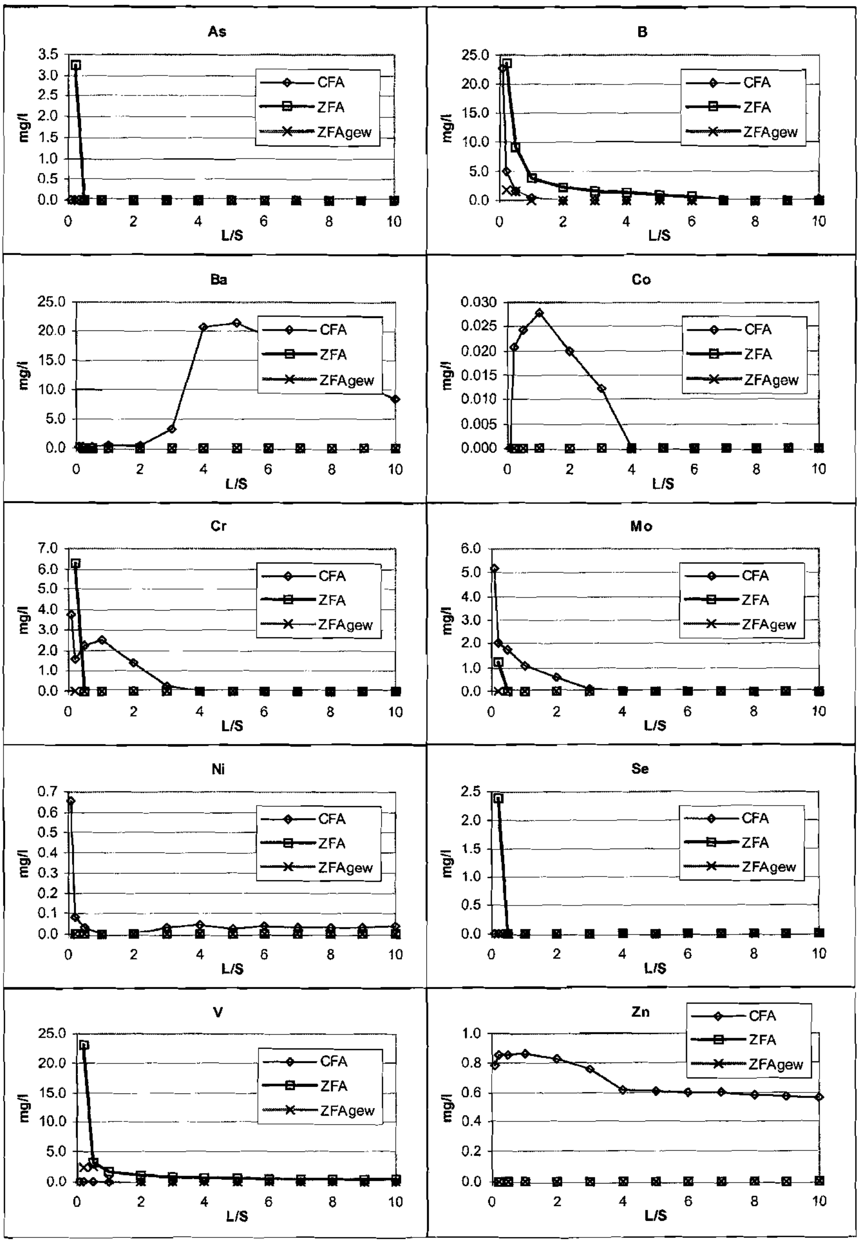

Figure 2 Concentration of elements in the leachate as a function of the amount of leachate passed through a column filled with fly ash (CFA), zeolitized fly ash (ZFA) or zeolitized pretreated fly ash (ZFAgew). Values below the detection limit are plotted as 0

From table 5.3 and figure 5.2 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 5.4 shows amounts of a number of elements removed from CFA by the different pretreatments.

Table 4 Percentages extracted of a number of elements from coal fly ash by different extractants1)

Element	CFA	Extracted (%)					
	(mg/kg)	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 NH_4-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 5.4 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 tot 80% lower. Table 5.5 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 5.4 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 5.5) 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. % in stead 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 has been created by the acid extraction.

Table 5 Concentrations of elements (mg/l) in reaction fluids obtained from the zeolitization of pretreated and non-pretreated coal fly ash[1]

	zeolitization at 93°C					zeolitization at 150°C	
Pretreat-ment	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	<	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	<	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 5.1 for a description of the conditions of pretreatment. All analyses by ICP-AES

Results column leaching experiments pretreated zeolitized CFA

Table 5.6 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 the formulas (1) and (2) in the introduction. In figure 5.2 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 6 Column leaching experiments: leaching from zeolitized pretreated CFA and the limits allowed by the Dutch Decree on Building Materials (DDBM)

Element	Cumulative leaching cumulative at L/S 10 (mg/kg)				limits DDMD at L/S 10 (mg/kg) at layer thickness 1 m	
	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	0.38	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 cat. 1 limit of the DDBM ; ■ = leaching exceeds cat. 2 limit of the DDBM;
-- = No limit specified

From table 5.6 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.

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 5.2 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 (Hollman, 1999/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 $Cr(OH)_4^-$ and the solubility controlling solid $Cr(OH)_3$, 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 $Sb(OH)_4^-$ and $Sb(OH)_6^-$ and their solubility is probably controlled by Sb_2O_3 and/or $Sb(OH)_3$ (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.

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.

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6

Application oriented experiments with the zeolite product

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

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Abstract

Pilot investigations were carried out on the possible applications of pure zeolite Na-P1, produced by the two-step-zeolitization of coal fly ash (CFA).
Batch-experiments were carried out with wastewater contaminated with color pigments and reject water from a wastewater treatment plant containing a high concentration of ammonium (about 600 mg per liter). It appeared that in case the color pigments are not bound to colloidals or to organic molecules in the solution, the zeolite is able to take up the pigments from the wastewater and lower their concentration below the valid standards. The reject water was purified from ammonium for about 80% in 1 step, but for about 100% when carrying out this treatment in 4 steps.
In order to investigate whether this pure zeolite can be used as a regenerable filter, a column was filled with pure zeolite Na-P1 and percolated with an ammonium containing effluent of a wastewater treatment until complete breakthrough. Afterwards, it was percolated with a regenerating solution containing NaCl. After 5 cycles equilibrium was established, which means that the amount of ammonium-cations during the loading of the zeolite is about equal to the amount of ammonium cations that is desorbed during the regeneration.

Key words: coal fly ash, pure zeolite, adsorption, ammonium, color pigments

Introduction

Following the research on the properties of the zeolitized fly ash (chapter 2-5), a number of pilot studies on the application of the product were carried out. In this chapter a selection of these studies is described. These investigations were all carried out with pure zeolite Na-P1, the product of the two-step zeolitization of fly ash (Hollman et al., 1999). The choice of experiments was inspired by interest shown in the market for the use of ZFA. The topics were:

1) Purification of wastewater from the dyeing industry that contains color pigments;
2) Purification of the effluent of a waste water treatment plant that contains ammonium (reject water);
3) As a re-usable filter in the purification of the effluent from a wastewater plant which contains ammonium.

Batch-experiments were chosen for the first two topics while for the third topic column experiments with regeneration were carried out.

Materials and methods

Batch-experiments

The batch-experiments were carried out with three types of wastewater, two of them containing color pigments (called purple and yellow, both colors resulting from a mixture of three pigments, namely yellow, red and blue) and one containing ammonium (called reject-water). Table 1 and 2 give an overview of respectively the chemical and spectral analysis of the wastewater samples. All chemical analyses were carried out by ICP-AES (Optima 3000, PE). The spectral analyses were carried out by spectrophotometry (Dr. Lange, cuvet test).

Table 1 Chemical analyses of the used waste water samples

Waste water	constituent (mg/l)*				
Sample	NH_4-N	Ca	K	Mg	Na
Purple	0.3	33	< d.l.	6.0	62
Yellow	< d.l.	39	< d.l.	6.8	70
Reject-water	610	91	72	16	56

* The concentrations of elements not mentioned (f.e. Si) are below the detection limit

Table 2 Spectral characterization of the samples purple and yellow

Waste water	Spectral absorption (A, dimensionless) of sample at wavelength		
Sample	436 nm (yellow)	525 nm (red)	620 nm (blue)
Purple	0.29	0.25	0.22
Yellow	0.071	0.044	0.028

An overview of the experimental conditions whereby the batch-experiments were carried out is given in table 3. All experiments were carried out in duplo.

Table 3 Performed batch-experiments with the waste water samples

Sample	batch experiment					Analysis		
	sample (ml)	Zeolite (g)	time (min)	present CEC (meq)	present cations (meq)	ICP	NH_4-N	spect.
Purple	50	1.0	1	4.30	0.24	X	x	x
	50	0.5	1	2.15	0.24		x	x
Yellow	50	1.0	1	4.30	0.28	X	x	x
	50	0.5	1	2.15	0.28		x	x
Reject	50	1.0	1	4.30	2.7	X	x	
Blank	50	1.0	1	4.30	0	X	x	x
	50	0.5	1	2.15	0	X	x	x

To investigate whether the color pigments of the waste water 'purple' and 'yellow' were bound or absorbed to colloids or to other particles bigger than 0.45 or 3 μm, small parts of these samples were filtrated using membrane filters with these pore sizes and subsequently analyzed by spectrometry.

Additional batch experiments to remove ammonium in more than one step

As was known from previous research (chapter 2 and Hollman et al, 1999), in case of high concentration of ammonium the adsorption has to be carried out in more than one step. Therefore, in addition, the same batch experiments as mentioned above were carried out with reject water, however this time in 4 steps. After each step the suspension was filtered and an unused sample of the zeolite was suspended in the filtrate of the next adsorption step.

Column-experiment

The column-experiment was carried out in a column (diameter 5-cm) with 30 g pure zeolite Na-P1. The CEC of this product was determined to be 4.3 meq/g (determined by the International Soil Reference and Information Center in Wageningen, the Netherlands, applying the ammonium acetate method (ISRIC, 1992) after samples were washed with 80% alcohol in order to remove excess salt). This material was upflow percolated with effluent of a wastewater treatment plant (for the chemical analysis see table 4) to which about 600 mg NH_4/ l was added.

Table 4 Composition of the wastewater treatment plant effluent

Element	Concentration	
	mg/l	meq/l
Ca^{2+}	33.6	1.66
K^+	15.9	0.4
Mg^{2+}	3.66	0.3
Na^+	208	9.0
NH_4^+-$N^{*)}$	596	42.6
Ni^{2+}	0.03	$1.0*10^{-3}$
Zn^{2+}	0.12	$3.6*10^{-3}$
Total cations		54

*) The concentration ammonium is increased by the addition of NH_4Cl

After filling the column, the material was percolated with the waste water treatment plant (wwtp) -effluent with a flow rate of 500 ml/h. Ten ml (10 ml) samples of the percolate were collected at time intervals of 1 hour and analyzed together with the total of percolate collected in between. At the moment the NH_4-N concentration in the percolate was equal to the concentration in the wwtp-effluent (the starting solution), the starting solution was replaced by a regenerating solution (NaCl solution, containing 17.5 gram NaCl per liter demineralized water (= 0.3 mol Na / l or 300 meq Na / l)), maintaining the same flow-rate. At the time the NH_4-N concentration in the percolate reached levels below the detection limit of the analytical method used, the regenerating solution was replaced by the wwtp-effluent again, and so on. Thus one complete cycle consisted of the loading and regenerating of the zeolite. The duration of the loading-part of one cycle varied from 7 hours in case of the first two cycles, to 6 hours for the third and 5 hours for the two last cycles. The regeneration time was 4 hours during the first cycle, 5 hours during the second, and 6 hours for the rest. Every cycle was repeated 5 times. The 500 ml fractions of the first and second cycle were analyzed by ICP-AES as well.

Results

Filtration of the colored samples

Table 5 gives the results of filtration test that was carried out, before the batch-experiments. It appears that in case the 'purple' is filtrated over a 0.45 μm filter, the purple color of the sample remains for a large part behind on the filter. Even after filtration over a paper filter (3 μm), a part of the color pigments remains in the filter. Compared to the purple sample, if the yellow sample is filtrated, a much smaller part of the pigments remains on the filter. For the purple sample the absorption at 436 nm decreases with 15%, at 525 nm with 20% and at 620 nm with 76%. After the filtration over the paper filter (3 μm) no pigments remains on the filter.

Thus the purple solution contains particles larger than 0.45 μm to which the color pigments are absorbed, or the color pigments are that large themselves (DHV, 1992). In the yellow solution the pigment is either dissolved, adsorbed to colloids or is a colloid, but mainly smaller than 0.45 μm. The chemical composition remained unchanged.

Table 5 Spectral absorption analyses of the filtrated waste water samples

Sample	filter	Absorption (A, dimensionless)		
		436 nm (yellow)	525 nm (red)	620 nm (blue)
purple	none	0.293	0.249	0.222
	0.45 μm	0.081	0.053	0.051
	3 μm	0.250	0.200	0.053
yellow	none	0.071	0.044	0.028
	0.45 μm	0.064	0.038	0.026
	3 μm	0.070	0.044	0.027

Batch-experiments

The results of the experiments carried out as mentioned in table 3 are shown in table 6. The data given in table 6 are converted to amounts adsorbed per gram zeolite in table 7.

Table 6 Concentration of elements (in mg/l) in the samples before and after the batch-experiments

Sample	before / after the test	Component in mg/l				
		NH_4-N	Ca	K	Mg	Na
Purple	before	0.3	33.4	< d.l.	6.0	61.7
	after	< d.l.	< d.l.	< d.l.	< d.l.	131.5
Yellow	before	< d.l.	38.9	< d.l.	6.8	69.7
	after	< d.l.	< d.l.	< d.l.	< d.l.	117.5
Reject water	before	613	91.1	72.3	16.4	55.8
	after	140	26.8	10.4	21	72

Table 7 Adsorption of elements by pure zeolite from the samples: the adsorbed amounts in mg/g and meq/g

Sample	Component									
	NH_4-N		Ca		K		Mg		Na	
	mg/g	meq/g	mg/g	meq/g	mg/g	meq/g	mg/g	meq/g	mg/g	meq/g
Purple	0.015	0.001	1.67	0.084	-	-	0.30	0.025	-3.5	-0.152
Yellow	-	-	1.95	0.098	-	-	0.34	0.028	-2.4	-0.104
Rej.water	23.7	1.69	3.22	0.161	3.10	0.080	-0.23	-0.018	-0.8	-0.034

A negative value means that the cation is released to the solution instead of adsorbed

In case of the colored samples, all NH_4, Ca and Mg were adsorbed from the solution by the zeolite. Overall, 0.11 meq cation per gram zeolite was taken from the solutions, this means that 100% of the total cations that was present in the original sample was adsorbed, see table 8. Table 8 gives an overview of the total quantity of elements adsorbed by 1 gram zeolite and of the theoretical, i.e. based on the CEC, quantity that can be adsorbed.

Table 8 Adsorption of elements by pure zeolite Na-P1 during the batch-experiments

Sample	Components reaction mixture (1 gram zeolite in 50 ml)		Adsorption by 1 gram zeolite		Occupation of the exchange sites (%)
	zeolite (meq)	cations*) (meq)	in meq*)	in %	
Purple	4.3	0.110	0.110	100	2.5
Yellow	4.3	0.126	0.126	100	2.5
Reject-water	4.3	2.59	1.93	75	45

*) The sum of the elements in the samples, except Na (exchange element)

From table 8 it is clear that a large excess of exchange sites is available compared to the quantity of cations in solution. This is the reason that 100% occupation of the exchange sites was not within the range of these experiments. This implies as well that in case the color pigments would not be completely taken up by the ZFA, the cause could not be that there were insufficient sites available. The results of the spectral absorption analysis are shown in table 9.

Table 9 Results of the spectral analysis of the samples after the batch-experiments

Sample	Composition reaction mixture		Absorbance (A, dimensionless) measured at		
	Zeolite (g)	Sample (ml)	436 nm (yellow)	525 nm (red)	620 nm (blue)
			A	A	A
Purple	0	50	0.293	0.249	0.222
	0.5	50	0.306	0.253	0.228
	1	50	0.282	0.242	0.220
Yellow	0	50	0.071	0.044	0.028
	0.5	50	0.046	0.024	0.016
	1	50	0.047	0.026	0.018

From this table it can be seen that the used ZFA does not adsorb the color-pigments of sample 'purple', but does of sample 'yellow'.

The spectral absorption coefficient is the used unity in standard norms, and can be calculated from the following formula (DHV, 1992):

$$\alpha(\lambda) = A(\lambda)*f/d$$

In which:

$\alpha(\lambda)$ = spectral absorption coefficient (m^{-1})
$A(\lambda)$ = absorbance of the sample by wavelength λ
f = factor, in this case 1000 mm/m
d = diameter of the cuvet (mm)

Table 10 gives the calculated spectral absorption coefficients, which thus can be compared with norms. The spectral absorption coefficients from the sample 'yellow' decreases at the three measured wavelengths to below the permitted standards (DHV, 1992).

Table 10 The spectral absorption coefficients of the samples before and after the batch-experiment

Sample	comp reaction-mixture		Spectral absorption coefficient ($\alpha(\lambda)$ in m^{-1})*)								
	zeolite (g)	sample**) (ml)	436 nm (yellow)			525 nm (red)			620 nm (blue)		
			before test	after test	% purified	before test	after test	% purified	before test	after test	% purified
Purple	0.5	50	29.3	30.6	0	24.9	25.3	0	22.2	22.8	0
	1.0	50	29.3	28.2	4	24.9	24.2	3	22.2	22	1
Yellow	0.5	50	7.1	4.6	35	4.4	2.4	45	2.8	1.6	43
	1.0	50	7.1	4.7	34	4.4	2.6	41	2.8	1.8	36
Norm***)			7			5			3		

*) Calculated by the formula $\alpha(\lambda) = A(\lambda)*f/d$

**) The batch-experiments are carried out with the untreated (unfiltrated) samples

***) From: 'Voorschrift Kleurstoffenanalyse' from DHV

Additional batch experiments to remove ammonium in more than one step

It appeared that is was possible to purify the used SWTP-effluent (containing 10 mg NH_4-N /l), but not in one step. In this case 3 successive steps were necessary to adsorb about 100 wt. % of the NH_4 ions in the effluent (see table 11)

Table 11 Ammonium adsorption by pure zeolite Na-P1 in four concessive batch experiments: adsorbed per batch experiment

Step	Conc. NH_4-N in effluent		Uptake NH_4-N by zeolite (wt.%)	
	before step	after step	compared to former step	cumulative
1	613	145	77	77
2	145	17	88	98
3	17	2	88	99.8
4	2	0.05	88	~100

Column experiment

An overview of the results of the NH_4-N concentrations in the fractions of the column experiment cycles is given in appendix 6.1. Besides the concentrations in mg/l the percentages NH_4-N adsorbed by the zeolite (the loading part of the cycle) and the percentages desorbed NH_4-N (the regeneration part of the cycle) are given. Figure 1a–d pictures these results. Appendix 6.2 contains the results of the ICP-AES analysis of the cumulative fractions from the first and the second cycle. From these results it can be seen that only the concentrations of

Na, Ca, Mg, S and Si were above the detection limit of the ICP-AES analytical method. The concentrations of Na and NH_4-N are compared with each other in figure 2 a-d. While Na and NH_4 compete with each other for the exchange sites in the zeolite, a behavior in reversed order can be expected from these two cations. The concentrations of the other cations are too low to be of interest in these experiments.

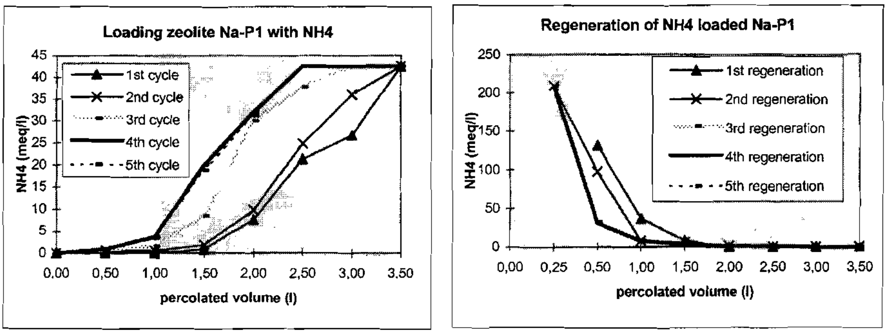

Figure 1a-b *Adsorption and desorption of NH_4-N by zeolite during the loading and regeneration of the cycles of the column experiment: concentration in the percolate in meq/l*

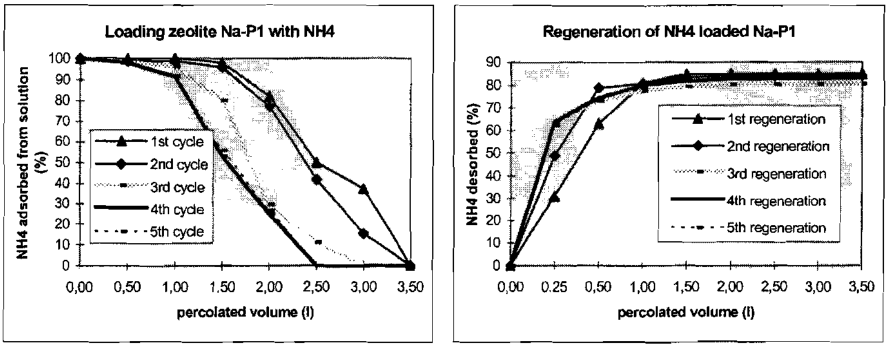

Figure 1c-d *Adsorption and desorption of NH_4-N by zeolite during the loading and regeneration of the cycles of the column experiment: percentages of NH_4 adsorbed from the starting solution and percentage NH_4 desorbed during the regeneration from the zeolite*

The total exchange capacity available in the column experiment was 129 meq. Table 11 gives an overview of the changes in the occupation of the adsorption sites by ammonium during the cycles. Noteworthy is that from the second cycle about as much cations are adsorbed as desorbed. However, the absolute quantity of ammonium cations that can be adsorbed decreases, and stabilizes finally at ca. 60 meq. During the 5 cycles of the experiment in total 377 meq NH_4 is adsorbed and 365 meq NH_4 is desorbed.

The values given in table 11 are based on a complete breakthrough of ammonium. Appendix 6.1 contains a table in which the breakthrough per cycle is given. From these tables, as well as from the figures 1 and 2, it can be seen that during the first loading the breakthrough of ammonium starts after 3 hours. In the other cycles, breakthrough starts already after 1 hour. After 2 hours the concentration in the percolate starts to increase with high amounts.

Table 11 Alterations in the occupation of the adsorption sites in the zeolite by NH4 during the cycles of the column experiment

Cyclus	Available (meq)	Adsorbed (meq)	Regenerated (meq)	% occupied exchange sites by NH_4 before start of the regeneration
1	129	104	88	81
2	113	91	90	83
3	112	67	68	65
4	113	57	61	57
5	117	58	58	54
6	117	-	-	-

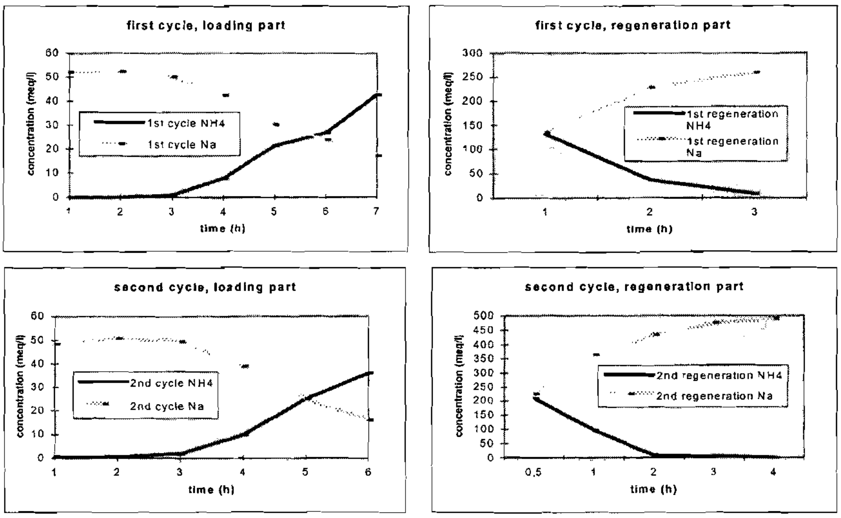

Figure 2a-d *Comparison of the Na and NH_4 concentrations during the first and second cycle of the column experiment*

Discussion

Batch-experiments with ammonium

The results of the batch-experiments show that the ZFA is able to lower the concentration of NH_4 considerably. All batch-experiments discussed here agree with this. However, since there was an excess exchange sites a complete removal of the ammonium from the solution by the zeolite could be expected. This does not occur, but it was found by additional batch experiments was found that the wastewater could be purified for about 100% in 4 steps.

Results here, like in previous research (Hollman, 1999) suggest that there has to be a relatively high concentration difference between the NH_4 in solution and in the exchanger.

Batch-experiments with colored samples
From the batch-experiment with the purple sample, it appears that almost no color pigment is taken from the solution by the zeolite. The spectral absorption coefficients virtually do not change. Because the color pigment does disappear after the filtration test, the pigments must be (or adsorbed on) particles larger than at least 0.45 μm, which are too large to fit in the zeolite channels (only about 3 Ångstrom).

The batch-experiment to remove the color from the yellow sample is much more effective in this case. All spectral absorption coefficients are below the norms after the experiment. Obviously, the color pigments in this sample consist of components with the capacity to adsorb on the zeolite. The filtration test showed that these pigments did not consist of particles larger than 0.45 μm, the composition of the yellow sample is the same before and after the filtration.

Column experiments (with NH_4, regeneration with Na)
From table 11 can be concluded that the degree of occupation decreases from 81% in the first cycle to 54% in the fifth and last cycle. Apparently, every next regeneration cycle less NH_4 is released to the percolate than was adsorbed in the loading part before that regeneration. Thus, a part of the ammonium is permanently adsorbed on the zeolite, and this means a change in structure. This change in structure is the reason as well for the fact that trials to model (with a computermodel based on Charon) this column experiment did not succeed.

During the regeneration the time in which the concentration of NH_4 in the percolate decreases to zero lasts about 3 hours. Taking more time for the regeneration is useless, since this will increase desorption of ammonium only with 0, 0.6, 1.0, 1.2 and 1.1% for the cycles 1 to 5. Thus, for an optimal application of zeolite as a filter to remove ammonium from wastewater, after 2 hours loading the filter has to be regenerated for 3 hours, when using an experimental setup like here.

After the synthesis of the zeolite the exchange sites are completely occupied with Na-ions. During the loading part of the cycle the NH_4 will push the Na from the exchange sites. During the regeneration part of the cycle this process takes place in the reverse order. That is why it is expected that during the loading and the regeneration the Na and NH_4 ions behave in opposed way. From figure 2 can be seen that this is indeed the case.

During the first regeneration, 139 meq Na remains in the column. Looking at the total exchange sites present in the column (129 meq), it suggests that besides adsorption of sodium other processes play a (small) role as well. An amount of 88 meq NH_4 is desorbed. Supposed that NH_4 in all cases is pushed away from the exchange sites by Na, 63% of the sodium is adsorbed by the exchange process and the rest (37%) taken away by other processes. However, the second cycle shows something different. More sodium is released from the zeolite (862 meq) than is put in by the starting solution (600 meq). In addition 90 meq NH_4 is removed from the column. Possibly sodium salts have formed in the material in the column, which start to dissolve again. Figure 2 points to the exchange between Na and NH_4, which is expected to take place. However, the data are not in perfect harmony to conclude that this is the only process, which takes place. Other processes may play a role as well.

Results in literature

In the present experiment regeneration is carried out by percolating the loaded zeolite with a sodium solution. In the literature, more methods are presented to regenerate zeolites. These presented methods can be divided in physical/chemical (this work) and biological methods. Physical/chemical methods can be used for the removal of ammonium as well as for the removal of heavy metals. The biological methods can only be used for the removal of ammonium. In the latter case, bacteria nitrify NH_4^+ to NO_3^- which will be converted into N_2 by other bacteria (denitrification).

Physical/ chemical methods: Hlavay et al (1982) loaded natural clinoptilolite with ammonium and regenerated it with an 20 grams per liter NaCl solution at pH 12.3. He reports a almost complete regeneration (98-99%) when the rate of loading is 5-7 Bed Volumes (BV) per hour or in total 10-200 BV per regeneration. De pH was kept constant through the addition of $CaCO_3$. In this research we applied about 100 BV per regeneration. Unfortunately, Hlavay did not supply more than one cycle, making comparison difficult.

Liberti et al. (1986) describes a process to remove ammonium and phosphate at the same time from water, forming a fertilizer ($MgNH_4PO_4$). Ammonium is removed from the wastewater by using clinoptilolite as an exchanger. Recirculating 6 BV's of 0.6 M NaCl 4 times regenerates this clinoptilolite. The average removal of ammonium was at least 90%. In comparison with this research the concentration Na is double, but the BV's much lower.

Loizidou (1989) used 20 ml 1M $NaNO_3$ for the regeneration of 0.3 g clinoptilolite. She found the heavy metals (Pb, Cd, Cu, Ni, and Cr) for more than 50% released to the solution.

Zhang et al (1988) as well as Zamzow and Murphy (1992) used a NaCl solution to regenerate clinoptilolite that was loaded with heavy metals. In both publications it is described that the zeolite can be regenerated for more than 80%, depending on the concentration of the NaCl solution and the rate of the regeneration.

Biological methods: The biological regeneration has also been applied successfully. Choudhary (1993) describes the possibility to regenerate the zeolite loaded with ammonium with the help of the bacterium *Escherichia Coli.* After regeneration 96% of the exchange sites can be used for adsorption again.

Green et al (1996) used the loaded zeolite as a carrier for the nitrifying biomass. Adding a NaCl solution (10 g/l) release the adsorbed ammonium which is nitrified to nitrate by the biomass The regenerating solution is reusable, while it isn't necessary to add new chemicals.

Conclusion

Batch-experiments with ammonium

From the result of the batch-experiments can be concluded that the zeolite Na-P1 is able to lower the ammonium concentration. If the batch-experiment is carried out in more than one step, the zeolite is able to remove all the ammonium. The reason for this behavior is that there has to be a difference in concentration of one order of magnitude between the exchanger and the solution before the reaction stops.

Batch-experiments with colored samples

It appears that samples with color pigments can be decolored by zeolite only in case they consist of small molecules that are not adsorbed on bigger particles. In the latter case the zeolite channels are too small for the color pigments to migrate into.

Column experiments (only with ammonium, regeneration with Na)

Alternating loading and regenerating zeolite Na-P1 with ammonium leads to the situation that about as much cations are adsorbed as desorbed. However, the absolute amount of ammonium cations that can be adsorbed decreases in the cycles. The degree of occupation decreases from 81% in the first cycle to 54% in the fifth and last cycle. The regeneration was successfully carried out with a 0.3 M (300 meq/l) NaCl solution, performance is similar to results in literature. However from the literature can be concluded that there are biological alternatives to regenerate the material as well.

Altogether it can be concluded that cleaning wastewater which is contaminated with ammonium is possible with zeolite Na-P1, and that the zeolite is (partly) regenerable as well. However, the costs of regenerating the zeolite will determine whether this method will be successful in practice.

Acknowledgments

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Appendix 6.1:

Results column experiments: NH4 analyses

Loading pure zeolite Na-P1 with NH4

cum.volume percolated solution	(l)	0	0,5	1	1,5	2	2,5	3	3,5
time	(h)	0	1	2	3	4	5	6	7
1st cycle, NH4-N in percolate	(mg/l)	0	0	0	11,9	107	298	373	596
2nd cycle, NH4-N in percolate	(mg/l)	0	7,5	8,2	25,8	137	347	505	596
3rd cycle, NH4-N in percolate	(mg/l)	0	8,1	23,2	119	420	530	596	596
4th cycle, NH4-N in percolate	(mg/l)	0	12,2	51,9	280	448	596	596	596
5th cycle, NH4-N in percolate	(mg/l)	0	13,8	48,6	263	437	596	596	596
1st cycle, NH4-N adsorbed	(%)	100	100	100	98	82	50	37,4	0
2nd cycle, NH4-N adsorbed	(%)	100	98,7	98,6	95,7	77,1	41,8	15,3	0
3rd cycle, NH4-N adsorbed	(%)	100	98,6	96,1	80,1	29,5	11,1	0	0
4th cycle, NH4-N adsorbed	(%)	100	98	91,3	53	24,8	0	0	0
5th cycle, NH4-N adsorbed	(%)	100	97,7	91,8	55,9	26,7	0	0	0

Loading is carried out with a solution containing 596 mg NH4-N/l and a flow of 500 ml/h

Regenerating of the NH4-loaded zeolite with NaCl

cum.volume percolated solution	(l)	0	0,25	0,5	1	1,5	2	2,5	3	3,5
time	(h)	0	0,5	1	2	3	4	5	6	7
1st reg., NH4-N in percolate	(mg/l)	-	-	1840	520	115	0	0	0	0
2nd reg., NH4-N in percolate	(mg/l)	-	2930	1360	115	80	19,9	0	0	0
3rd reg., NH4-N in percolate	(mg/l)	-	2930	460	105	48	16,2	5,4	0	0
4th reg., NH4-N in percolate	(mg/l)	-	2930	440	112	39	18,3	6,2	0	0
5th reg., NH4-N in percolate	(mg/l)	-	2930	450	115	44	16,7	4,9	0	0
1st reg., NH4-N desorbed	(%)*	0	31	63	80,9	84,8	84,8	84,8	84,8	84,8
2nd reg., NH4-N desorbed	(%)*	0	57,5	84,2	94,9	98	98,8	98,8	98,8	98,8
3rd reg., NH4-N desorbed	(%)*	0	79,3	91,5	97,1	99,6	100,5	100,8	100,8	100,8
4th reg., NH4-N desorbed	(%)*	0	82,3	96,1	103,1	105,6	106,7	107,1	107,1	107,1
5th reg., NH4-N desorbed	(%)*	0	75,8	89,7	96,8	99,5	100,5	100,8	100,8	100,8
1st reg., NH4-N desorbed	(%)**	0	31	63	80,9	84,8	84,8	84,8	84,8	84,8
2nd reg., NH4-N desorbed	(%)**	0	49	78,9	80,8	83,5	84,1	84,1	84,1	84,1
3rd reg., NH4-N desorbed	(%)**	0	63,3	73,1	77,5	79,5	80,2	80,5	80,5	80,5
4th reg., NH4-N desorbed	(%)**	0	63,8	74,6	80	81,9	82,8	83,1	83,1	83,1
5th reg., NH4-N desorbed	(%)**	0	62,5	73,9	79,8	82	82,8	83,1	83,1	83,1

Regeneration is carried out with a solution containing 17.5 gram NaCl /l and a flow of 500 ml/h

*) Percentage is calculated in respect of the NH4 adsorption in the zeolite in the preceding loading part of the cycle

**) Percentage is calculated in respect of the NH4 adsorption in the zeolite in the preceding loading part of the cycle PLUS the remaining NH4 in the zeolite from the former cycles

APPENDIX 6.2

Results column experiments: ICP analyses (1st and 2nd cycles)

		1st loading								d.l.
cum.volume percolated solution	(l)	0,5	0,8	1,3	1,7	2,1	2,6	3	3,5	
time	(h)	1	1,6	2,6	3,4	4,2	5,2	6	7	
S	(mg/l)	9,9	11,3	11,1	11,3	10,8	10,1	11,8	9,6	2,5
Mg	(mg/l)	<d.l.	2,1	2,8	3,1	3,1	3	2,9	2,9	0,5
Ca	(mg/l)	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	5	9	14,9	1,5
Si	(mg/l)	6,3	6,5	6,7	6,8	6,8	6,9	7,2	6,4	0,9
Na	(mg/l)	1171	1193	1204	1151	975	695	546	394	0,1

		2nd loading						d.l.
cum.volume percolated solution	(l)	0,5	1	1,5	2	2,5	3	
time	(h)	1	2	3	4	5	6	
S	(mg/l)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2,5
Mg	(mg/l)	<d.l.	2,1	2,7	2,7	2,8	2,7	0,5
Ca	(mg/l)	<d.l.	<d.l.	<d.l.	<d.l.	7,4	15,9	1,5
Si	(mg/l)	6,1	6	6,1	6,1	6,4	6,5	0,9
Na	(mg/l)	1116	1171	1140	902	574	364	0,1

		1st regeneration			d.l.
cum.volume percolated solution	(l)	0,5	1	1,5	
time	(h)	1	2	3	
S	(mg/l)	<d.l.	<d.l.	<d.l.	25
Mg	(mg/l)	<d.l.	<d.l.	<d.l.	5
Ca	(mg/l)	<d.l.	<d.l.	<d.l.	15
Si	(mg/l)	<d.l.	<d.l.	<d.l.	9
Na	(mg/l)	3106	5252	5962	1

		2nd regeneration					d.l.
cum.volume percolated solution	(l)	0,25	0,5	0,75	1	2	
time	(h)	0,5	1	1,5	2	4	
S	(mg/l)	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	25
Mg	(mg/l)	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	5
Ca	(mg/l)	94	<d.l.	<d.l.	<d.l.	<d.l.	15
Si	(mg/l)	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	9
Na	(mg/l)	5166	8400	10011	10951	11266	1

d.l. = detection limit
n.a. = not analyzed

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HET is af!

CURRICULUM VITAE

Arian Steenbruggen is op 20 januari 1969 in Deventer geboren. Na het behalen van het diploma Atheneum-B (Deventer) en de propedeuse Chemische Technologie (Enschede) is zij Milieukunde gaan studeren aan het Professor H.C. van Hallinstituut te Groningen. Gedurende deze studie heeft ze stage gelopen bij de Grontmij in De Bilt en het Zuiveringsschap West Overijssel in Zwolle. Het afstudeeronderzoek (reinigen van met zware metalen verontreinigde baggerspecie) is uitgevoerd bij TNO MeT in Apeldoorn. In 1991 studeerde zij af. Aansluitend is ze Geochemie gaan studeren aan de Universiteit Utrecht. In 1992 nàm ze deel aan een oceaanexpeditie over de Indische Oceaan, in 1993 deed ze haar afstudeeronderzoek bij het RIVM te Bilthoven. In januari 1994 ontving ze haar bul in de Exogene Geochemie. Van januari tot en met juni 1994 was ze werkzaam bij het Algemeen Geochemisch Laboratorium van de faculteit Aardwetenschappen, Universiteit Utrecht. Op 1 juli 1994 werd ze aangesteld als toegevoegd onderzoeker op het project 'Zeolitisatie van Vliegassen'. Gedurende 3 jaar werkte ze aan dit project. In augustus 1997 kwam ze in dienst bij de stichting GOA (Geologisch, Oceanografisch en Atmosferisch Onderzoek) van NWO. Van mei 1998 tot mei was ze werkzaam bij het Laboratorium voor Anorganische Chemie van het RIVM in Bilthoven. In deze periode startte ze tevens met het schrijven van dit proefschrift. Sinds mei 1999 is Arian werkzaam als beleidsmedewerker bij NWO, Aard- en Levens-wetenschappen (ALW), ontstaan uit het samengaan van GOA en SLW.