

BIJLAGE C

**RAPPORTAGE VAN DE SCHUDPROEVEN
(THE 'ACTIVE BARRIER' - BATCH EXPERIMENTS)**

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SUMMARY

The 'Active Barrier' - Batch experiments

The purpose of the present study is to define the optimized composition of a permeable active barrier. For that purpose experimental data are necessary in order to compare the adsorption ability of various materials towards a set of ionic pollutants. Experimental conditions were based on field data from an industrial site in the Rotterdam harbour area. Parameters known as important for the adsorption process like the synthetic groundwater composition, ionic strength, temperature and contact time were kept constant. The pH of the system was determined by the sorbing materials. Batch experiments were performed using glauconite, pyrolusite and zeolite as materials and arsenic, copper, nickel and zinc as adsorbents. In order to foresee the adsorption behaviour of a contaminant according to a type of material, experimental data were compared to the best-fit theoretical isotherm adsorption.

With respect to the ability of the investigated materials to reduce the contaminant concentrations 10 % of the initial concentrations or the 'intermediate value' glauconite will do for arsenic and zeolite will do for copper, assuming a barrier of 1 m width and a lifetime of minimal 30 years. A single material permeable active barrier will probably not be sufficient but a combination barrier might be required, for this case.

For the barrier materials a grain size of about 2.5 mm has to be used, glauconite fails because of its smaller grain size.

For the realization of a permeable active barrier for the (geo)chemical conditions as used for the experiments a combination of pyrolusite and zeolite is preferable.

1 Introduction

1.1 General

Solute transport of contaminants in natural soils is usually coupled with sorption processes. The main idea behind the permeable active barriers as used in environmental engineering is based on the use of this ability of certain mineral materials to reduce the mobility of contaminants thus decreasing the risk of spreading.

Since 1999 a research project 'the Active Barrier' has started on this topic in the research programme NOBIS (Dutch Research Programme In-Situ Bioremediation). The aim of this project is to investigate the ability of different type of mineral materials for the fixation of the contaminants, arsenic, copper, nickel and zinc and their geomechanical behaviour in relation to the application as permeable active barrier materials.

This report forms a part of the research study and is related to the sorption abilities of three types of mineral materials based on batch sorption experiments.

1.2 Purpose of the study

The purpose of the present study is to get experimental data in order to compare sorption ability of various solid materials in contact with the elements arsenic, copper, nickel and zinc, based on batch sorption experiments at constant test conditions. This to select one or more or a combination of the studied mineral materials for the following step of the project, the performance of column sorption tests.

Experimental conditions are taken from field measurements at an industrial site in the Rotterdam harbour area [1].

2 Materials and methods

2.1 Materials

Batch experiments have been performed with three types of barrier materials: zeolite (chabamin J), pyrolusite and glauconite. The barrier materials are supplied by Minerais de la Meditteranee S.A. via Ankerpoort n.v., Jan de Poorter and Mineral Development International A/S. The available physical and chemical properties of the materials are described in the following sections.

Two types of pH values are presented in the following sections. One is given by the provider of the materials and the second was measured in the laboratory at GeoDelft. The pH of the materials was measured with a ratio between water and solid (L/S) of 10. The system was shaken for 24 hours before the pH of the solution was measured. To distinguish the pH provided by the supplier and the one measured at GeoDelft, the latter will be called pH*.

2.1.1 *Glauconite*

Glauconite was used as it was received from the provider. Its grain size distribution is presented in appendix 1. The main characteristics of the materials are given in tables 1 up to 3.

Table 1. Chemical analysis. Results of XRF analysis on glauconite.

component	%	trace element	ppm
SiO ₂	53.65	V	183
TiO ₂	0.24	Cr	283
Al ₂ O ₃	10.06	Ni	30
Fe ₂ O ₃	19.84	Cu	6
FeO	n.d.	Zn	4
MnO	0.00	Rb	232
MgO	2.62	Sr	109
CaO	0.27	Y	105
Na ₂ O	0.04	Zr	163
K ₂ O	6.58	Nb	80
P ₂ O ₅	0.21	Mo	0
volatiles	5.80	Sn	0
		Ba	93
		La	188
		Ce	642

Table 2. pH and cation exchange analysis on glauconite.

pH* (L/S = 10)	exchange of Ca (cmol·kg ⁻¹)	exchange of Mg (cmol·kg ⁻¹)	exchange of Na (cmol·kg ⁻¹)	exchange of K (cmol·kg ⁻¹)	CEC (cmolkg ⁻¹)	base saturation (%)
4.65 ⁺	7.6	1.9	0.1	0.5	25.2	40

* pH is dependant on the contact time, because of the possible presence of pyrite

Table 3. Physical properties.

properties		units
density	2.91	g·cm ⁻³
porosity*	0.33	v/v
specific surface area	249	m ² ·g ⁻¹

* at 95 % compaction for the used grain size

2.1.2 Pyrolusite

The delivered pyrolusite (β -MnO₂) was sieved and the fraction between 2 and 2.8 mm was used for the experiments. The grain size distribution of the sieved pyrolusite is in appendix 2. The properties of the material are collected in tables 4 up to 6.

Table 4. Chemical analysis.

component	%	method
MnO ₂	74	ISO 312
MnO	3	XRF
Fe ₂ O ₃	8	XRF
Al ₂ O ₃	4	XRF
SiO ₂	5	XRF
Na ₂ O	0.2	XRF
K ₂ O	1	XRF
MgO	0.5	XRF
CaO	1	XRF

Soluble Mn 0.02 mg/l

Table 5. pH and cation exchange analysis on pyrolusite.

pH (5 % in H ₂ O)	pH* (L/S = 10)	exchange of Ca (cmol·kg ⁻¹)	exchange of Mg (cmol·kg ⁻¹)	exchange of Na (cmol·kg ⁻¹)	exchange of K (cmol·kg ⁻¹)	CEC (cmol·kg ⁻¹)	base saturation (%)
8	6.3	0.4	0.0	0.0	0.0	3.6	11

Table 6. Physical properties.

property		units	method
density	4.24	g·cm ⁻³	
tapped app. density	1.7	g·cm ⁻³	105 °C/24 h
porosity*	0.54	v/v	
specific surface	32	m ² ·g ⁻¹	
hardness Mohr's scale	5		

* at 95 % compaction for the used grain size

2.1.3 Zeolite

Zeolite was sieved to be used in the range of grain sizes between 2 and 2.8 mm. The grain size distribution of it is presented in appendix 3.

The chemical data of zeolite, partly based on data provided by the supplier of the material, are collected in the tables 7 and 8. The concentrations in the right column of table 7 are concentrations measured in the liquid phase after 24 hours of shaking in water (L/S = 10). The physical properties of zeolite are collected in table 9.

Table 7. Chemical properties.

composition solid phase		concentrations in water	
Na ₂ O	0.60 %	Al	< 0.02 mg/l
MgO	2.30 %	B	1.32 mg/l
Al ₂ O ₃	15.00 %	Ca	12 mg/l
SiO ₂	46.50 %	Cd	< 0.01 mg/l
K ₂ O	6.00 %	Cl	14.2 mg/l
CaO	10.00 %	Co	< 0.01 mg/l
Ti ₂ O	0.50 %	Cr	< 0.01 mg/l
Fe ₂ O ₃	3.00 %	Cu	0.13 mg/l
P ₂ O ₅	0.10 %	Fe	3.55 mg/l
SO ₃	0.30 %	H ₂ PO ₄	< 1 mg/l
Cr ₂ O ₃	- %	HCO ₃	73 mg/l
ZnO	- %	Hg	0.01 mg/l
As ₂ O ₃	- %	K	15.6 mg/l
SrO	0.10 %	Mg	2.4 mg/l
BaO	0.05 %	Mn	0.1 mg/l
lost in analysis	15.00 %	Mo	< 0.01 mg/l
		Na	9.2 mg/l
		Ni	< 0.01 mg/l
		NH ₄	< 2 mg/l
		NO ₂	< 0.1 mg/l
		NO ₃	< 0.1 mg/l
		Pb	< 0.01 mg/l
		Si	17.7 mg/l
		SO ₄	10 mg/l
		V	0.01 mg/l
		Zn	0.004 mg/l

Table 8. pH and cation exchange analysis on zeolite.

pH (5 % in H ₂ O)	pH* (L/S = 10) (1 hr)	pH* (L/S = 10) (24 hrs)	CEC (cmol·kg ⁻¹)
7.8	8.2	7.1	170

Table 9. Physical properties.

moisture (at 100 °C)	10	%
water absorbing capacity	50	%
density	2.2	g/cm ³
internal pore size	3.7 · 4.2	Å
porosity*	0.65	v/v
specific surface (110 °C)	14	m ² /g
specific surface (250 °C)	250	m ² /g

* at 95 % compaction for the used grain size

2.2 Methods

2.1.2 Introduction

The test conditions were chosen so that they enable valuable comparisons between the various materials. Ionic strength, pH, temperature, contact time, liquid/solid ratio are crucial parameters which can influence the adsorption process. Therefore care is taken to keep them identical between comparative tests.

Batch experiments are performed for each of the three types of barrier materials, discussed in section 2.1, with 4 contaminants dissolved in synthetic groundwater. Experiments are carried out in duplicate.

2.2.2 Liquid phase

The metal containing solutions that were used at the experiments were based on a synthetic groundwater. The macro chemical composition of the groundwater from reference [1] was chosen for the background composition of the synthetic groundwater. The synthetic groundwater was prepared by dissolving the following components in tap water:

- excess of calcium sulphate (± 1.00 g/l);
- excess of calcium carbonate (± 0.15 g/l);
- 1.97 mmole/l potassium chloride (0.1469 g/l);
- 0.59 mmole/l potassium nitrate (0.0597 g/l);
- 0.51 mmole/l magnesium nitrate (0.1308 g/l);
- 2.78 mmole/l magnesium sulphate (0.6852 g/l).

At first, there was also used 3.35 mmole/l sodium chloride in the preparation of the synthetic groundwater but because the pH was stabilized with HCl, sodium chloride is no longer important to obtain the necessary concentrations of chloride.

As one of the aims of this study was to investigate the adsorption behaviour of the elements at different pH values, the pH of the (basic) synthetic groundwater had to be adapted to the desired levels.

Firstly this was realized by pumping CO₂ through the solution to adapt the pH of the bulk solution of the synthetic groundwater. At first the used partial CO₂ pressures were 0.8 atmosphere and 0.024 atmosphere, resulted in pH ≈ 6.0 and pH ≈ 6.4, respectively (in agreement with the results

of calculations by the program MINTEQA). When the solution is in equilibrium with its chemicals (in the solution and in the solid phase) and its atmosphere, it is separated from the solid phase and can now be used to prepare solutions containing various contaminants. The prepared synthetic groundwater is used to prepare the metal containing solutions.

However, when the synthetic groundwater (after CO₂ treatment) is exposed to the normal atmosphere, the dissolved CO₂ will come out and the pH will increase to 7.9. To prevent the various contaminants from precipitation at higher pH levels, the pH is adjusted to the desired level by adding hydrochloric acid.

This way of preparing the synthetic groundwater background solution, however, results in different background concentrations, resulting in not a constant background solution for the sorption experiments, which is necessary to analyse and compare the results of the batch experiments.

To avoid this problem the following solution has been chosen.

About 150 litres of synthetic groundwater are prepared under atmospheric conditions (pH ± 7.9). When the system (liquid/solid phase interactions) is in equilibrium, the water is siphoned to three containers in which the solutions were adjusted to pH values of 5.75, 6.5 and 7.25 by using HCl. The addition of chloride is compensated with addition of an equivalent amount of NaCl in the containers with a higher pH.

To control the pH of the synthetic groundwater seemed to be reasonable but as the minerals to be investigated strongly influence the pH of the system and wash and condition them to the desired pH levels was not possible without changing their behaviour (see paragraph 2.2.3), the need for three types of synthetic groundwater turned out to be of less importance. Moreover when these type of materials should be used as a permeable active barrier in practice, conditioning them to a desired pH level will increase the cost of realization of permeable active barriers.

The elements, used for the batch experiments are copper (Cu), zinc (Zn), nickel (Ni) and arsenic (As). For Cu, Zn and As the proposed concentration ranges were 0, 5, 10, 15, 20 and 25 ppm while Ni was used in a range of 0, 1, 2, 3, 4 and 5 ppm, based on the maximum concentrations found from reference [1].

Unfortunately, the initially proposed concentration ranges were not feasible. In figure 1 the influence of the pH on the metal solubility in the synthetic groundwater is shown. On the y-axis is plotted the metal concentration, dissolved in the liquid phase. On the x-axis is plotted the pH. The dots at pH 5.7 are representing the concentrations, measured in the groundwater from the industrial site. Calculations have been made involving the effect of a raise of the pH on the solubility of the metal ions in the synthetic groundwater, used in the batch experiments. From the graphs can be concluded that only for As and Ni, it is possible to maintain the proposed concentration ranges.

For Zn, the range is limited to a maximum concentration of 15 ppm due to precipitation above pH 6.0. Input data for figure 1 are calculated by the program MINTEQA and are collected in table 10. Cu is also limited, but in a more extreme form by comparison with Zn.

Cu will already precipitate at pH ≈ 5.7 (for instance, at pH ≈ 6 copper precipitates as malachite (Cu₂(OH)₂CO₃) [4] and the maximum dissolved concentration drops till 0.3 ppm. Therefore, only

the concentration ranges for As and Ni can be the same as before and the ranges for Cu and Zn have to be changed.

Therefore, finally, only the synthetic groundwater with pH 5.75 was used in the experiments because at this pH level, copper can still be used (even though the maximum concentration equals 15 ppm) and Zn can also be used in the initial concentration range.

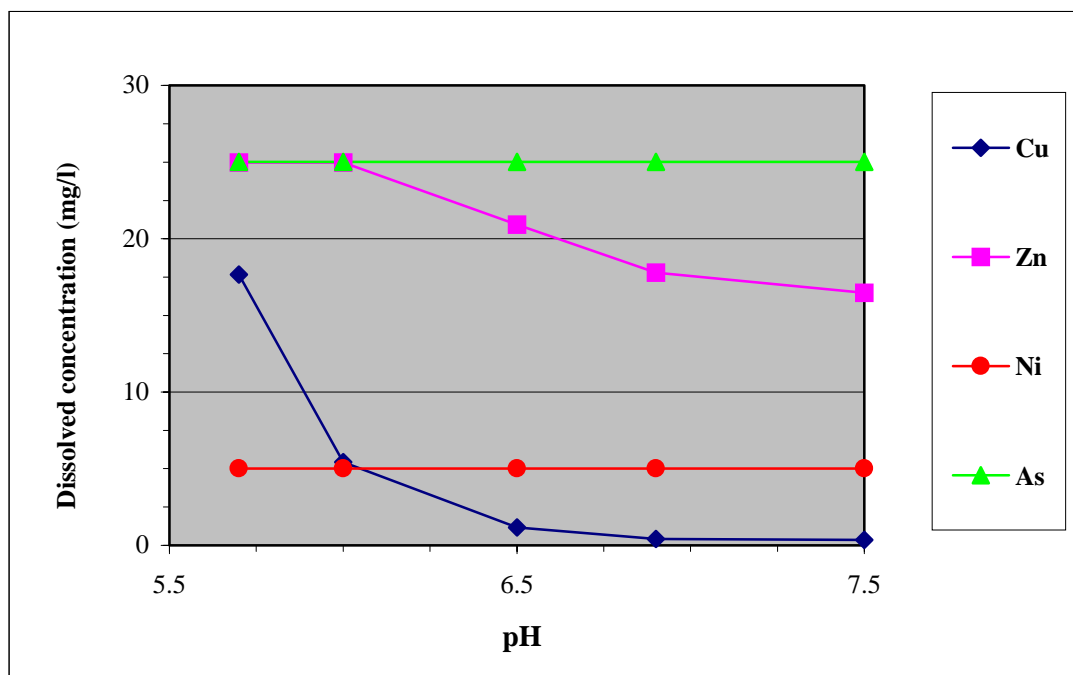


Fig. 1. Metal solubility in the synthetic groundwater as a function of pH.

Table 10. Maximum amount of dissolved metal in the synthetic.

P _{CO2} (atm)	pH	Cu (mg/l)	Zn (mg/l)	Ni (mg/l)	As (mg/l)
3.0	5.7	17.7	25.0	5.0	25.0
0.8	6.0	5.4	25.0	5.0	25.0
0.1	6.5	1.2	20.9	5.0	25.0
0.015	6.9	0.4	17.8	5.0	25.0
0.001	7.5	0.3	16.5	5.0	25.0

2.2.3 Solid phase

To minimize the influence of the pH on the system during the experiments, the materials are washed with water (same pH as used in the experiment). The reason for coming to this method is because prior to the experiments the materials were shaken in tap water for 24 hours in the same L/S ratio that is used in the experiments. pH measurements showed a large difference among the different materials. The pH values after shaking are 7.92, 4.65, 6.30 and 7.57 for water, glauconite, pyrolusite and zeolite, respectively (see table 11).

Firstly, all the three materials were washed several times with tap water (pH ≈ 8). Glauconite and pyrolusite are also washed with a water solution containing 0.01 M NaOH. After this treatment, the influence of the materials on the pH is different; after shaking with synthetic groundwater of pH 6.5 for 2.5 hrs. The pH changes are presented in table 12.

Table 11. pH values for three types of materials, before preparation.

mixture (L/S = 5)	pH liquid before	pH liquid after
glauconite/tap water	7.90	4.65
pyrolusite/ tap water	7.90	6.30
zeolite/ tap water	7.90	7.57

Table 12. pH values for three types of materials, after preparation.

mixture (L/S = 5)	pH liquid before	pH liquid after
glauconite/tap water	7.90	5.87
glauconite/synthetic groundwater	6.50	5.00
pyrolusite/tap water	7.90	6.3
pyrolusite/synthetic groundwater	6.51	6.0
zeolite/tap water	7.90	6.95
zeolite/synthetic groundwater	6.50	6.60

Washing out the materials was not enough to change and to keep the desired pH.

This shows the high buffer property of these materials. For glauconite and pyrolusite the exchangeable acids have been estimated by the difference between the CEC and base saturation (see tables 2 and 5) and have values of 25.1 cmol/kg and 3.2 cmol/kg. Because of this reason, the materials were used in the same state as delivered by the supplier. Therefore care was taken to measure the pH before and after the batch experiments.

2.2.4 Batch experiments

To execute the batch experiments, 10 grams of solid material were shaken in 50 ml polypropylene bottles in an end-over-end shaker with a solution of metal in the synthetic groundwater. The experiments were carried out with a contact time of 24 hours, at a constant temperature of 10 °C and a liquid/solid ratio of 5.

After the experiment, the samples were centrifuged and filtered. The sorbed amount of metal can be calculated using equation (2.1) when the concentrations of metal in the liquid phase were measured by Atomic Adsorption Spectrometry:

$$S = \frac{(C_r - C_t) \cdot V}{M} \quad (2.1)$$

where:

- S is the sorbed amount (mg/kg);
- C_r is the initial concentration in the solute (mg/l);
- C_t is the concentration in the solute (mg/l);
- V is the volume of the solute (l);
- M is the mass of the sand (kg).

3 Results and discussion

3.1 Experimental results

Data obtained from the batch experiments are presented in the following tables (see table 13 up to 24). For clarity concern, graphs relating the adsorbed amount and the final concentration of the ionic solute are presented after the tables (see fig. 2 up to 13).

The measurement based on a mixture of groundwater and the solid materials show some negative sorption of desorption. This may be explained by the desorption of the relevant ion present in the solid materials.

3.1.1 *Glauconite*

Table 13. Arsenic.

arsenic	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.005	0.005	0.000	5.02	5.64	4.33
	5	0.005	24.937	5.01	4.34	4.12
	10	0.01	50.055	5.01	4.06	4.06
	16	0.0145	79.704	4.99	3.85	4.06
	20	0.0265	99.795	5.00	3.69	4.03
	26	0.0485	130.021	5.01	3.64	3.99
	26	13	691.714	53.21	3.64	3.88

Table 14. Copper.

copper	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.0675	0.2095	-0.708	4.99	5.63	3.77
	4.769	1.449	16.621	5.01	5.57	3.86
	8.8125	2.88	29.653	5.00	5.55	3.91
	13.5715	4.611	44.820	5.00	5.54	3.89
	-	-	-	-	-	-
	-	-	-	-	-	-
	13.5715	13.1875	18.780	49.13	5.543	4.08

Table 15. Nickel.

nickel	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.051	0.155	-0.519	4.99	5.69	4.22
	1.1	0.596	2.529	5.02	5.56	4.2
	2.257	1.09	5.829	5.00	5.72	4.15
	3.622	1.726	9.495	5.01	5.77	4.14
	4.533	2.159	11.895	5.01	5.7	4.15
	5.334	2.5785	13.710	4.98	5.79	4.12
	5.334	4.757	32.237	56.11	5.79	4.27

Table 16. Zinc.

zinc	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.082	0.1955	-0.568	5.01	5.64	3.89
	5.007	1.90	15.562	5.01	5.59	3.89
	10.1125	3.06	35.225	5.00	5.480	3.9
	15.599	4.675	54.811	5.02	5.35	3.87
	20.35	5.975	71.627	4.98	5.2	3.86
	25.823	7.696	90.594	5.00	5.12	3.89
	25.823	14.830	555.460	50.55	5.12	4.07

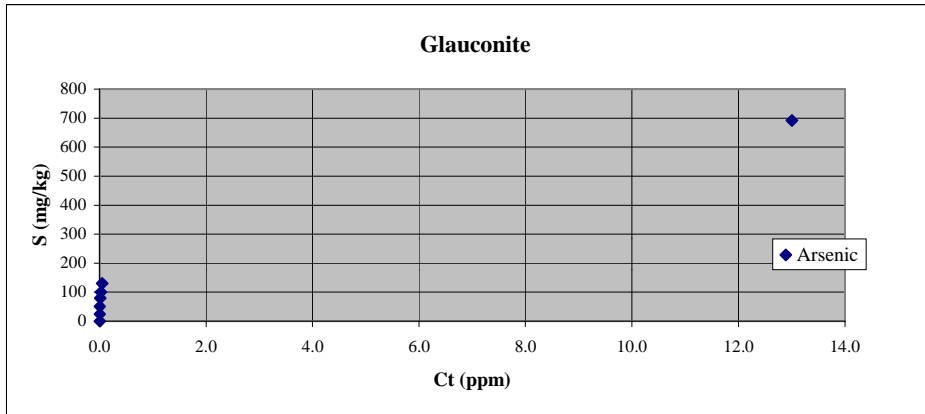


Fig. 2. Sorption of arsenic on glauconite (T: 10 °C).

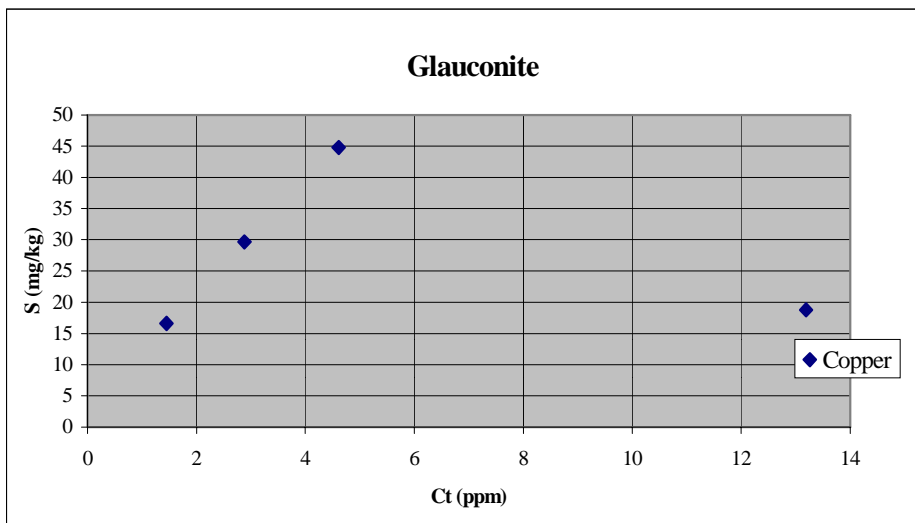


Fig. 3. Sorption of copper on glauconite (T: 10 °C).

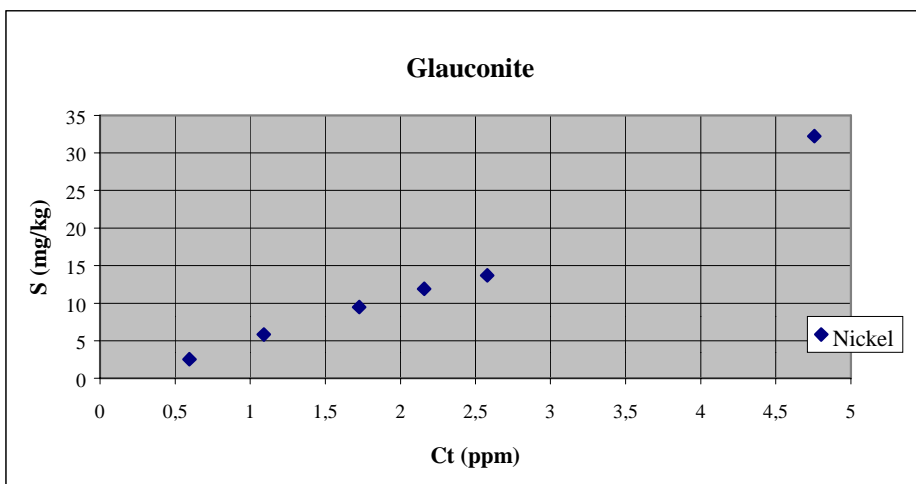


Fig. 4. Sorption of nickel on glauconite (T: 10 °C).

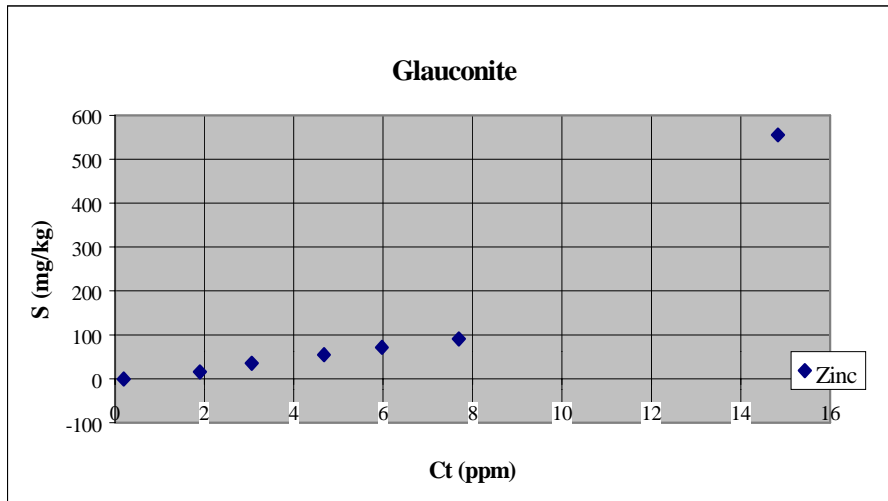


Fig. 5. Sorption of zinc on glauconite (T: 10 °C).

3.1.2 Pyrolusite

Table 17. Arsenic.

arsenic	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.005	0.005	0.000	5.02	5.64	5.41
	5	0.005	25.211	5.05	4.34	5.33
	10	0.01	50.111	5.02	4.06	4.41
	16	0.029	80.179	5.02	3.85	5.32
	20	0.0565	99.773	5.00	3.69	5.36
	26	0.081	129.372	4.99	3.64	5.33
	26	18	406.268	50.78	3.64	4.66

Table 18. Copper.

copper	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.0675	0.1605	-0.464	4.99	5.63	5.28
	4.769	0.222	22.623	4.98	5.57	5.13
	8.8125	0.36	42.231	5.00	5.55	5.1
	13.5715	0.746	65.036	5.07	5.54	5.08
	-	-	-	-	-	-
	-	-	-	-	-	-
	13.5715	2.7525	108.647	10.04	5.543	4.93

Table 19. Nickel.

nickel	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.051	0.066	-0.075	4.99	5.69	5.67
	1.1	0.3855	3.634	5.09	5.56	5.67
	2.257	0.85	7.053	5.01	5.72	5.59
	3.622	1.54	10.409	5.00	5.77	5.6
	4.533	2.182	11.671	4.96	5.7	5.55
	5.334	2.788	12.732	5.00	5.79	5.55
	5.334	5.031	16.277	54.70	5.79	5.53

Table 20. Zinc.

zinc	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.0475	0.015	0.166	5.10	5.98	5.97
	4.968	1.362	18.017	5.00	5.51	5.85
	9.95	4.30	28.704	5.08	5.550	5.73
	15.238	7.508	39.127	5.06	5.43	5.68
	19.85	10.560	46.582	5.01	5.28	5.64
	24.955	14.820	50.605	5.00	5.16	5.56
	24.955	21.600	61.882	18.56	5.16	5.57

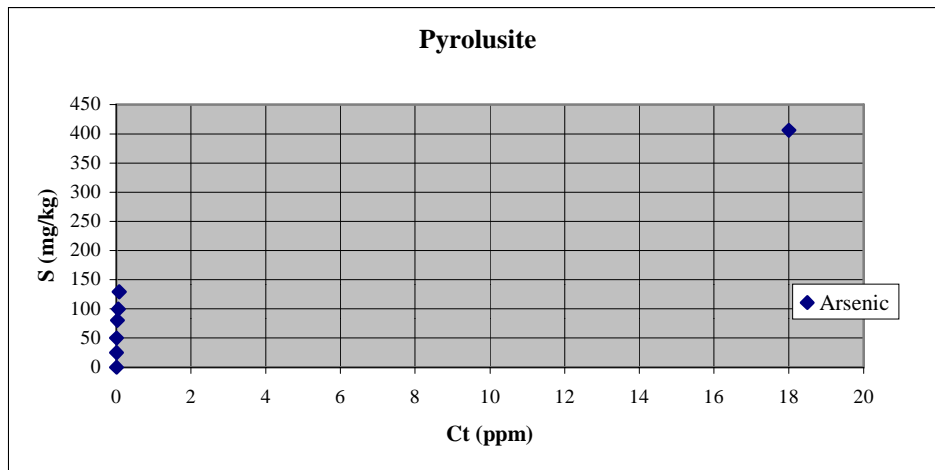


Fig. 6. Sorption of arsenic on pyrolusite (T: 10 °C).

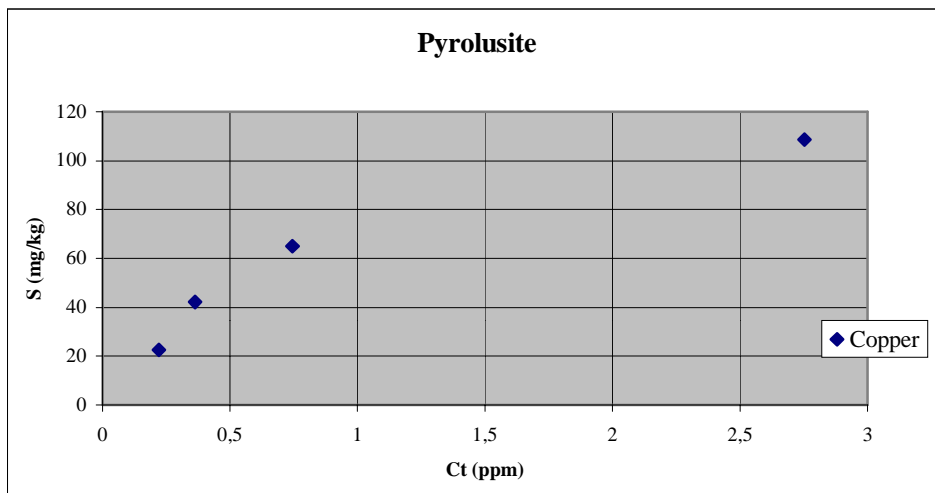


Fig. 7. Sorption of copper on pyrolusite (T: 10 °C).

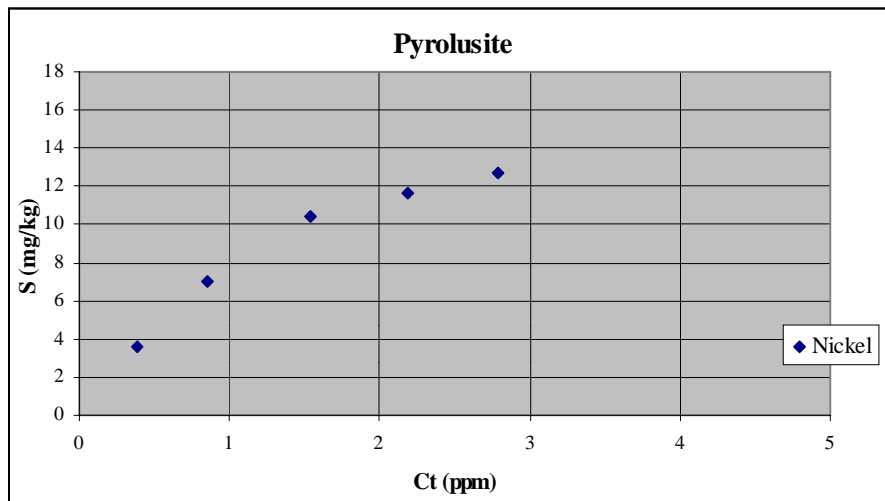


Fig. 8. Sorption of nickel on pyrolusite (T: 10 °C).

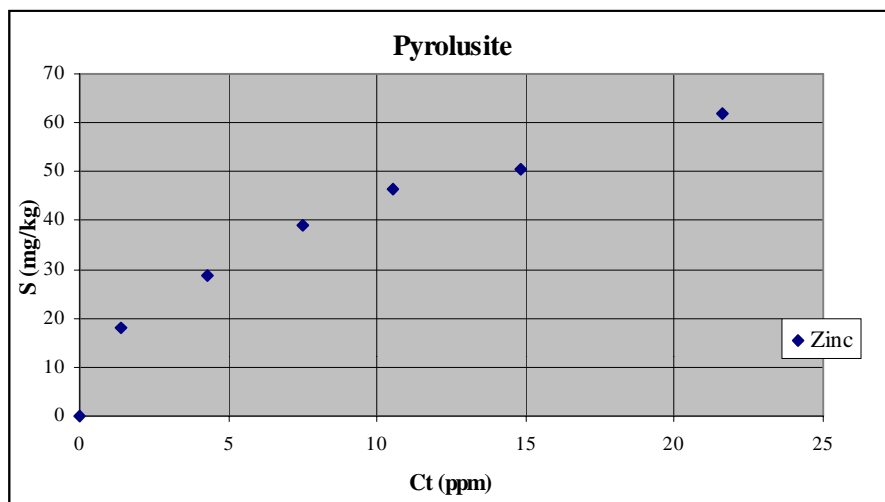


Fig. 9. Sorption of zinc on pyrolusite (T: 10 °C).

3.1.3 Zeolite

Table 21. Arsenic.

arsenic	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.005	0.00685	-0.009	4.99	5.69	6.8
	5	2.4	12.998	5.00	5.56	7.07
	10	5.35	23.284	5.01	5.72	7.23
	16	9.3	33.565	5.01	5.77	7.26
	20	11.3	43.571	5.01	5.7	7.32
	26	17	45.040	5.00	5.79	7.26
	26	24	108.481	54.24	5.79	7.33

Table 22. Copper.

copper	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.074	0.0725	0.008	5.01	5.84	7.25
	4.79875	0.0835	24.108	5.11	5.57	7.39
	8.9125	0.08	44.263	5.01	5.67	7.49
	14.3925	0.0975	71.443	5.00	5.64	7.54
	-	-	-	-	-	-
	-	-	-	-	-	-
	14.3925	0.403	271.203	19.39	5.64	7.22

Table 23. Nickel.

nickel	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.051	0.0315	0.098	5.01	5.69	7.07
	1.1	0.192	4.552	5.01	5.56	7.16
	2.257	0.42	9.212	5.00	5.72	7.12
	3.622	0.7645	14.329	5.01	5.77	7.11
	4.533	0.986	17.752	5.00	5.7	7.1
	5.334	1.218	20.727	5.04	5.79	7.06
	5.334	4.339	53.860	54.10	5.79	6.85

Table 24. Zinc.

zinc	C ₀ (ppm)	C _t (ppm)	S (mg/kg)	L/S	pH ₀	pH _t
	0.0475	0.0095	0.190	5.01	5.98	7.53
	4.968	0.095	24.628	5.03	5.51	7.54
	9.95	0.31	48.171	4.99	5.550	7.5
	15.238	0.587	73.014	4.98	5.43	7.5
	19.85	0.889	95.057	5.01	5.28	7.46
	24.95965	1.524	117.437	5.01	5.16	7.49
	24.95965	8.590	310.060	18.94	5.16	7.11

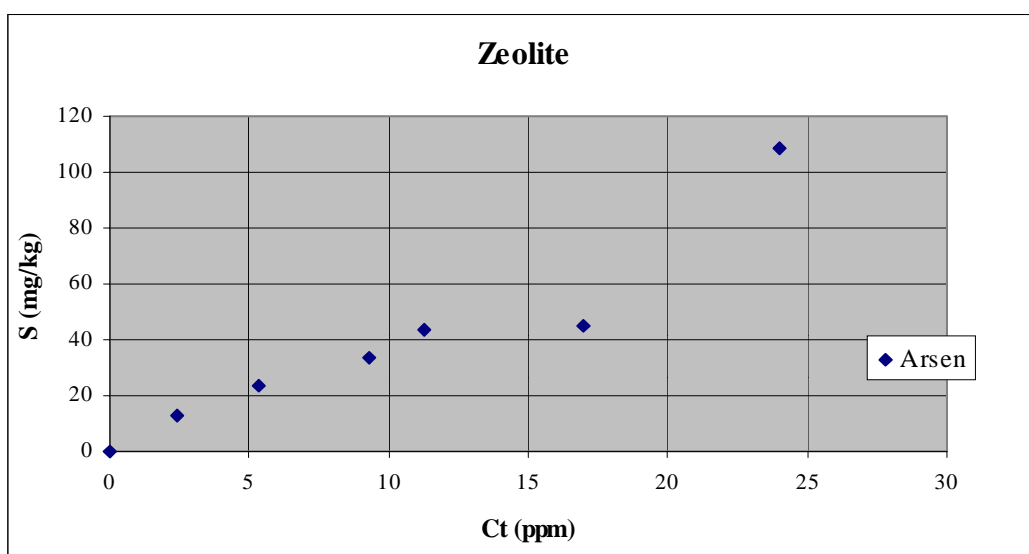


Fig. 10. Sorption of arsenic on zeolite (T: 10 °C).

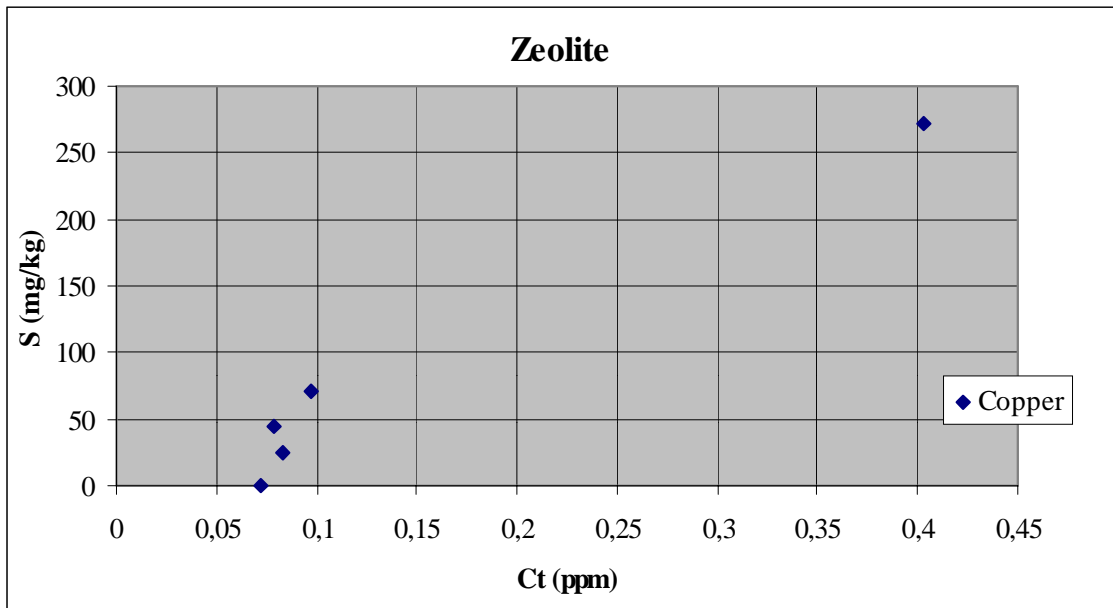


Fig. 11. Sorption of copper on zeolite (T: 10 °C).

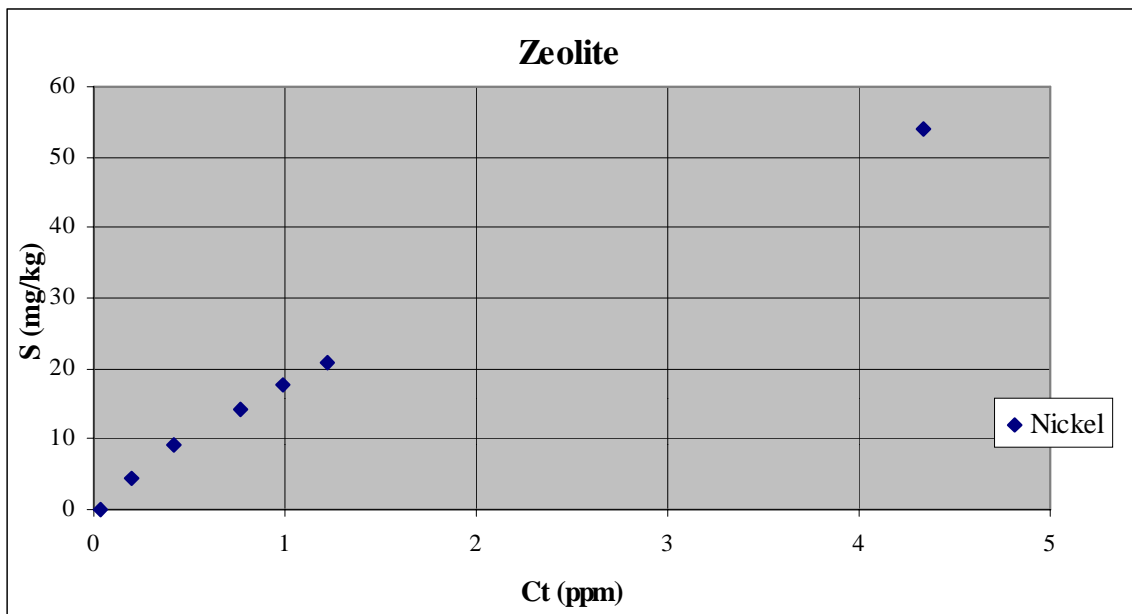


Fig. 12. Sorption of nickel on zeolite (T: 10 °C).

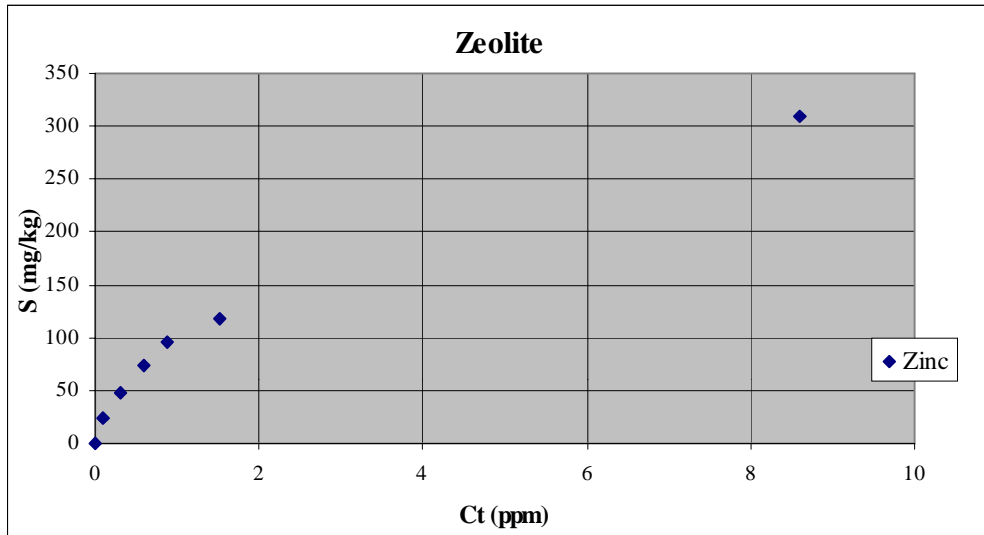


Fig. 13. Sorption of zinc on zeolite (T: 10 °C).

3.2 Sorption isotherms and breakthrough curves

In order to transform the experimental results in a sorption ability ranking for the materials, adsorption isotherms were derived from the experimental data. These isotherms have been used to model the breakthrough times of As, Cu, Ni and Zn, assuming a permeable barrier of 1 meter thickness and a groundwater velocity of 8 m/j [1].

The following assumption is taken: the adsorption equilibrium is reached for all our tests. Two arguments enable this assumption. Firstly, to allow the above-mentioned assumption, the chosen contact time is 24 hours. The latter should be reasonably long enough especially for batch experiments. Secondly, to get closer to the adsorption maximum, adsorption of samples with a higher liquid/solid ratio (L/S:10, 20 or 50) were also determined. Fitting was performed for all the results of the batch experiments except for the highest L/S experiments. In table 25 the derived adsorption parameters for the materials are summarized, based on the linear sorption equation: $S = K_{lin} \cdot C_{eq}$ or the Freundlich sorption equation: $S = K_f \cdot C_{ev}^n$ or the Langmuir equation: $S = S_m \cdot K_{lan} \cdot C_{eq} / (1 + K_{lan} \cdot C_{eq})$. In appendices 4, 5 and 6 the curves fitted for the isotherms are given for glauconite, pyrolusite and zeolite respectively.

Table 25. Material sorption parameters.

glauconite		n	S_0^*	S_m	K	R^2
As	Freundlich	0.48			572.93	0.9862
Cu	Freundlich	0.86			12.07	0.999
Zn	linear		4.45		12.51	0.9963
Ni	linear		0.55		5.67	0.9956
pyrolusite		n	S_0^*	S_m	K	R^2
As	Freundlich	0.31			203.42	0.9071
Cu	Freundlich	0.59			66.35	0.9317
Zn	Langmuir			67.6	0.19	0.9807
Ni	Langmuir			22.17	0.426	0.9949
zeolite		n	S_0^*	S_m	K	R^2
As	Freundlich	0.83			5.83	0.9246
Cu	linear		41.3		822.89	0.9825
Zn	Freundlich	0.51			100.74	0.9613
Ni	Langmuir			59.88	0.43	0.9805

* amount of sorbed elements at $C_0 = 0$

The results of the breakthrough curves are presented in the figures 14 through 16.

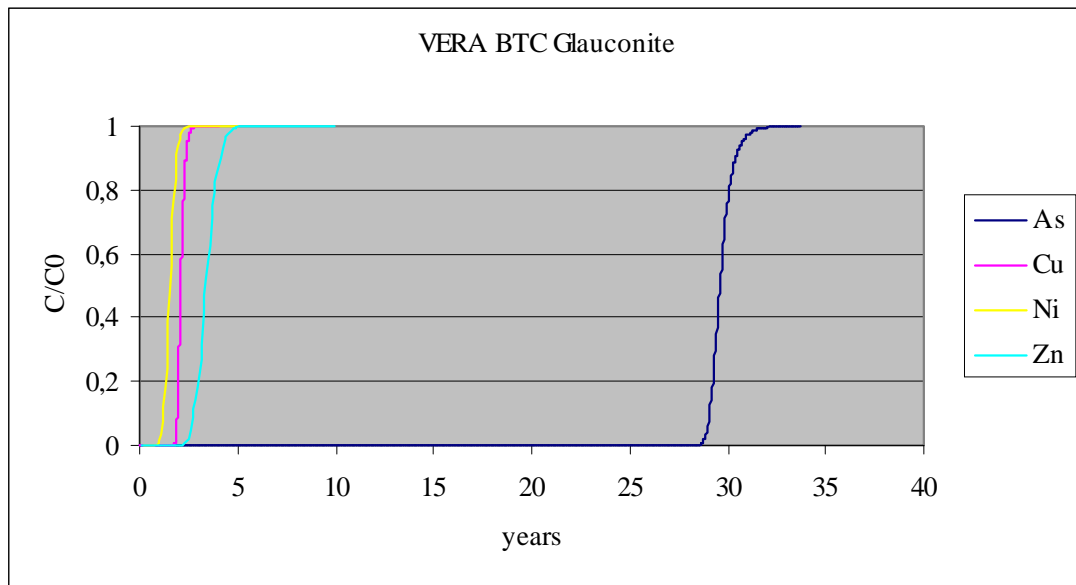


Fig. 14. Breakthrough curves for glaucosite.

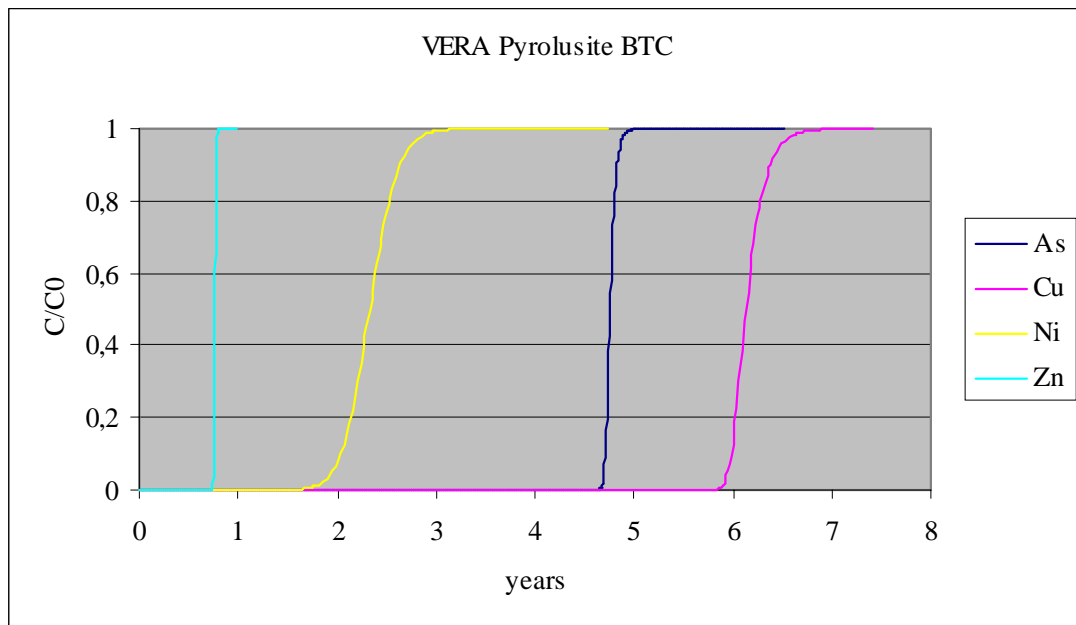


Fig. 15. Breakthrough curves for pyrolusite.

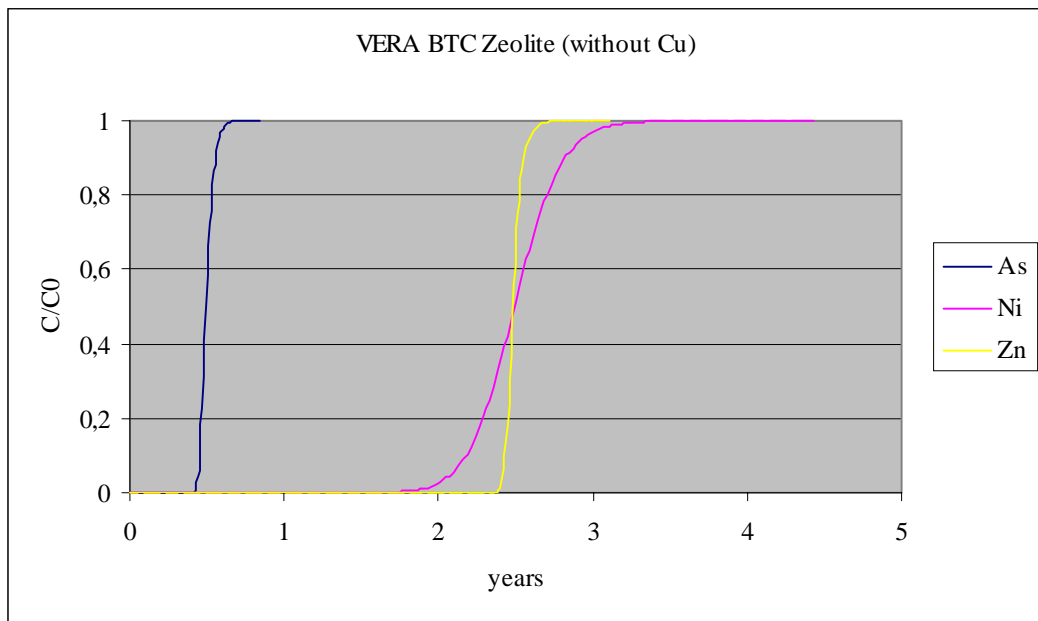
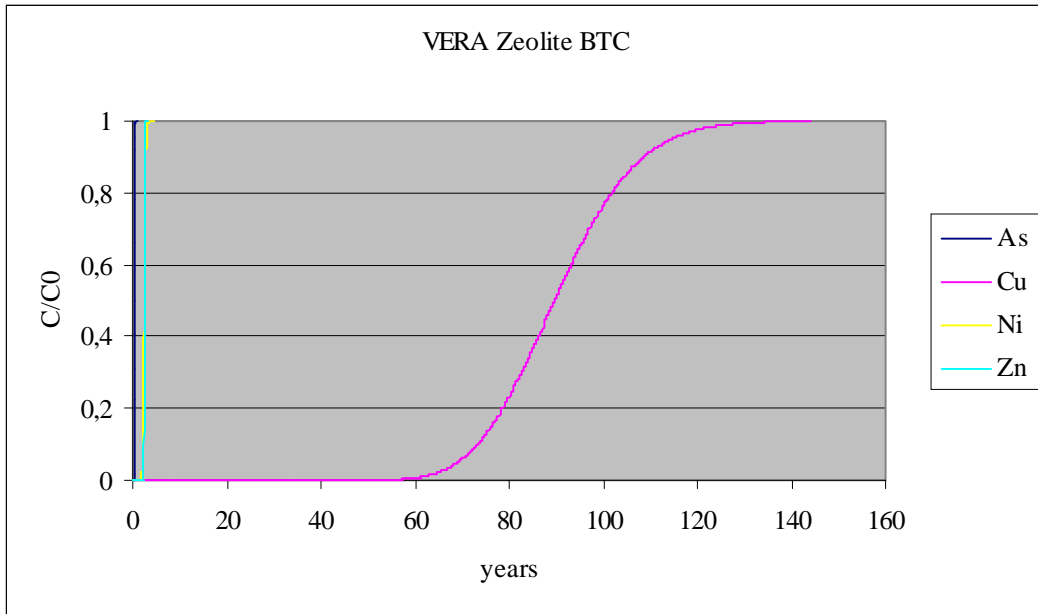


Fig. 16. Breakthrough curves for zeolite.

3.3 Discussion

Based on the results of the batch experiments the sorption ability ranking for the different materials can be derived from the modelled breakthrough curves. The results are presented in table 26.

Table 26. Material sorption ability ranking.

material/ions	arsenic	copper	nickel	zinc
glauconite	++	-	-	+
pyrolusite	++	++	+	-
zeolite	-	++	+	+

The evaluation of the ability to reduce the contaminant concentrations to 10 % of the initial concentration and the 'tussenwaarden' of the different materials is presented in table 27. The evaluation for the 'tussenwaarden' are presented between brackets.

Table 27. Ability of materials to reduce concentrations to 10 % of the initial concentration and the 'T(ussen)waarden'.

	C_{max} (ppm)	10 % · C_{max}	T-waarde (ppm)	glauconite	pyrolusite	zeolite
arsenic	14	1.4	0.035	+(+)	++(++)	-(-)
copper	23	2.3	0.04	(-)	-(-)	++(++)
nickel	0.39	0.04	0.04	(-)	-(-)	-(-)
zinc	22	2.2	0.4	(-)	-(-)	-(-)

- ++ breakthrough > 30 years
- + breakthrough 20 - 30 years
- breakthrough < 10 years

As can be seen from table 27 only glauconite and pyrolusite is able to reduce the arsenic concentration to it's 'tussenwaarde' or lower at these initial concentration levels, just as only zeolite is able to do this for copper. Although for pyrolusite the elements copper, nickel and for zeolite copper, nickel and zinc are adsorbed, these materials contain some of the elements, that will be desorbed at concentrations 2 or 3 times their T-waarden.

For application purpose, the local pH influence is important to determine the composition of the permeable active barrier as the latter can be made of a mixture of various materials.

A compromise between the materials is necessary to optimize the chemical wall especially when the groundwater is spoiled with a mixture of various contaminants and the groundwater quality requirements. In the conditions of the experiments, a mixture of zeolite and pyrolusite is the most interesting composition in order to adsorb a blend of arsenic, copper, nickel and zinc. Pyrolusite should be preferred to glauconite because his buffering pH is higher. Moreover, pyrolusite and zeolite are commercially available in the desirable size range. To work with glauconite, it has to be pretreated, as the grain sizes might be to small for direct application in a permeable active barrier which is to be considered for the cost evaluation.

4 Conclusions

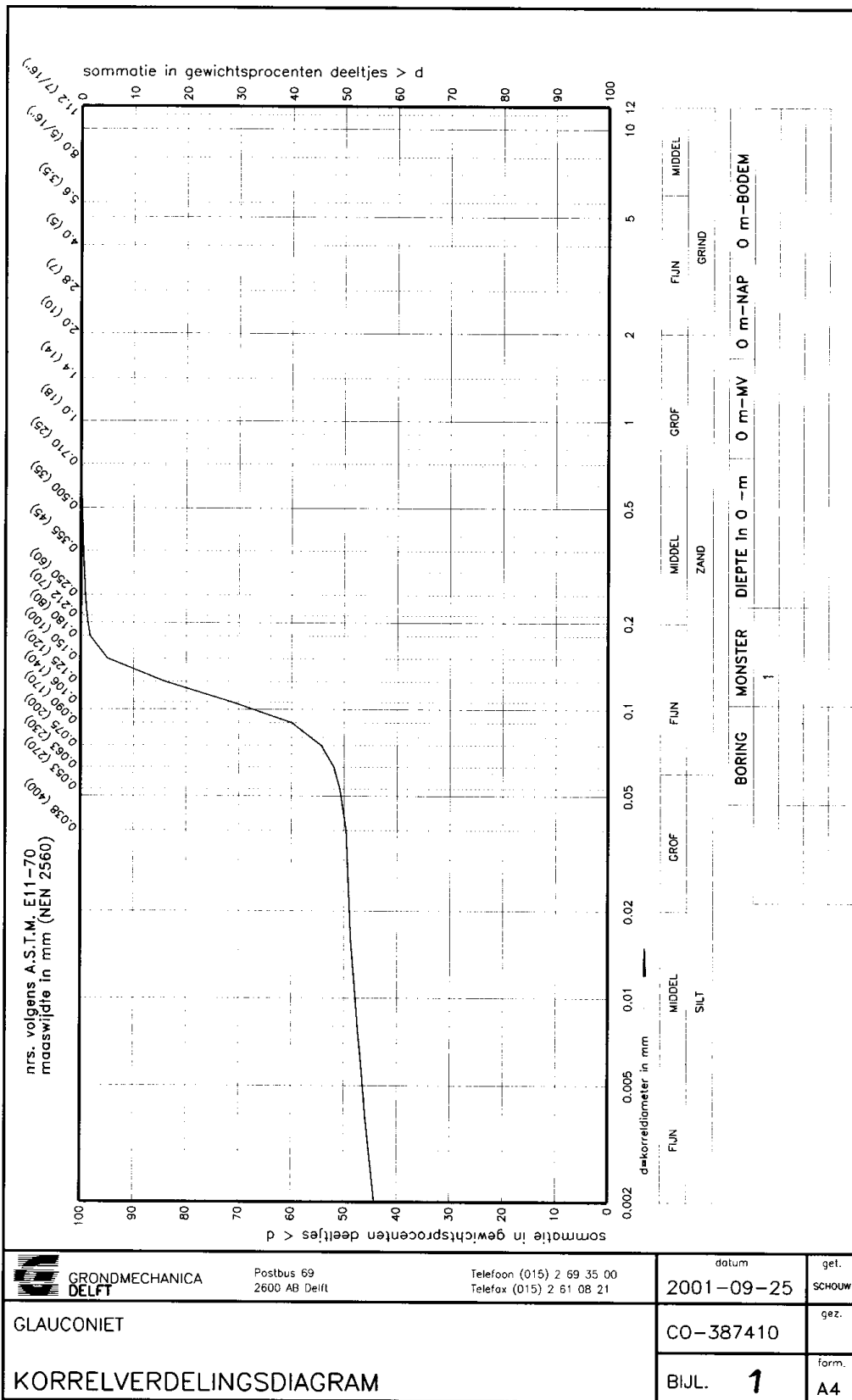
Batch experiments have been performed in order to compare adsorption of arsenic, copper, nickel and zinc, dissolved separately into a synthetic groundwater, on glauconite, pyrolusite and zeolite. The test conditions were based on fields' measurement at an industrial site. pH was not kept constant but was determined by the sorbing materials. Data sets fit different sorption isotherms. Several adsorbent/contaminants systems show high adsorption levels compared to the others. Arsenic adsorbs preferentially on acid materials like glauconite and pyrolusite whereas copper, zinc and nickel (in decreasing adsorption order) prefers basic materials like zeolite as well as pyrolusite except for nickel. The materials buffering pH is of importance for the adsorption of some of the materials.

With respect to the ability of the investigated materials to reduce the contaminant concentrations, for this case, to 10 % of the initial concentrations glauconite will do for arsenic, zeolite will do for copper assuming a barrier of 1 m width and a lifetime of minimal 30 years. A single material permeable active barrier will probably not be sufficient but a combination barrier might be required, for this case. As for the barrier materials a grain size of about 2.5 mm has to be used, glauconite fails because of its smaller grain size.

5 References

1. Materiaal- en veldgegevens 'Chemische Barrière' Kemira Agro, Pernis.
CO-387410/52, 1999 (bijlage A bij het eindrapport van dit NOBIS-project).
2. Weber, W.J. et al.
Sorption and retardation of organic contaminants in subsurface systems: effects on transport and fate.
Advances in Groundwater Pollution Control and remediation, Kluwer Academic Publishers, pp 1-31, 1996.
3. Sposito, G.
The chemical of soils.
Oxford University Press, New York; 1989.
4. Benjamen, M.M., and J.O. Leckie.
Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxide.
Journal of colloid and interface science, vol. 79, nr. 1, pp 209-221, January 1981.
5. Programma van eisen Actieve barrière.
CO-378410/20, 1999 (bijlage B bij het eindrapport van dit NOBIS-project).

Appendix 1 Grain size distribution of glauconite



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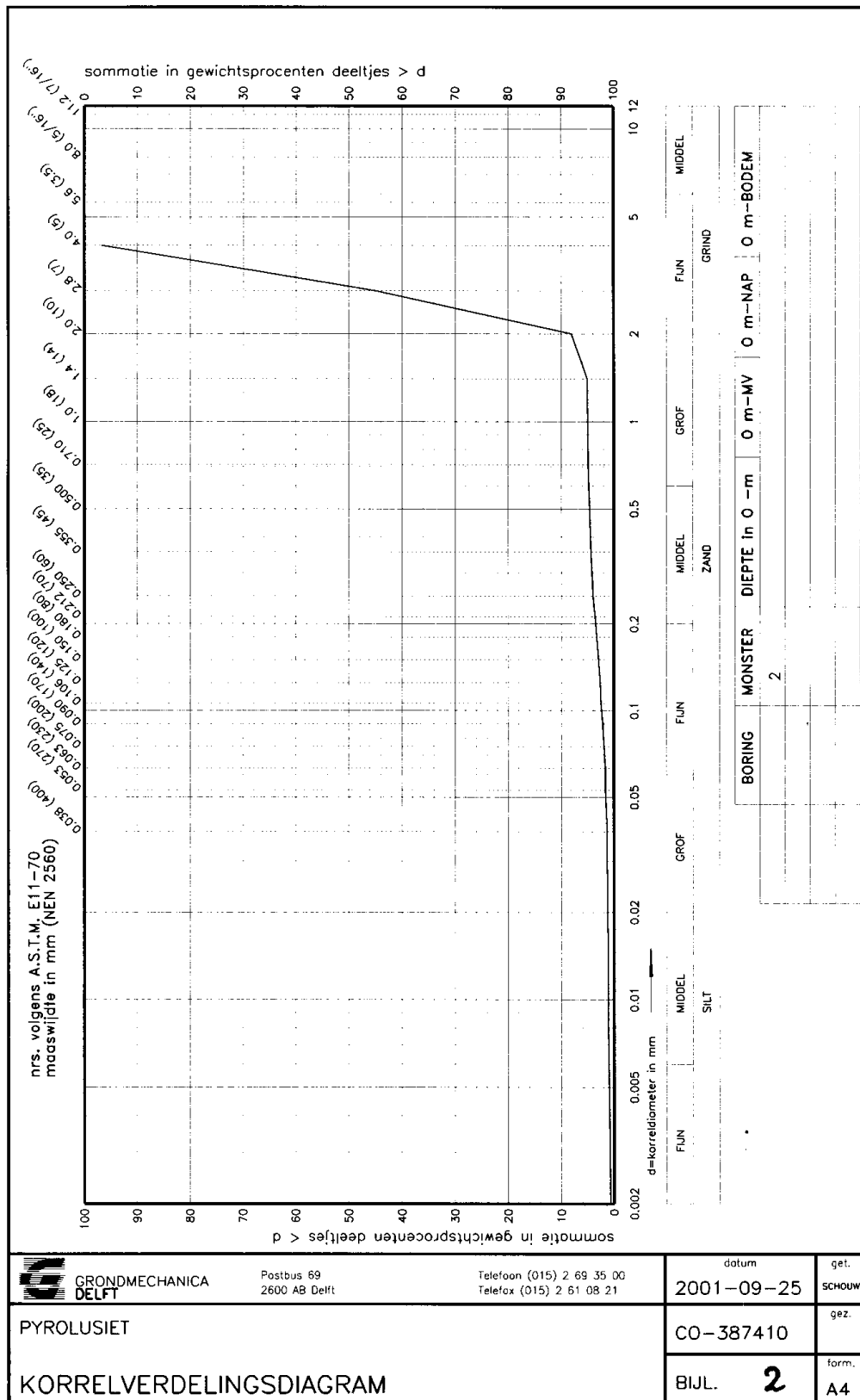
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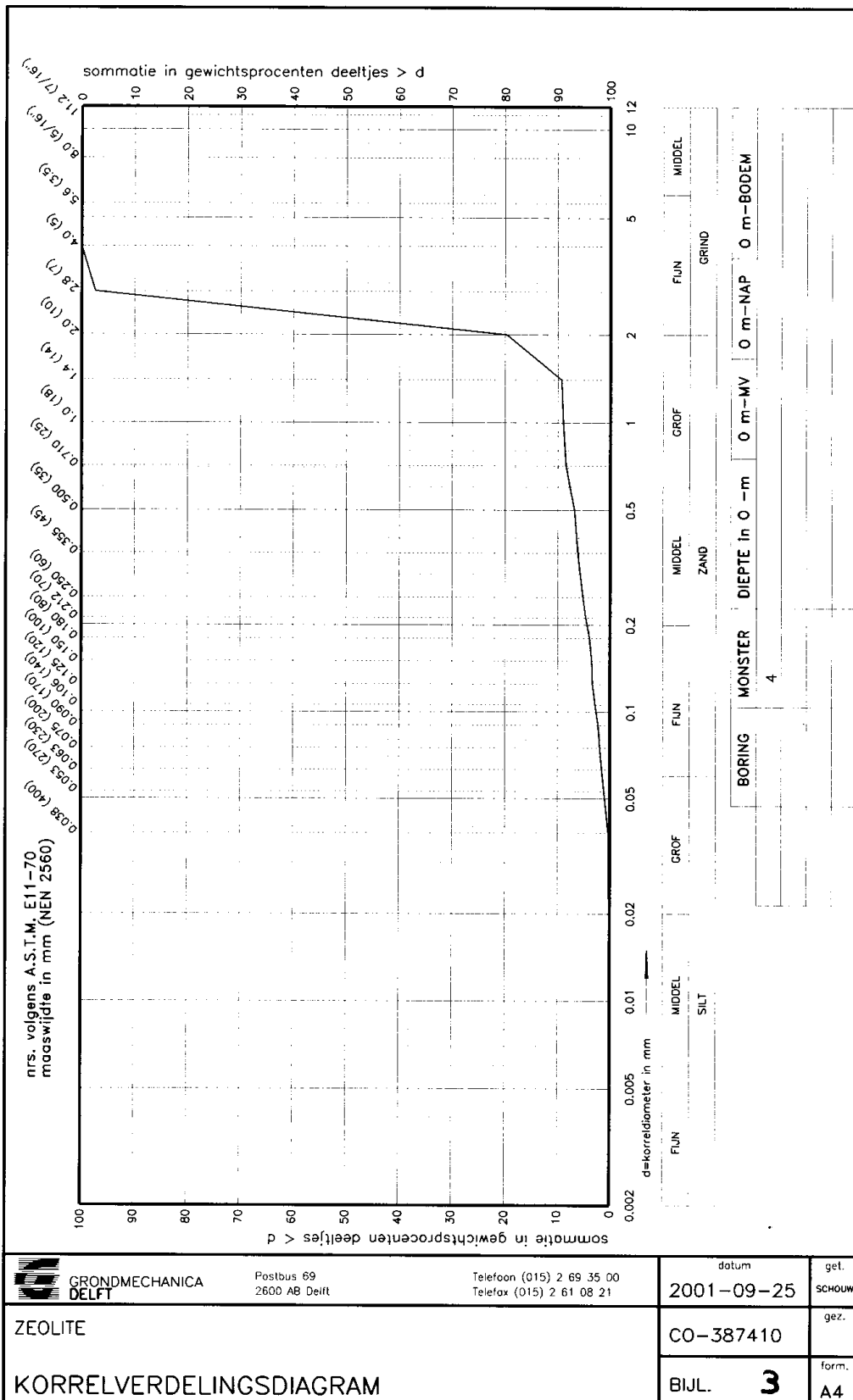
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Appendix 2 Grain size distribution of pyrolusite



Appendix 3 Grain size distribution of zeolite



Appendix 4 Adsorption isotherms on glauconite

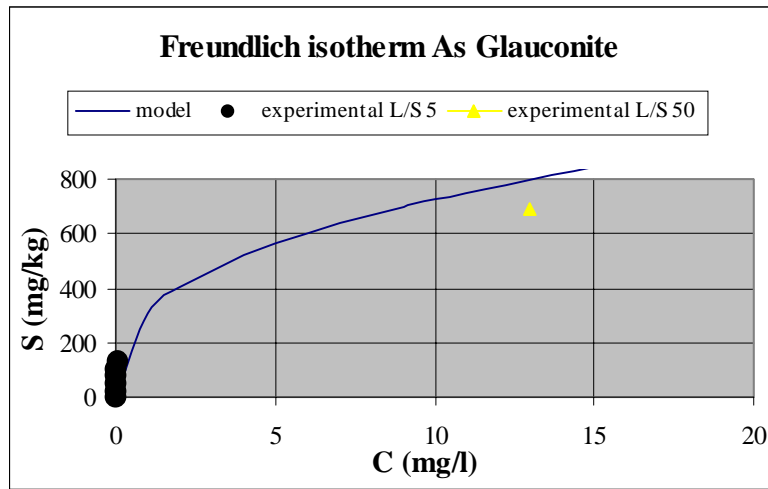


Fig. 4.1. Arsenic sorption.

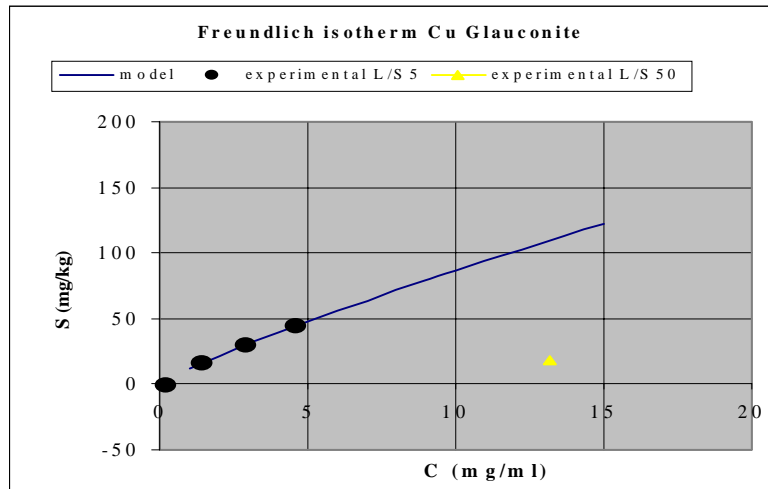


Fig. 4.2. Copper sorption.

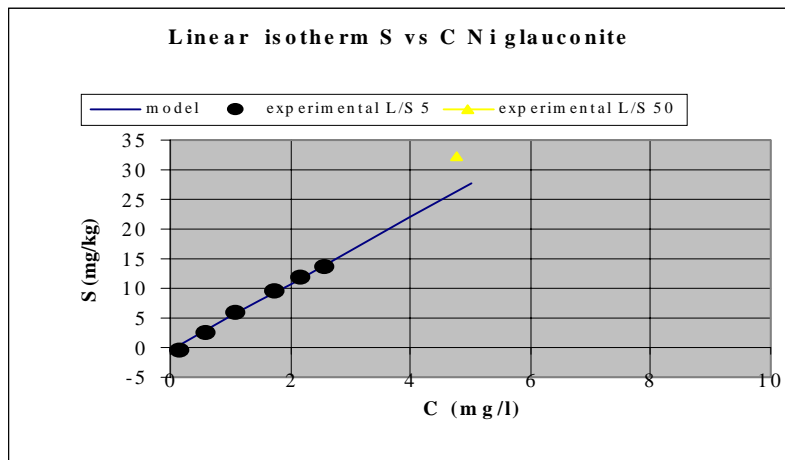


Fig. 4.3. Nickel sorption.

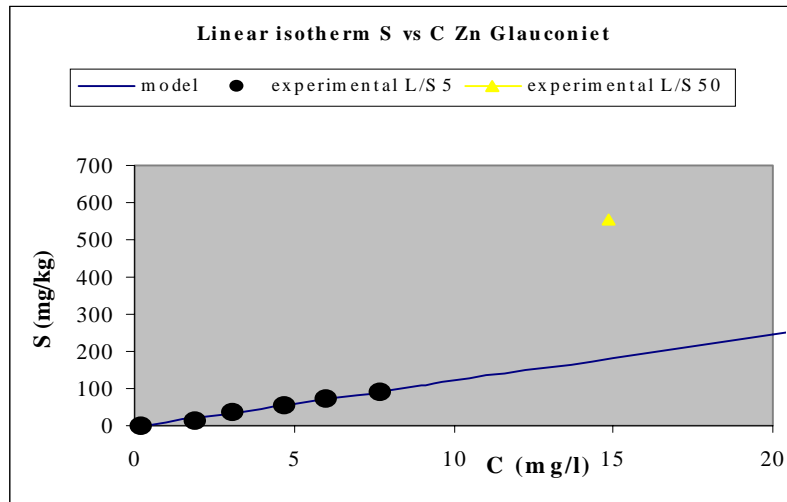


Fig. 4.4. Zinc sorption.

Appendix 5 Adsorption isotherms on pyrolusite

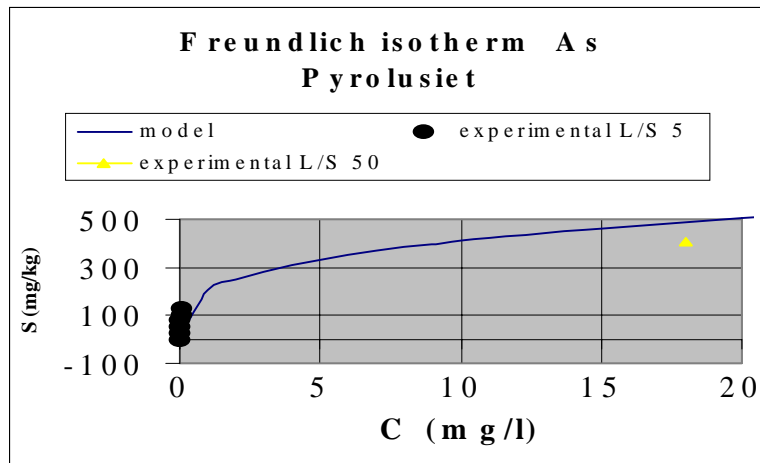


Fig. 5.1. Arsenic sorption.

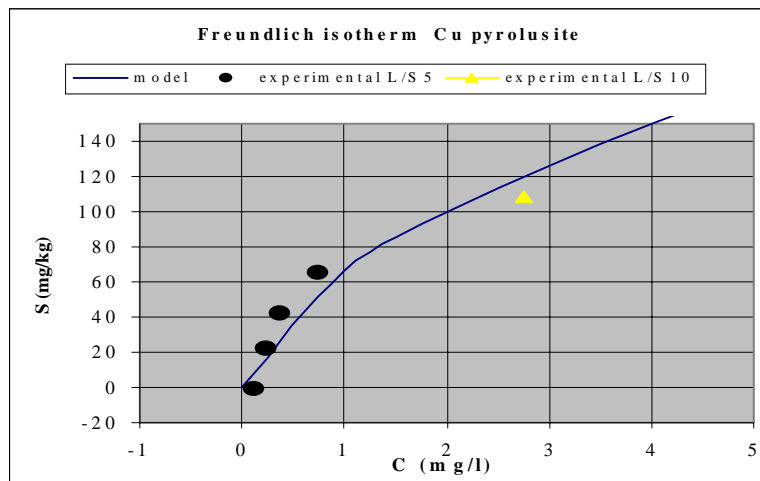


Fig. 5.2. Copper sorption.

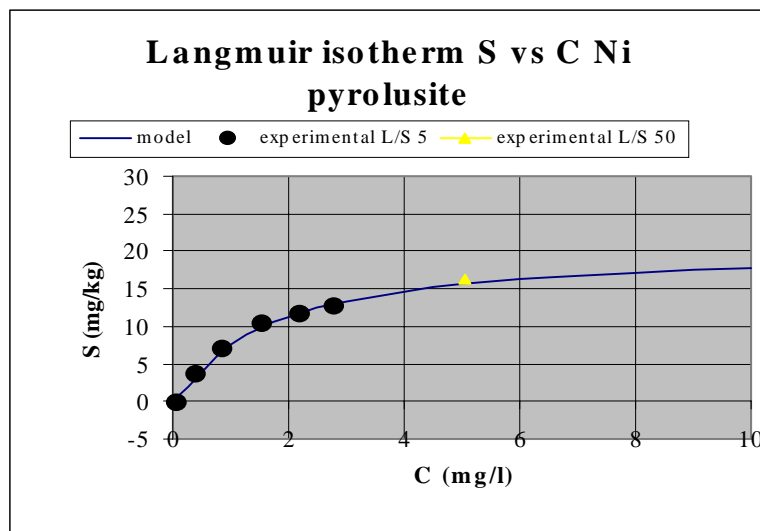


Fig. 5.3. Nickel sorption.

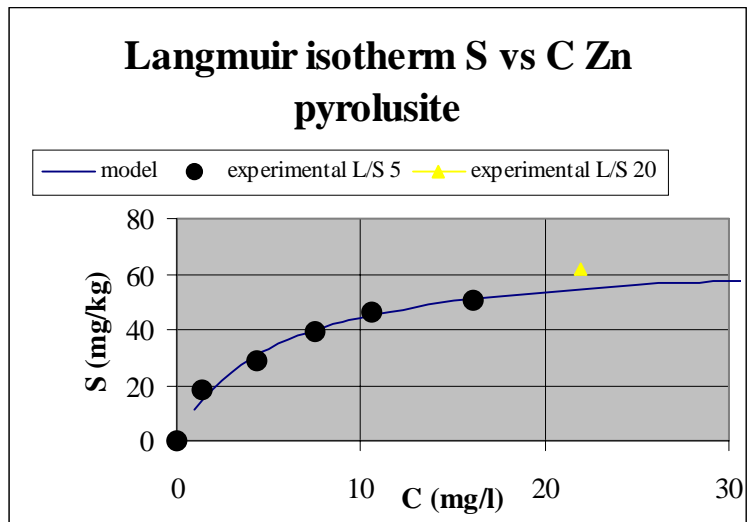


Fig. 5.4. Zinc sorption.

Appendix 6 **Adsorption isotherms on zeolite**

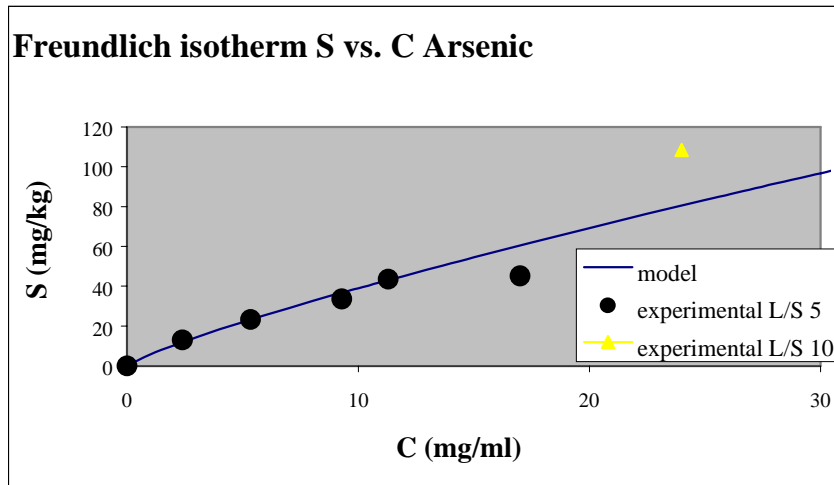


Fig. 6.1. Arsenic sorption.

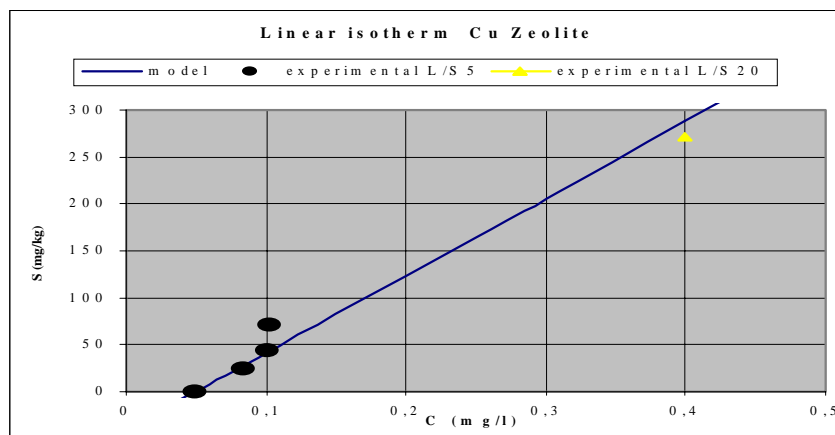


Fig. 6.2. Copper sorption.

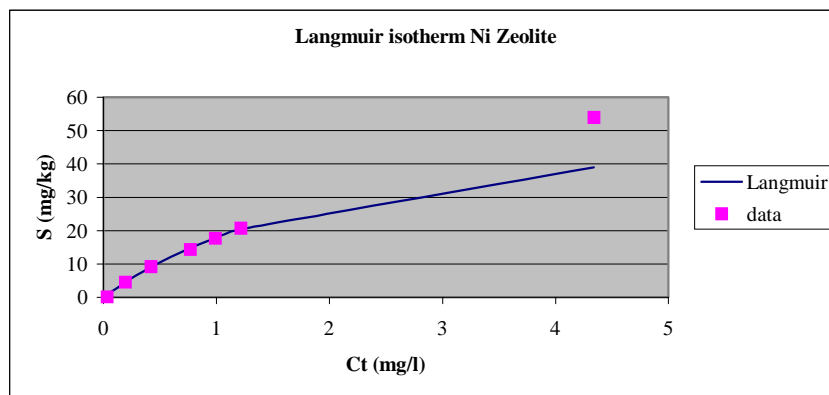


Fig. 6.3. Nickel sorption.

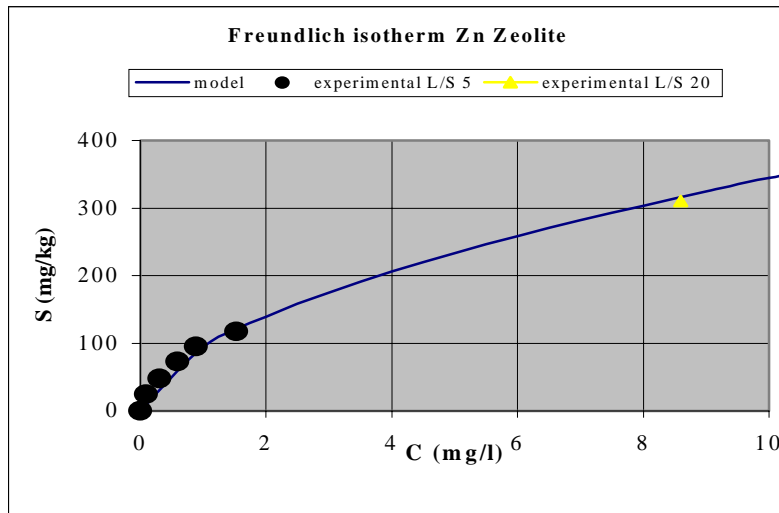


Fig. 6.4. Zinc sorption.