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Diffusion of organic colloids in compacted bentonite

**The influence of ionic strength on
molecular size and transport capacity
of the colloids**

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September 2000

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Abstract

Diffusion of radionuclides in compacted bentonite can be affected by inorganic and organic colloids if the radionuclides form complexes with the colloids. Formation and mobility of the colloid-radionuclide complexes will be governed by the properties of the colloids as well as the competition between complexation and sorption of the radionuclides on bentonite.

This report presents the results of experiments with organic colloids humic acid (HA) and lignosulfonate (LS). The aim of the experiments have been to describe the HA and LS properties:

- size distribution,
- acidity,
- sorption on bentonite,
- diffusivity in compacted bentonite,
- complexation with strontium, and
- diffusion of strontium in bentonite in the presence of HA.

This study indicates that the diffusion of cationic radionuclides like Sr^{2+} is not affected by the presence of HA in high ionic strength solution. In 0.1 M NaClO_4 solution, HA is most probably not available for complexation due to coiling and shielding of the negative sites.

Sammanfattning

För att undersöka rörligheten av organiska kolloider i kompakterad bentonitlera och hur detta i sin tur påverkar transporten av radionuklider i leran, har en serie experiment genomförts. Som modellsystem valdes två organiska kolloider humussyra (HA) och lignosulfonat (LS) samt radionukliden strontium. Inom ramen för detta karakteriserades kolloiderna och sorptionen av HA och LS på bentonit mättes. Det visade sig att HA sorberar i en miljö med 0,1 M NaClO₄ men inte LS.

Vidare framgick av sorptionsstudierna med strontium på bentonit med HA närvarande att sorption och komplexering till HA är konkurrerande processer. Vid den lägre jonstyrkan (0,01 M NaClO₄) befinner sig en stor del av strontiet i lösning, dvs i kolloidfasen. Vid den högre jonstyrkan (0,1 M NaClO₄) finner man mycket mindre mängd strontium i lösning. Det är uppenbart att komplexeringen är underordnad vid höga jonstyrkor.

Storleksmätningar på HA i lösningar med varierande pH och jonstyrka visade att jonstyrkan påverkar kolloidernas konformation. Vid höga jonstyrkor drar kolloiderna ihop sig ifrån stora utsträckta molekyler till mindre enheter.

LS och HA uppvisar diffusiviteter i samma storleksordning som Cl⁻ och I⁻ vilket är högre diffusiviteter än väntat med tanke på att de är negativt laddade kolloider. Detta kan troligtvis förklaras av följande: kolloidernas medelstorlek är stor ~150–200 nm, men storleksfördelningarna är mycket breda. Fraktionerna av små kolloider är rörliga och diffunderar därmed genom bentoniten och lämnar de större kolloiderna bakom sig. I höga jonstyrkor (0,1 M NaClO₄) är kolloiderna dessutom ihopdragna till mindre enheter där de negativa laddningarna är skärmade, vilket ger lägre jonexklusion i bentonitporerna.

Närvaron av HA påverkade inte mobiliteten av Sr²⁺ i diffusionsförsöken. I 0,1 M NaClO₄ lösning verkar HA inte i någon större utsträckning vara tillgänglig för komplexering. Humussyrans negativa laddningarna är skärmade och tar därför inte del i någon komplexbildningen. Dessutom är det möjligt att Na⁺ är bundet till kolloiderna. HA koncentrationen är högre i diffusionsförsökens inlösningar än i porvattnet varför komplexen troligen bryts. I framtida försök kommer bentonit att mättas med HA innan diffusionsförsöken startas.

Hydratiserade radionuklider såsom strontium påverkas troligen inte nämnvärt av närvaron av HA i någon jonstyrka. Försök med Eu³⁺, som binder hårt till organiska kolloider är planerade. Co²⁺, som sorberar starkt till bentonitlera, och Tc^(IV) som har mycket låg löslighet ($\approx 10^{-8}$ M) är intressanta för framtida studier.

Summary

The study reports on the mobility of organic colloids through compacted bentonite, the effect of organic colloids on diffusing radionuclides like Sr^{2+} , and the behavior of the organic colloids lignosulfonate (LS) and humic acid (HA) at different chemical conditions.

Sorption of HA and LS on bentonite have been studied. LS does not sorb on bentonite but HA sorbs to bentonite in 0.1 M NaClO_4 electrolyte solution.

The results from sorption of strontium on bentonite with HA in the system show that sorption on bentonite competes with complexation with HA. At low ionic strength (0.01 M NaClO_4) of the supporting electrolyte a large fraction of strontium is found in the colloidal phase. At higher ionic strength (0.1 M NaClO_4) a smaller fraction of strontium is found in the colloidal phase. Taking into account sorption data for strontium, it is clear that there is no complexation of strontium to HA at higher ionic strength.

Size measurements were performed on HA solutions with varying pH and ionic strength of supporting electrolyte. Ionic strength has a big impact on the colloids. At high ionic strength the colloids seem to coil into smaller units.

The results from the diffusion studies with LS and HA show that the organic colloids have higher diffusivities than first expected, when taking into account the charge and size of the colloids. There are probably two reasons for this. The mean sizes of the colloids are large but the size distributions are broad and smaller sized colloids diffuse faster than large molecules. The supporting solutions in the diffusion experiments contained 0.1 M NaClO_4 , therefore the colloids are most likely coiled into small units with the negative charges shielded. Ion exclusion in the pores is therefore low.

Diffusion studies of Sr^{2+} in compacted bentonite with HA present in the saturation solutions, show that HA has no visible impact on Sr^{2+} diffusion behavior. The experiments were performed with 0.1 M NaClO_4 solutions where HA likely is not available for complexation. The negative sites in the HA are shielded in the coiled molecules, or are bound to Na^+ . Since the HA concentration is higher in the inlet solutions than in the pore water, complexes initially formed most likely break up in the pore space solution. A more realistic scenario with respect to expected repository conditions would be to saturate the bentonite with HA before starting diffusion experiments.

Diffusion of strontium sorbed by cation exchange mechanisms will only slightly be influenced by HA. Future work will include studies of Eu^{3+} that is known to bind hard to organic colloids. Also included are studies of Co^{2+} which sorb hard to bentonite by inner sphere surface complexation and/or surface precipitation, and $\text{Tc}^{(\text{IV})}$ which has a very low solubility ($\approx 10^{-8}$ M).

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1 Introduction

Characteristic features of bentonite to be used as buffer material in repositories for spent nuclear fuel is low permeability, high sorptivity and long term stability. The low permeability of compacted bentonite prevents material transport by hydraulic flow and makes diffusion the principal mechanism for transport of solutes. Diffusion is therefore important for the long-term safety because it will control the mass-transport of corrosive solutes to the surface of the waste canister or alternatively the migration of radionuclides released in the case of waste canister failure.

The diffusive transport of solutes through compacted bentonite is governed by the geometrical microstructure of the pore network i.e. the parameters porosity (θ), tortuosity (τ), constrictivity (δ), and the interaction between the three components diffusing solute, water and solid. Despite extensive studies several of the processes involved are, due to the complicated microstructure of the bentonite, not fully understood.

In porous media, like water saturated compacted bentonite, the diffusion coefficients directly obtained from through diffusion experiments are the apparent diffusivity D_a , i.e. the diffusive mobility of the diffusants, and the effective diffusivity D_e . For diffusants not interacting with bentonite the apparent diffusivity is given by equation (1).

$$D_a = D_p = D_w \times \delta / \tau^2 \quad (1)$$

D_p diffusivity in pore space solution (cm^2)

D_w the diffusivity in aqueous solution

δ / τ^2 a system dependent factor accounting for the geometry of the pores

The effective diffusivity D_e , obtained from the steady state diffusion through the bentonite, is given by equation (2).

$$D_e = D_a \times \alpha \quad (2)$$

α is a capacity factor, taking into account the total concentration in the pore space

$\alpha = \theta$ for non sorbing species θ is the porosity

$\alpha = \theta + \rho \times K_d$ for sorbing species ρ is the dry density of the compacted bentonite
 K_d is the distribution coefficient

$\alpha < \theta$ for negatively charged species

The effect of organic colloids on the mobility of radionuclides in natural systems, like bentonite clay and bedrock has been studied and discussed but is still not fully understood [1, 2, 3, 4, 5, 6 etc]. Numerous complexation studies of different radionuclides with HA and fulvic acids are performed and complexation constants obtained. A number of questions must be answered when introducing the complexes into a system with bentonite clay or bedrock. How does complexation compete with sorption to the clay or the bedrock? If the complexes diffuse through a bentonite medium, how is the

pore system built up? Is the pore size distribution of the clay needed to define the diffusion path in sufficient detail? How does the complexes adapt to the heterogeneous environment in bentonite clay? Complexation of radionuclides with colloids may change the diffusive pattern for the radionuclides. Possible radionuclide carrying colloids in compacted bentonite are for example fine clay particles and complex forming solutes e.g. humic substances (HA). HA is a potential complexing agent because of its negative charge and high specific area at neutral pH. Being reducing HA also may change the radionuclide speciation [7]. HA is a group of naturally occurring polyelectrolytes with no defined chemical structure, containing a variety of functional groups such as carboxylate, phenolate etc. Deep groundwaters in Sweden contain dissolved organic carbon (DOC) levels of 1 mg/l of which ~15% is HA [8]. Since HA has a complicated three-dimensional structure metal ions can probably diffuse into the structure and be retained without specific chemical bonding.

An important parameter for diffusive transport in porous media is the pore size distribution. The relative proportion between intra and inter particle porosity depends on compaction and ionic strength of the equilibrating solutions. According to the GMM-model [9] the inter lamellar based spacing for water saturated compacted bentonite with density 2,000–2,200 kg/m³ is 13.7–16.5 Å and the average number of inter lamellar hydrates 1–2. The diameter of inter particle void is 1–5 µm, these voids may however be partly gel filled.

The present work reports on diffusion studies of the organic colloidal anions lignosulfonate (LS), and HA. Lignosulfonate is chosen since it forms colloidal polyelectrolytes at neutral pH, is structurally related to HA since HA is degraded lignin and LS is sulfonated lignin, and is less complicated to work with. The experimental work comprises measurement of charge, size, sorption and diffusive properties for organic colloids. Sorption and diffusion of Sr²⁺ are also measured, with and without HA in the system.

2 Experimental

2.1 Materials

The bentonite used in this investigation is the American Colloid Co type MX-80 (Wyoming Na-bentonite). The bentonite (MX-80) has a clay content ($< 2\mu\text{m}$) of approximately 85% and a montmorillonite content of 80–90 weight % of this fraction. The remaining silt fraction contains quartz, feldspar and some micas, sulfides and oxides [10]. Two solutions with different perchlorate concentrations were used in the experiments, see Table 1. All solutions were prepared from analytical grade chemicals and Millipore deionized, triple distilled water.

HA in the form of soil humic standard from International Humic Substances Society (IHSS) was used. The molecular weight for the HA is not known hence the concentration is always given in g/l. Since HA is not completely soluble in water it was initially dissolved in 0.1 M NaOH solution. The element composition of HA is given in Table 2, and one of several suggested structures is shown in Figure 1.

Table 1. Composition of groundwater and perchlorate solutions used in the sorption, diffusion, size and titration experiments. Allard solution was used in earlier performed diffusion experiments.

Perchlorate		Allard	
NaClO ₄	100 mM	NaHCO ₃	2 mM
	50 mM	CaCl ₂	0.45 mM
		KCl	0.1mM
		NaSiO ₄	0.2 mM
pH	7–8	MgSO ₄	0.1mM
		MgCl ₂	0.78 mM
		NaCl	10 mM
		pH	8–8.2

Table 2. Element composition of the HA used in the experiments.

C	H	O	N	S	P	Total	Water	Ash
58.13%	3.68%	34.08%	4.14%	0.44%	0.24%	100.7%	8.2%	0.88%

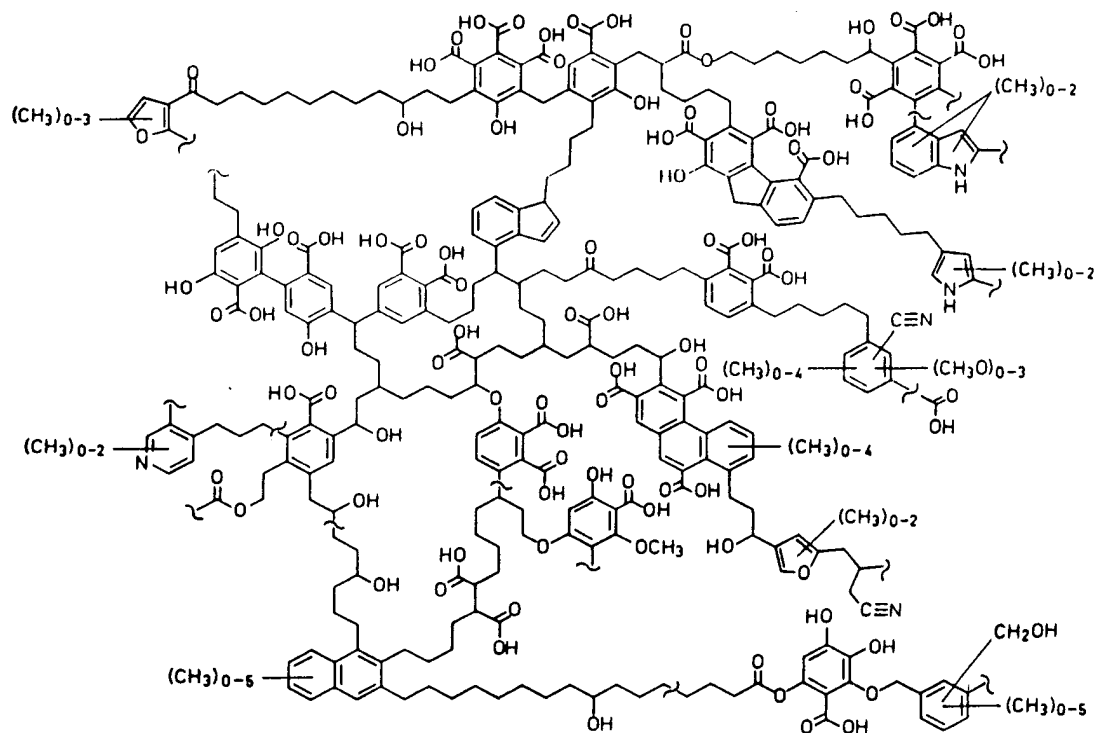


Figure 1. A general picture of HA, one suggestion among many others [11].

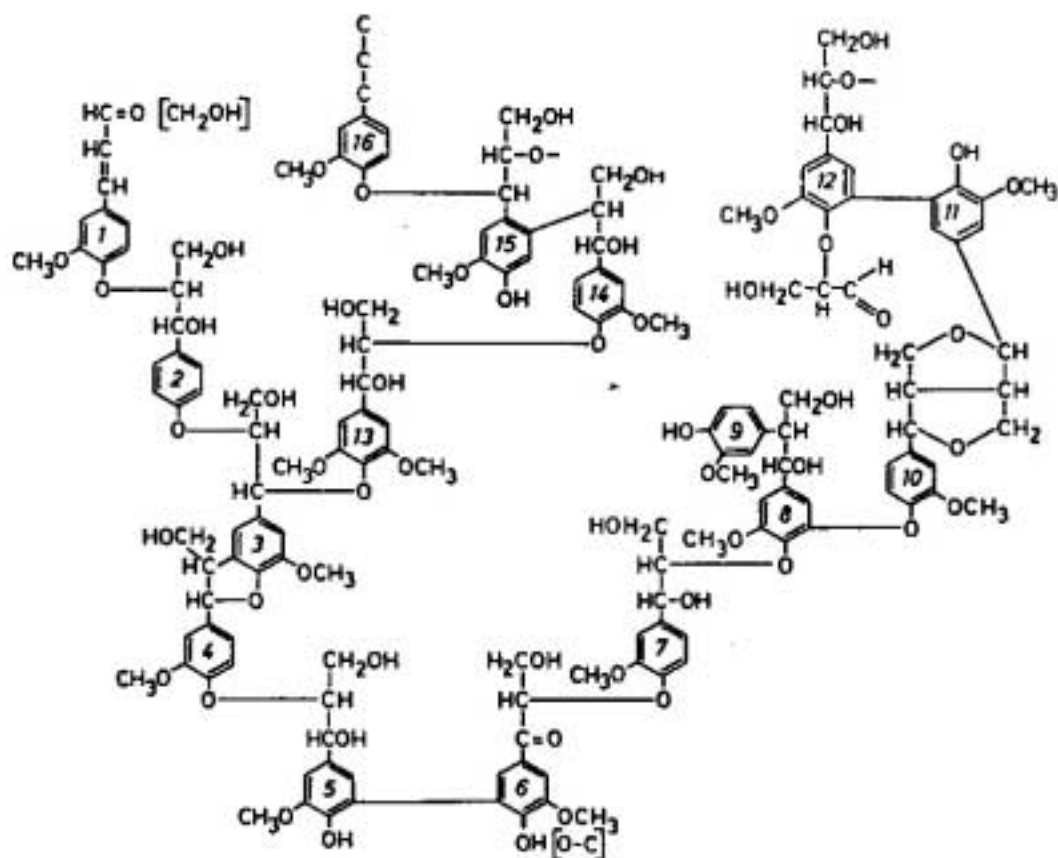


Figure 2. General structure of lignin, LS with sulfonated phenyl-propane units [12].

Table 3. The cumulative weight distribution of Wanin SL 2 as measured by Lignotech with gel permeation chromatography using a sephadex G75 column.

Wanin SL 2						
Molecular weight, g/mol	<59,000	<38,000	<16,000	<6,600	<2,755	<1,740
Cumulative percent	96%	92%	81%	69%	51%	39%

The LS used in the experiments, Wanin SL, is supplied by Lignotech Sweden. The LS product used contains approximately 65% sodium LS and the remaining part is, according to Lignotech, a mixture of organic acids and inorganic salts. The structure of the macromolecule LS is not fully explored, but a general picture of LS is lignin with sulfonated phenyl-propane units. LS being anionic at neutral pH and soluble in water is used as received. The molecular weight based on gel chromatography analysis performed by Lignotech is given in Table 3, and a general picture is presented in Figure 2. The mean molecular weight is approximately 11,500, see Table 3.

2.2 Sorption of organic colloids on bentonite

Sorption of LS and HA on bentonite was measured in batch experiments with dry bentonite suspended in 20 cm³ NaClO₄ solution of differing concentrations, 0.05 M in the LS and 0.01 and 0.1 M in the HA solutions respectively. In the experiments 0.1 g, and 0.01, 0.1, 1 g bentonite was used in the LS and HA case respectively. The solutions were shaken for more than one week. Prior to analysis the suspensions were centrifuged for 10 minutes at 17,000 rpm for LS, and 6,000 rpm for HA solutions to separate the bentonite phase from the colloid containing solution. All solutions were analyzed by optical absorption using a UV-Vis type LKB, Biochrom, Utrospec 4050 spectrophotometer for the LS and UV-Vis type Jasco V-530 for the HA solutions. Spectra were observed in the UV-region and the peak heights were read at 278 nm for LS, and 258, 278 and 300 nm for HA.

Six LS concentrations in the range 0.001 to 0.1 g/l were used. A total of 0.1 g bentonite was added to 20 cm³ solution. After addition of LS the pH in the solutions was 8. Six tubes with only LS were prepared as blanks. The experiments were carried out in duplicate.

Six solutions with HA concentrations of 0.1 g/l were prepared. 0.01–1 g bentonite was added to the tubes. The ionic strength was controlled by perchlorate solutions. The electrolyte concentrations 0.01 and 0.1 M NaClO₄ were used. The measured pH in the tubes was in the range of 7–9 after 7 days, Table 4.

Table 4. The experimental conditions for sorption of strontium with and without HA present in the system.

Sample	Volume (cm ³)	NaClO ₄ conc. (M)	HA conc. (g/l)	Sr ²⁺ (M)	Clay (g)	pH
1	20	0.01	0.1	0.000001	0.01	7.3
2	20	0.1	0.1	0.000001	0.01	7.2
3	20	0.01	0.1	0.000001	0.1	7.8
4	20	0.1	0.1	0.000001	0.1	7.7
5	20	0.01	0.1	0.000001	0.98	8.7
6	20	0.1	0.1	0.000001	1	8.2
7	20	0.01	0	0.000001	0.01	7.4
8	20	0.1	0	0.000001	0.02	7.3
9	20	0.01	0	0.000001	0.13	8
10	20	0.1	0	0.000001	0.13	7.9
11	20	0.01	0	0.000001	0.98	8.9
12	20	0.1	0	0.000001	0.99	8.2
standard	20	0	0	0.000001	0	7

2.3 Sorption of strontium on bentonite with HA present

Sorption of strontium on bentonite was measured in batch experiments with dry bentonite suspended in 20 cm³ aqueous NaClO₄ solution with and without HA in the system. The tracer ⁸⁵Sr with its inactive carrier of Sr²⁺ was added to all the tubes. The solutions were shaken for twelve days. The suspensions were centrifuged for 10 minutes at 6,000 rpm to separate the bentonite phase from colloids in the solution. 5 ml samples were drawn at time intervals for γ -counting using a germanium detector and multi-channel analyzer. The samples were returned to the batch solutions after measurement. A review of the experimental conditions experimental is given in Table 4.

2.4 Titration

All titrations were performed in a dark box thermostated to 25 ± 0.1°C. The titrations were carried out in an aqueous solution purged with argon washed in acid (H₂SO₄), base (NaOH), and the ionic medium (NaClO₄). The titrants 0.1 M HCl and 0.1 M NaOH solutions were added to 50 ml solution in steps of 25 μ l for LS and 10 μ l for HA using a computerized system consisting of a Metrohm 713 pH-meter and a Metrohm 665 dosimat. The pH was measured by a combined double junction glass electrode (Metrohm AG 9101 Herisau, 8.109.1166), with 3 M KCl and saturated KNO₃ solutions as inner and outer electrolyte respectively. The solutions were titrated in the pH-range 3–10.

HA, dissolved in 1 ml 0.1 M NaOH solution, was diluted with 0.1 M NaClO₄ to a concentration of 0.1g/l and pH 9.5. The solution was titrated in duplicate, from high to low pH with 0.1 M HCl. One of the solutions was back titrated with 0.1 M NaOH.

LS was dissolved in 0.1 M NaClO₄ to a concentration of 1g/l and the pH adjusted to 9.5 (to get the same starting point as for HA) with 0.1 M NaOH. The solution was titrated from high to low pH with 0.1 M HCl and back titrated from low to high pH with 0.1 M NaOH.

2.5 Size measurements

The ionic medium 0.1 M NaClO₄ was mixed with a small volume of dissolved HA and placed in an ultrasonic bath at room temperature for about 15 minutes. The pH of the solutions was adjusted with 0.01–0.1 M NaOH and 0.01–0.1 M HCl. The time between preparation and analysis should be minimized to avoid aggregation. For all samples to be analyzed in one run, the shortest time between preparation and analysis is one day. The solutions were therefore prepared one day and analyzed the next. All samples were filtered three times to remove dust and other contaminant particles. A filter of 0.8 μm was chosen to avoid interference in the natural size contribution. The samples were analyzed immediately after filtering using polystyrene cuvettes. Dynamic light scattering technique was employed using a 90 Plus Particle Size Analyzer from Brookhaven equipped with a 2 W Lexus Laser Model 95 Ion Laser. Readings at 488 nm were evaluated with the Brookhaven particle size software.

The dynamic scattering technique displays difficulties in analyzing non-homogenous and polydisperse solutions because large molecules have a tendency to suppress the detection of smaller molecules. Another drawback with the method is multi-scattering effects in concentrated solutions; the measurements will give a smaller mean size than the “true” size. For this reason the concentration is fixed to a level where repeatable data are obtained. All solutions in the experiment series were measured for 10 minutes. Each measurement was repeated 5 times.

Therefore, this method was applied to the experiments with factorial design of pH and ionic strength as variables, since it is an efficient way of determining the influence of the factors varied and also interaction effects [13]. The pH was varied between 4 and 8 and the ionic strength of the added electrolyte between 0 and 0.1 M in the experiment, see Figure 3. Eleven series of HA solutions were analyzed, three of these are replicates. The replicates in the middle are chosen to be as representative as possible for the whole experimental domain. The experimental conditions and results are given in Table 5.

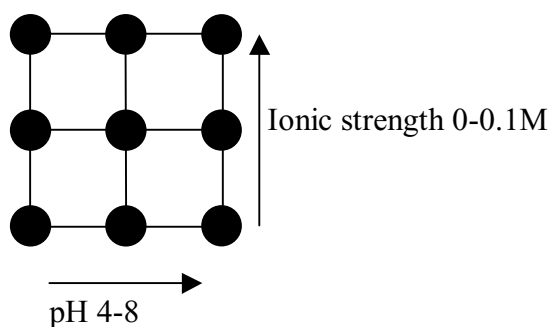


Figure 3. The figure shows the experimental domain and design for the different HA series.

Table 5. Experimental conditions for size distribution measurements.

Experiment	pH	Ionic strength (M)	HA (g/l)
1	4	0	0.01
2	7.94	0	0.01
3	4	0.1	0.01
4	7.97	0.1	0.01
5	3.85	0.05	0.01
6	8.328	0.05	0.01
7	5.95	0	0.01
8	6.1	0.1	0.01
9	6.08	0.05	0.01
10	6.08	0.05	0.01
11	6.08	0.05	0.01

2.6 Diffusion of HA and LS colloids

The design of the diffusion cells used is shown in Figure 4. Bentonite is statically compacted to the desired dry density of 1.8 g/cm^3 into the diffusion cylinder. The cylinder is assembled with end plates containing in and outlet channels fitted with metallic filters. PEEK cells with ϕ 10 mm and steel oedometers with ϕ 50 mm were used. The length of the cells was 5 mm in both cases. The experimental setup for the through-diffusion experiments is shown in Figure 5. The bentonite was equilibrated with aqueous perchlorate solutions for more than three weeks.

The solution used in the equilibrating process was also used to prepare the colloid solutions. Six small and three large diffusion cells were used. Unfortunately, the inlet filters in three of the small and one large cell were clogged during the experiments leaving five series for evaluation. One of the clogged cells contained HA the others LS. Filters were installed between the pump and the inlet solutions in the oedometer experiments to avoid clogging of the metal filters.

In the experiments with the small cells initial pH in the inlet solutions was measured. With the solid to solution ratio used, the final pH was approximated to 8 due to bentonite buffering. In the large cell experiments the pH in the inlet solutions was adjusted to about 8 before connecting them to the diffusion cells. Afterwards a series of solutions were analyzed for size distribution. The following conditions for the solutions were obtained, see Table 6.

The volume of the initial solution was 35 ml in the PEEK-cell and 50 ml in the oedometer experiments. The volume of the outlet solution was 10 ml in all experiments. Diffusion of organic colloids was studied for 169 days in the small cells and 36 days in the oedometers. The concentrations in the outlet solution were at time intervals measured in a spectrophotometer of UV-Vis type JASCO V-530. For the small cells the absorption was read at 278 nm. For the oedometers the absorption was read at 258, 278 and 300 nm. Since the concentration calculated from these three readings matched well, a mean value for the three observations was used.

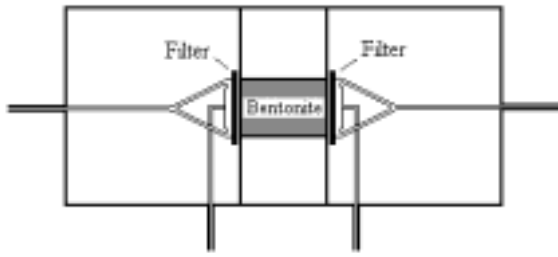


Figure 4. Schematic draws of diffusion cell [14].

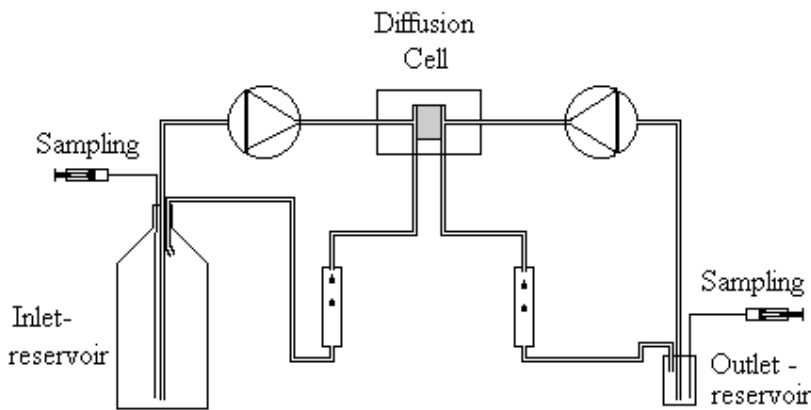


Figure 5. Arrangement of through-diffusion experiments. The setup is the same for both PEEK-cells and oedometers [15].

Table 6. Initial conditions for diffusants in different experiments.

Solutions in the PEEK cells	Initial pH	Perchlorate ionic strength (M)	*Mean size (nm) in solutions pH 9	Concentration (g/l)
LS	8.5	0.1	142	6.1
LS	8.5	0.1	142	6.1
HA	3.2	0.1	137	0.7
Solutions in the oedometers	Initial pH	Perchlorate ionic strength (M)	*Mean size (nm) in solutions pH 9	Concentration (g/l)
LS	8	0.1	142	2
LS	8	0.1	142	2

* Size measurements were obtained from analyzing solutions similar to the solutions in the diffusion experiment. The size measurements are approximate since the concentrations in the solutions are not optimal for measuring.

2.7 Diffusion of strontium with organic colloids in the system

The design of the diffusion cells used is shown in Figure 4. Bentonite was statically compacted with a hydraulic press to the desired dry density 1.8 g/cm^3 in the diffusion cylinder, and the cylinder assembled with end plates (0.82 mm thick) containing inlet and outlet channels fitted with metallic filters. PEEK cells with length 5 mm and ϕ 10 mm were used. The experimental setup for the through diffusion experiments is shown in Figure 5. The bentonite was equilibrated with electrolyte solution for more than three weeks.

After equilibration small amounts of diffusant with ^{85}Sr as tracer and HA in 0.1 M NaClO_4 solution were added to the inlet solutions. The inlet and outlet volumes were in all experiments 60 and 40 ml respectively. The ^{85}Sr activity of the solutions in inlet and outlet reservoirs was monitored by γ -spectrometry on small sample volumes using a germanium detector and multichannel analyzer. The volume of the inlet reservoir was sufficient to keep the concentration nearly constant (within a few percent) throughout the experiments. The diffusion properties of the filters are previously measured in separate through-diffusion experiments, using a package of five filters. The filter porosity was obtained from the weight of dry and water saturated filters respectively [16].

The experiments were carried out with factorial design for varying the Sr^{2+} and HA concentrations and initial pH of the inlet solutions. The Sr^{2+} concentration was varied between 10^{-6} and 10^{-4} M, the HA concentration between 0 and 0.2 g/l and the initial pH between 7 and 8. At the end of the diffusion period the bentonite plugs were sliced into 0.05 cm thick discs and weighed. The bentonite samples were mixed with 2 cm^3 water in the measuring vial. The water was slowly evaporated at 70°C to obtain a thin layer at the bottom of the vial for ^{85}Sr analysis by γ -counting. The data are corrected for differences in counting geometry for solid and liquid samples. The inlet filters for cell 3, 5, 6, 10 and 11 were shaken in water and treated in the same way as the bentonite samples. The experimental conditions for the 16 diffusion cells are shown in Table 7, column 1–5.

3 Data evaluation

3.1 Sorption of organic colloids on bentonite

The concentration of LS in the blanks was compared with the mean values of two sorption samples for every concentration. Regression analysis was performed on blanks and suspension samples, and regression lines including standard errors were compared.

The HA concentration in the blank was compared to the values of the sorption samples; $< \pm 20\%$ difference from the blank is treated as if no sorption has occurred.

3.2 Sorption of strontium on bentonite with HA present

The distribution coefficient K_d was calculated using equation 1:

$$K_d = (C_0 - C_1) / (C_1) \times V / w \text{ (cm}^3/\text{g)} \quad (1)$$

V volume of solution, in this case 20 cm³

C₀ initial activity in solution (cps)

C₁ activity in solution at equilibrium (cps)

w weight of dry bentonite (g)

K_d -values obtained in experiments with and without HA were compared.

3.3 Titration

The data obtained were pH of solution as function of titrant (0.1 M HCl, 0.1 M NaOH) added. The titration curves are derived to find inflexion points. Gran-plots are used for the evaluation. Acidity of LS and HA is given in meq/g.

3.4 Size measurements

The data obtained are treated statistically with multi linear regression (MLR) analysis of mean size distribution of the colloidal with respect to ionic strength or/and initial pH of the inlet solutions. The software calculates a combined mean value where the 5 repetitions overlap, and another mean value that treats the 5 runs as separate runs. If the combined value correspond with the mean value the solutions contain particles with homogenous size distributions. An example of size measurement is shown in Figure 6.

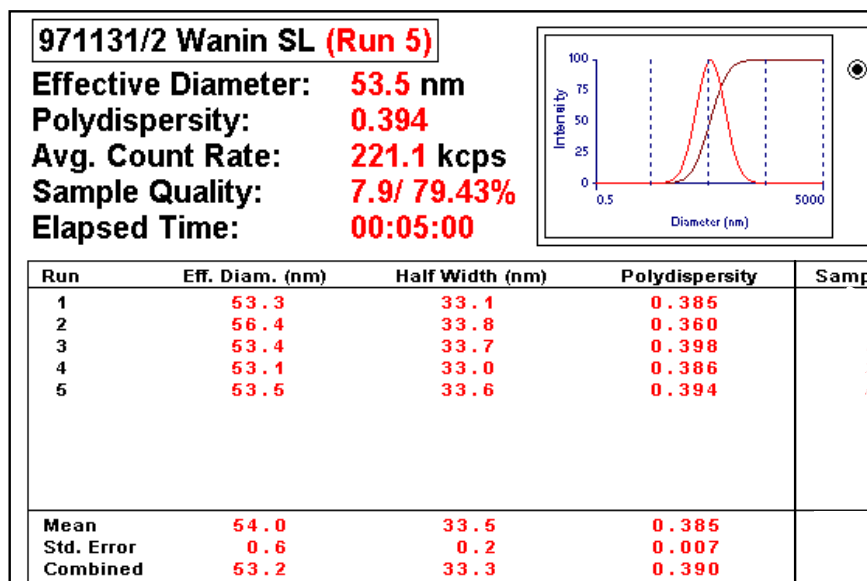


Figure 6. Typical size measurement data.

3.5 Diffusion experiments

The filters were judged to have but a slight effect on the diffusion of negatively charged diffusants through the diffusion cell. The effective and apparent diffusion constants were therefore evaluated using the equation (1) and (2) respectively [17].

$$D_e = J L / A[C_o - C_i] \quad (1)$$

$$D_a = L^2 / 6 t_e \quad (2)$$

D_e effective diffusion constant (cm^2/s)

D_a apparent diffusion constant (cm^2/s)

J flux through the diffusion cell (cps/s, g/s)

L thickness of the bentonite plug (cm)

A surface area perpendicular to the diffusion direction (cm^2)

C_o concentration in the inlet reservoir (const) (cps/ cm^3 , g/ cm^3)

C_t concentration in the outlet reservoir (cps/ cm^3 , g/ cm^3)

t_e time lag, i.e the point where the asymptote of the break through curve intercepts the time axis

For sorbing diffusants e.g. Cs^+ and Sr^{2+} the evaluation of diffusion parameters using equations 1 and 2 will be strongly influenced by the presence of filters in the diffusion cell. In evaluating the experimental diffusion data for sorbing diffusants analysis of the complete diffusion system, as represented schematically in Figure 7 is required.

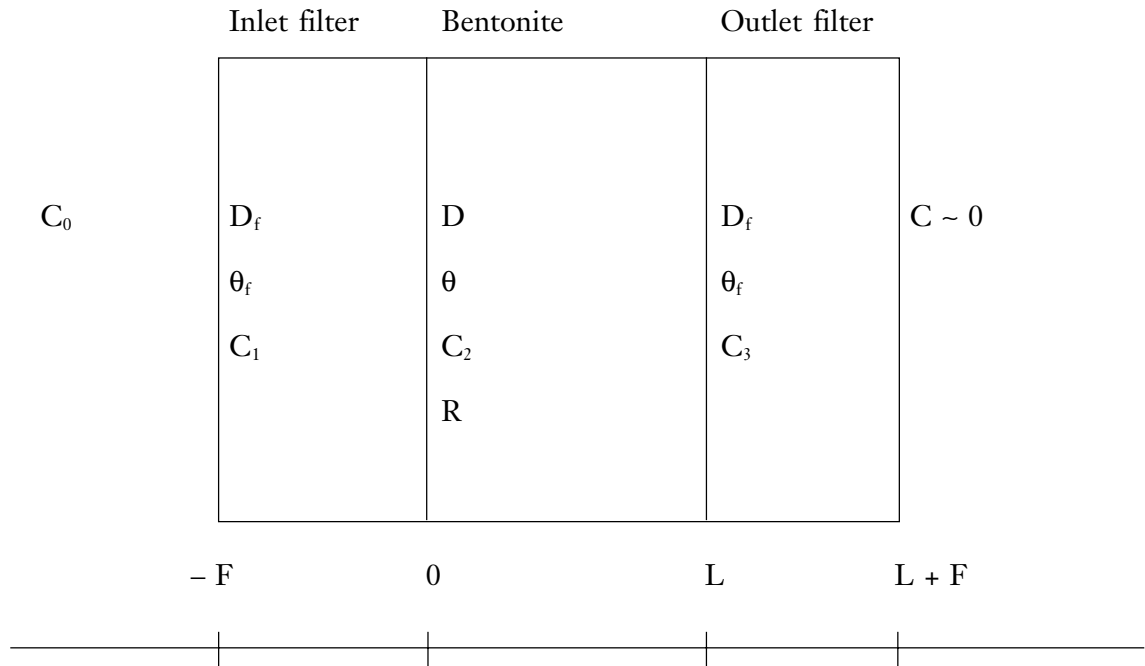


Figure 7. Schematic representation of the barriers in the diffusion cell.

The diffusive transport through the inlet filter ($-F < x < 0$) is given by equation (3)

$$J = -A \theta_f D_f \left(\frac{\partial C_1}{\partial x} \right) \quad (3)$$

and the boundary conditions

$$C(-F, t) = C_0$$

θ_f filter porosity

D_f apparent diffusion constant in filter

F filter thickness

C_1 concentration in filter

C_0 concentration in inlet solution

The diffusive transport through the compacted bentonite ($0 < x < L$) is given by equation (4)

$$J = -A \theta D_a R \left(\frac{\partial C_2}{\partial x} \right) \quad (4)$$

R capacity (retardation) factor defined as the ratio of the overall concentration of diffusant in the compacted bentonite to the concentration in the pore solution accessible for diffusion, ($R = \theta + \rho K_d / \theta$)

C_2 concentration in pore solution (Bq/cm^3 , g/l).

At the boundary between the inlet filter and the compacted bentonite we have the following conditions

$$C_1(0,t) = C_2(0,t)$$

$$\theta_f D_f (\partial C_1 / \partial x)_{x=0} = \theta D_a R (\partial C_2 / \partial t)_{x=0} \quad (\text{no storage in the boundary})$$

The corresponding transport equation and boundary conditions for the outlet filter are given by

$$J = -A \theta_f D_f (\partial C_3 / \partial x) \quad (5)$$

$$C_2(L,t) = C_3(L,t)$$

$$\theta D_a R (\partial C_2 / \partial x)_{x=L} = \theta_f D_f (\partial C_3 / \partial x)_{x=L}$$

$$C_3(L+F, t) = 0$$

The accumulated flow of diffusant through the outlet filter $Q(t)$ is given by the flux through the boundary $x = L + F$ integrated from time zero to t

$$Q(t) = A \theta_f D_f \int_0^t (\partial C_3(x,t) / \partial x)_{x=L+F} dt \quad (6)$$

An analytical solution to equation (6), defining the break through curve, can be obtained by the Laplace transform method [18]. However, to make use of all the experimental data i.e. the accumulated flow and the concentration profile within the compacted bentonite, we have decided to use a finite difference based simulation code (ANADIFF). Using the code ANADIFF the apparent diffusion coefficient D_a and the sorption coefficient for transport K_d are obtained by fitting of the breakthrough curve and activity profile in the bentonite. In the simulations A , θ_f , θ , D_f , C_0 , F , L and r are kept constant while D_a and K_d are varied.

The results from the diffusion experiments with HA present were statistically treated with MLR to see if the diffusion behavior of strontium is affected by the presence of HA in the inlet solution, that is if complexation influences the mobility of strontium. The activity profiles in the bentonite plug and diffusive flux, as given by the temporal change of activity in the outlet solution, are assumed to describe the diffuse transport of strontium. The factors used for statistical treatment are given in Table 7. The flux is given as the slope of the breakthrough curve (column 6), the “accprof” (column 7) represents the accumulated activity in the bentonite plug and “profin” (column 8) denotes the percentage of the initial activity that reached the outlet solutions.

Table 7. Data used for statistical treatment.

Exp No	In/Out	pH	Sr ²⁺ (M)	HA (g/l)	Flux (cps/day)	Accprof (cps)	Profin (%)
1	In	7.1	9.90E-07	0	8.17	1,433	2.47365
2	In	8.4	9.90E-07	0	9.09	2,137	2.16634
3	In	7.1	9.90E-05	0	2.72	1,432	0.857075
4	In	8.4	9.90E-05	0	14.95	1,771	2.50242
5	In	7.2	4.97E-05	0	2.94	1,206	1.33627
6	Out	8.1	9.90E-07	0.2	0.2	14	0.118285
7	Out	7.2	9.90E-05	0.2	0.05	3.85	0.0331201
8	Out	8.1	9.90E-05	0.2	0.09	3.05	0.0629738
9	In	7	9.90E-07	0.2	7.39	1,069	2.06183
10	In	8.2	4.97E-05	0.2	4.96	1,440	1.08006
11	In	7.7	9.90E-07	0.1	4.01	1,322	0.818865
12	In	7.7	9.90E-05	0.1	7.69	1,729	1.00332
13	In	7.5	4.97E-05	0.1	7.48	1,450	0.986116
14	In	7.4	4.97E-05	0.1	9.32	1,282	1.60644
15	In	7.5	4.97E-05	0.1	4.62	1,297	0.753518
16	In	7.5	4.97E-05	0.1	6.08	1,033	1.87038

4 Results

4.1 Sorption of organic colloids on bentonite

The sorption data are shown in absorbance versus concentration plots in Figure 8. As can be seen from the plots LS is not sorbing on bentonite. The regression analysis of the data show that data for blank and sorption samples, are on the same line when the uncertainties in the analysis are taken into account.

The sorption data for HA are shown in Table 8. The concentrations calculated from absorbances at 258, 278 and 300 nm match well and only the mean concentration is tabulated. The concentration of the standard solutions appears to have increased with

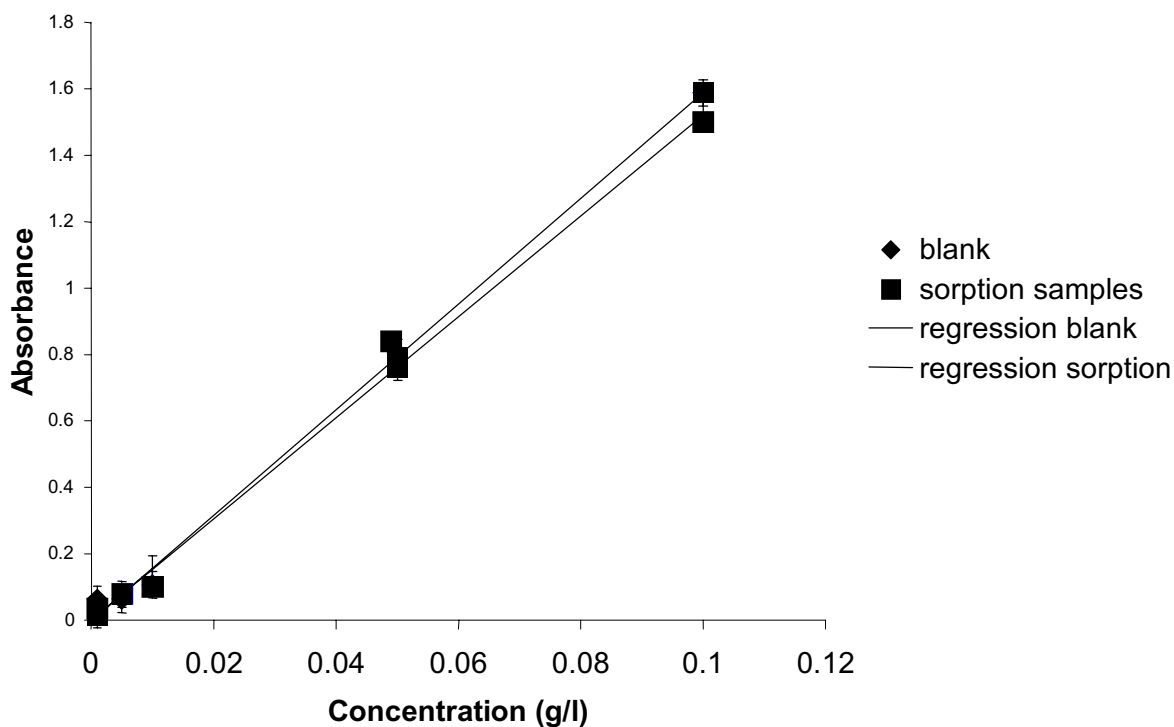


Figure 8. Absorbance against concentration for the blanks and the sorption samples.

Table 8. Sorption data for HA.

	NaClO ₄ (M)	Clay (g)	pH	HA (g/l)*	Colour change	Change in conc. (%)
1	0.01	0.01	7.2	0.05	–	0
2	0.1	0.01	7	0.05	–	0
3	0.01	0.1	8.7	0.05	–	0
4	0.1	0.1	8.3	0.02	brown to yellow	–60
standard		0	6.8	0.06	–	20
standard		0	6.5	0.06	–	20

* All samples and standards were diluted from 1 g/l to 0.05 g/l.

20%, Table 8, which is an artifact. This means that the samples with changes of concentration $\pm 20\%$ are treated as if no sorption occurred. In sample 1, 2 and 3 there is no sorption, but in sample 4 sorption is significant. The distribution coefficient for HA to bentonite is in the range 70–300 taking the uncertainties into account. Sample 5 and 6 has not been taken into account since bentonite in the amount of 1 g/20 cm³ gives substantial absorbance in the wavelengths for HA absorbance.

4.2 Sorption of strontium on bentonite with HA present

The HA clearly influences the sorption of Sr²⁺. At low ionic strength (0.01 M NaClO₄) electrolyte solutions the K_d-values are higher for strontium in the absence of HA, Figure 9. The gap between the sorption with and without HA is larger in the case with low solid to solution ratio.

At high ionic strength (1M) NaClO₄ the K_d-values for strontium are slightly higher in the presence of HA. The K_d-values are of the same magnitude, but the tendency at higher K_d in the presence of HA is valid through the whole experiment series. Complexes might to some extent sorb to the surface. The K_d-values for strontium in the absence of HA are in good agreement with data from the diffusion experiments.

4.3 Titration

Titrations of LS from high to low and from low to high pH gave the same acidity value, but different shapes of the titration curves. When titrating with HCl the two pKa:s 2.8 and 4 were obtained, and when back titrating with NaOH only one pKa (3.4) was found. Somehow the molecular structure changes by adding acid, but the total number of protonation/deprotonation sites remain the same. A similar phenomena is observed when titrating HA with HCl, but in this case the acidity increases with a factor 3. Two pKa values (4.0 and 2.7) were found when titrating with HCl and one pKa (3.7) when back-titrating with NaOH. This can be explained by assuming precipitation to occur at pH ≤ 4 . When titrating a solution containing precipitated humic with NaOH it dissolves and the structure of HA is changed. Since the interesting pH-range in the bentonite system is 7–9, this process can be ignored. The acidity of HA was obtained when titrating the solution in duplicate from high pH to low with NaOH. The mean value of the two acidities were calculated. Acidity is higher for HA and it contains more deprotonated sites than LS. The acidity for HA is 12.5 and for LS 2.3 meq/g respectively. Assuming acidity to be an approximate measure of the charge HA is more negatively charged than LS. It should be emphasized that titration of organic colloids is problematic, starting point, electrolyte concentration etc are critical parameters and the titrations in this study should be regarded as comparative and not absolute.

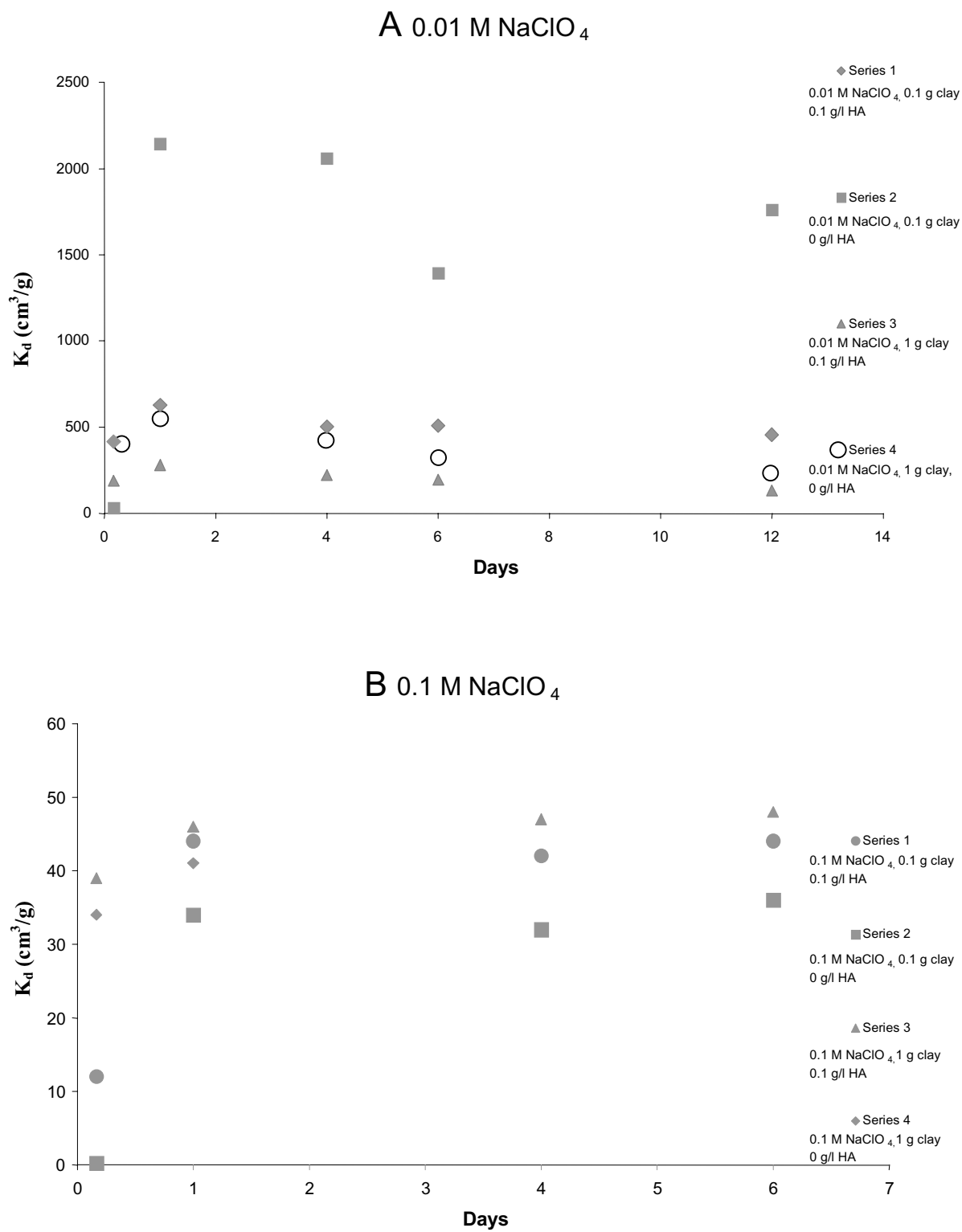


Figure 9. Sorption of strontium on bentonite with and without HA in the system.

4.4 Size measurements

The experimentally determined sizes vary from a few to almost 300 nm, Table 9. The size measurement equipment is claimed to be capable of analyzing molecules down to 2 nm, but it is questionable if this is the case. Looking at the results the method seems to break down around 10 nm. The interpretation of the small number should then be $d < 10$ nm. No precipitation was observed in the solutions and the laser signal is of the same magnitude for all the samples, Figure 10.

These experimental results indicate that pH and ionic strength affect the conformation and thereby the size of HA in this experimental domain. The most important factor for determining the size of the colloids is, according to this study, the ionic strength. Quantitatively, variation of ionic strength in the interval 0–0.1 M changes the size from about 200 nm to $d < 10$ nm. The ionic strength affects the size in the same manner at high and a low pH, but the colloids are larger at higher pH. It should be pointed out that experiment 8, see Table 9, is not included in the statistical treatment. That this data point is an outlier is confirmed by the raw-data from the size measurements. The uncertainty is high compared to the other measurements why it seems reasonable to exclude this experiment. Even when this point is included the trends are the same but with higher uncertainty attached to the results.

The experimental results match qualitatively with the theory of conformation of colloids. Macromolecules stretch out because of deprotonation at higher pH according to Jeffrey et al [19]. Deprotonated sites are negatively charged and give rise to electrostatic repulsion. At lower pH the electrostatic repulsion is much lower and the molecules coil. In a high ionic strength solution the molecules will coil due to charge shielding. If HA bind Na^+ provided by the ionic medium NaClO_4 , the electrostatic repulsion will decrease and the macromolecules will be able to coil into smaller units. Are these results valid at other pH-values and ionic strength-values than investigated? At pH below 4 the findings are not valid since colloids precipitate. The results are probably valid at higher pH but at $\text{pH} > 10$ HA start to fragment. When the ionic strength is high the colloids precipitate and it is questionable if the results are valid at ionic strength higher than 0.1 M.

Table 9. Measured mean sizes of HA.

Sample	pH	Ionic strengt (M)	Conc. (g/l)	Size (nm)
1	4	0	0.01	159
2	7.94	0	0.01	272
3	4	0.1	0.01	66
4	7.97	0.1	0.01	7
5	3.85	0.05	0.01	4
6	8.28	0.05	0.01	61
7	5.95	0	0.01	175
8	6.1	0.1	0.01	120
9	6.08	0.05	0.01	4
10	6.08	0.05	0.01	0.2
11	6.08	0.05	0.01	0.9

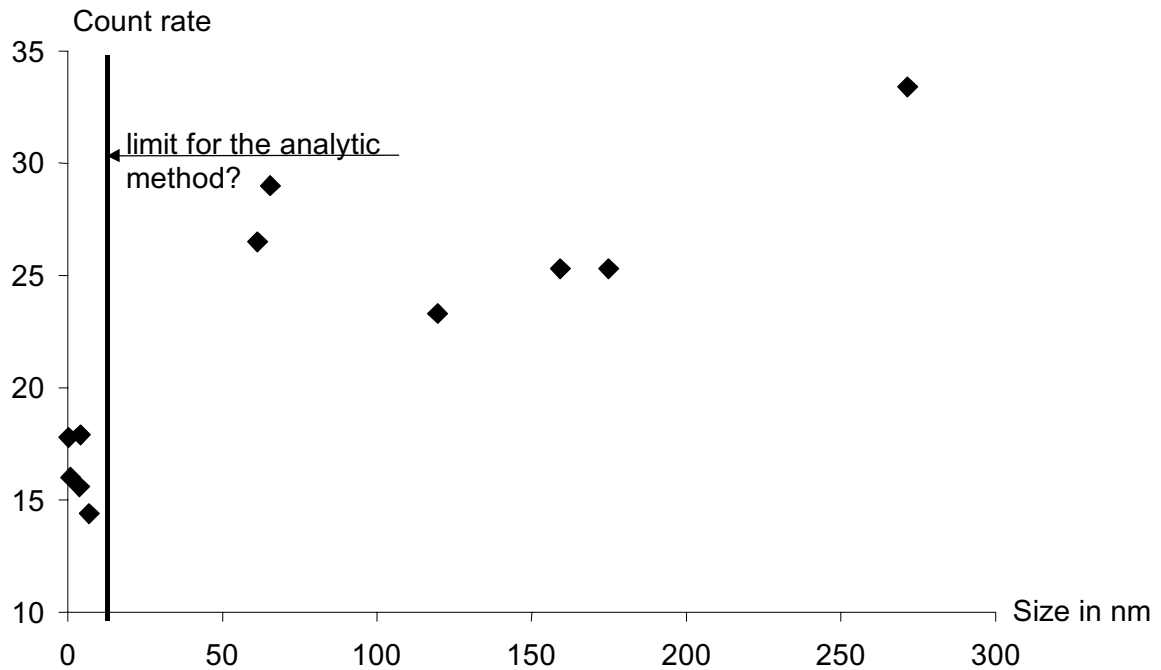


Figure 10. Signal size as a function of molecular size.

4.5 Diffusion of organic colloids

The parameters determining diffusive transport are in addition to diffusivity, flux area, porosity, length of the diffusion path, and concentration of the diffusant. The steady state diffusive transport in different diffusion experiments (A, B) with the same compaction, concentration of electrolyte solutions and solution to solid ratio can be normalized using the following ratio $(A \cdot C_0/l)_a / (B \cdot C_0/l)_b$. LS and HA diffuse through bentonite with time. The diffusive behavior of LS in the PEEK-cells and the oedometer match well when the differences in dimensions are taken into account. The data from the oedometer are normalized to the transport area of the PEEK-cells to be able to compare the results. The experimental breakthrough curve for one of the two PEEK-cells and one of the oedometer cells are plotted in Figure 12. The two series, not shown in the plots, match well with the others. In comparison with data from an earlier experimental series in Allard solutions performed by Eriksen and Jacobsson [20] the apparent diffusivities are of the same magnitude, Table 10. The breakthrough curve for HA can be seen in Figure 11, and α -values (D_e/D_s) are plotted in Figure 13.

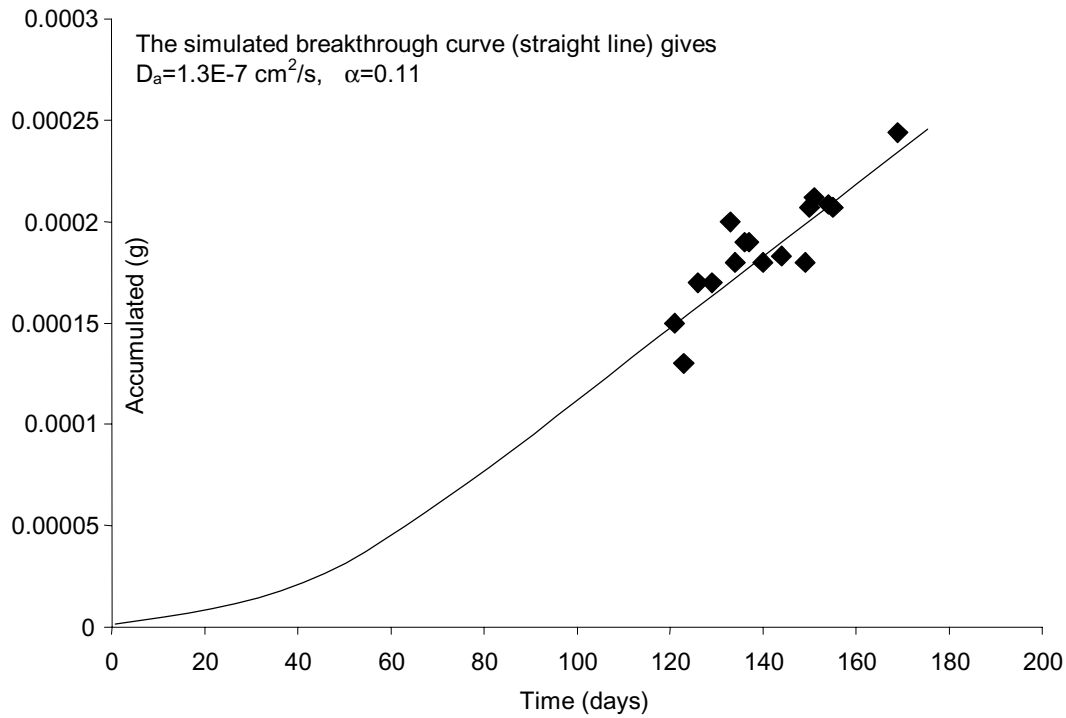


Figure 11. Breakthrough curve for diffusion of HA in bentonite.

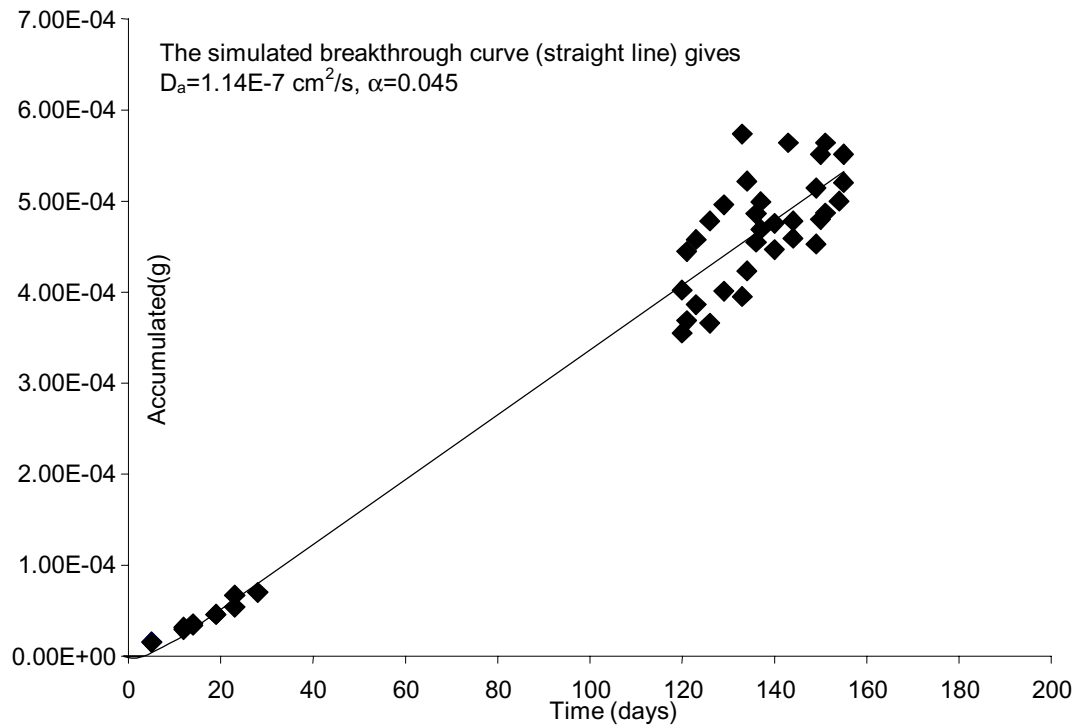


Figure 12. Breakthrough curve for diffusion of LS colloids in bentonite, the left cloud origin from the oedometer experiments and the right cloud from the PEEK-cell experiment.

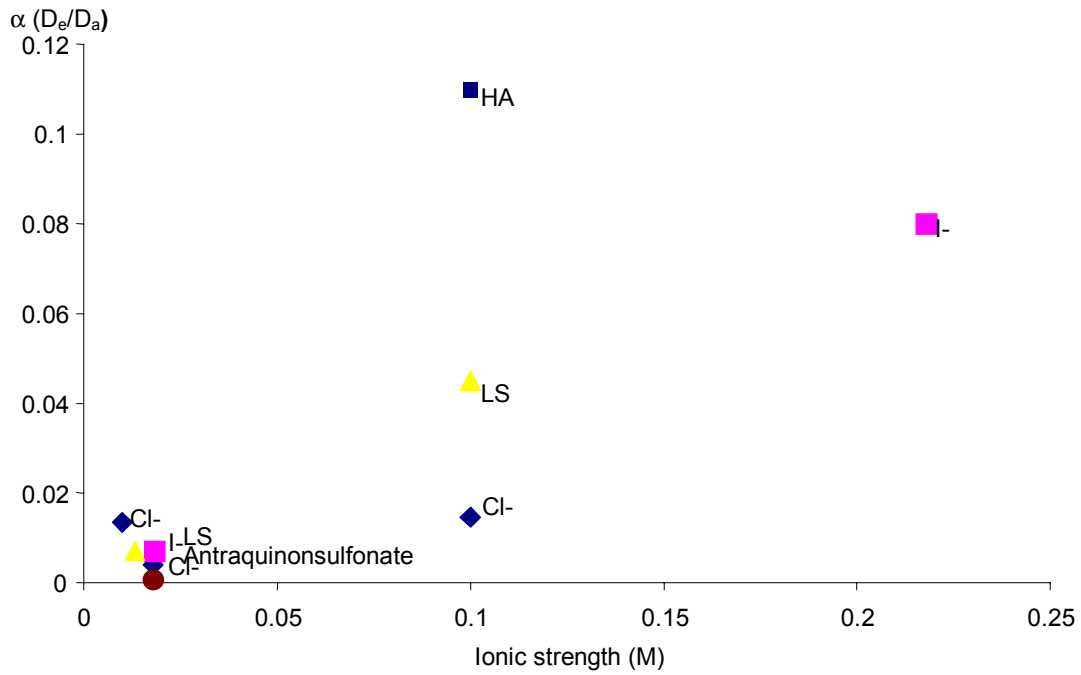


Figure 13. The transport capacity α plotted against ionic strength of the equilibration solution.

Table 10. Comparison of apparent and effective diffusivities in compacted bentonite (1.8 g/cm³).

Reference	Ion or molecule	Ion strength (M)	D_a (cm ² /s)	D_e (cm ² /s)	α	θ
From this study	HA	0.1 M, NaClO ₄	$1.3 \cdot 10^{-7}$	$1.4 \cdot 10^{-8}$	0.11	0.32
From this study	LS	0.1 M, NaClO ₄	$1.1 \cdot 10^{-7}$	$5.0 \cdot 10^{-9}$	0.045	0.32
Eriksen 1982 [20]	LS	0.018 M, Allard	$4.8 \cdot 10^{-8}$	$8.2 \cdot 10^{-11}$	0.0017	0.32
Eriksen 1982 [20]	Antraquinon-sulfonate (AQS)	0.018 M, Allard	$8.2 \cdot 10^{-8}$	$5.0 \cdot 10^{-11}$	0.0006	0.32
Jansson 1999 [16]	I ⁻	0.218 M, Nask	$8.6 \cdot 10^{-7}$	$6.8 \cdot 10^{-8}$	0.08	0.32
Eriksen and Jacobsson 1984 [17]	I ⁻	0.018 M, Allard	$3.5 \cdot 10^{-7}$	$2.1 \cdot 10^{-9}$	0.006	0.32
Muurinen et al 1987, 1989 [21, 22]	Cl ⁻	0.01 M, NaCl	$5.0 \cdot 10^{-7}$	$3.3 \cdot 10^{-9}$	0.007–0.02	0.32
Muurinen et al 1987, 1989 [21, 22]	Cl ⁻	0.1 M, NaCl	$5.4 \cdot 10^{-7}$	$4.8 \cdot 10^{-9}$	0.009–0.02	0.32
Muurinen et al 1987, 1989 [21, 22]	Cl ⁻	1 M, NaCl	$7.7 \cdot 10^{-7}$	$4.0 \cdot 10^{-8}$	0.24–0.38	0.32
Muurinen et al 1987, 1989 [21, 22]	Cl ⁻	Synthetic groundwater	$5.2 \cdot 10^{-7}$	$2.0 \cdot 10^{-9}$	0.004	0.32

4.6 Diffusion of strontium with HA in the system

The experiments were started with 16 cells, but unfortunately HA clogged the filters in three leaving thirteen cells for evaluation. All data were modeled using ANADIFF to obtain D_a and K_d -values. The best fits of the simulated breakthrough curves were obtained with the D_a :s and K_d :s given in Table 11.

It is impossible to distinguish the breakthrough curves for Sr^{2+} in experiments with and without HA present in the inlet solutions. The differences in D_a and K_d -values are in the same range as the uncertainties for the results. There are, however, three curves (6, 7, 8) that differ significantly, with almost no diffusive flux through the bentonite cells. The activity in the inlet filters for series 6 as well as for four other series were measured. The activity in the inlet filter for series 6 is about two orders of magnitude lower than for the other filters indicating that the inlet tubes, or the inlet filters for series 6, 7 and 8 were clogged. These series are therefore not taken into consideration in the data evaluation.

The flux and the time for breakthrough for the series with HA are in the same variance area as for the other series, Figure 14.

Comparison of the activity profiles in the bentonite plugs confirms these findings. The activity profiles from the series with HA present in the inlet solutions are hard to separate from those without.

Table 11. Apparent diffusivities and K_d :s from the best fitted simulated curves using the code ANADIFF.

Cell	HA (g/l)	D_a (cm ² /s)	K_d (cm ³ /g)
1	0	1.00E-07	8
2	0	1.00E-07	10
3	0	1.00E-07	77
4	0	2.00E-07	40
5	0	1.00E-07	60
6	–	–	–
7	–	–	–
8	–	–	–
9	0.2	1.00E-07	60
10	0.1	1.00E-07	77
11	0.1	8.00E-08	77
12	0.1	1.00E-07	75
13	0.1	1.00E-07	80
14	0.1	2.00E-07	60
15	0.1	8.00E-08	75
16	0.1	1.00E-07	31

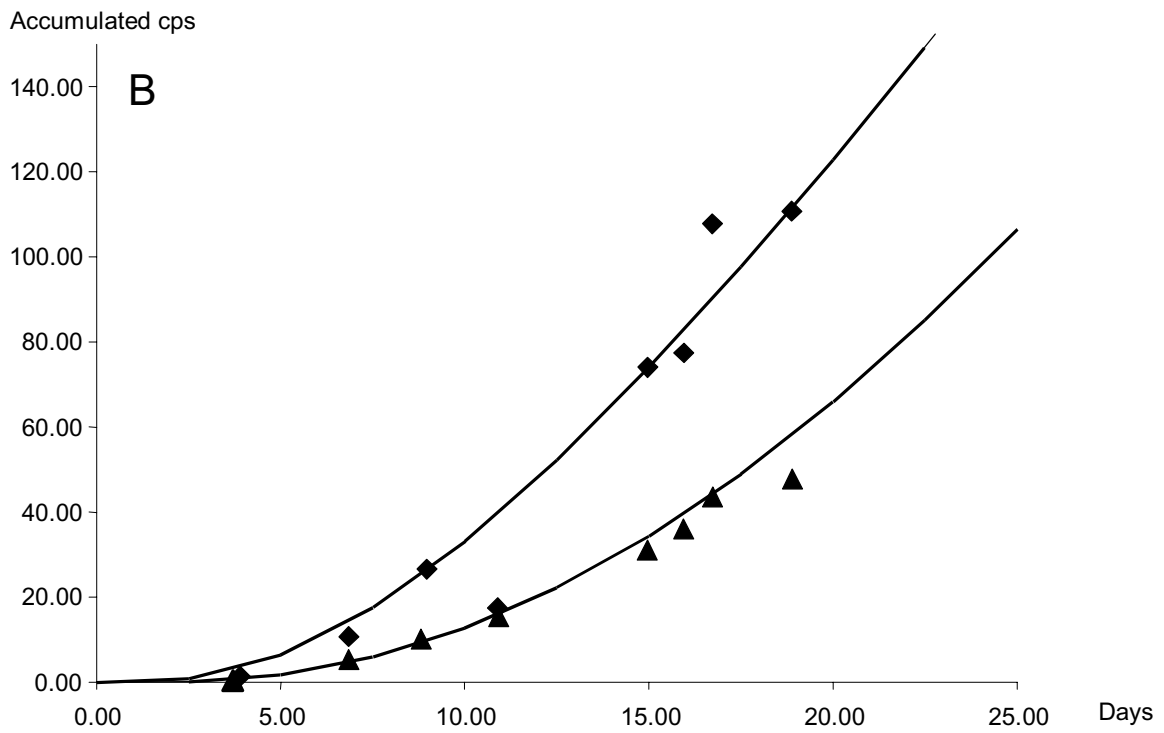
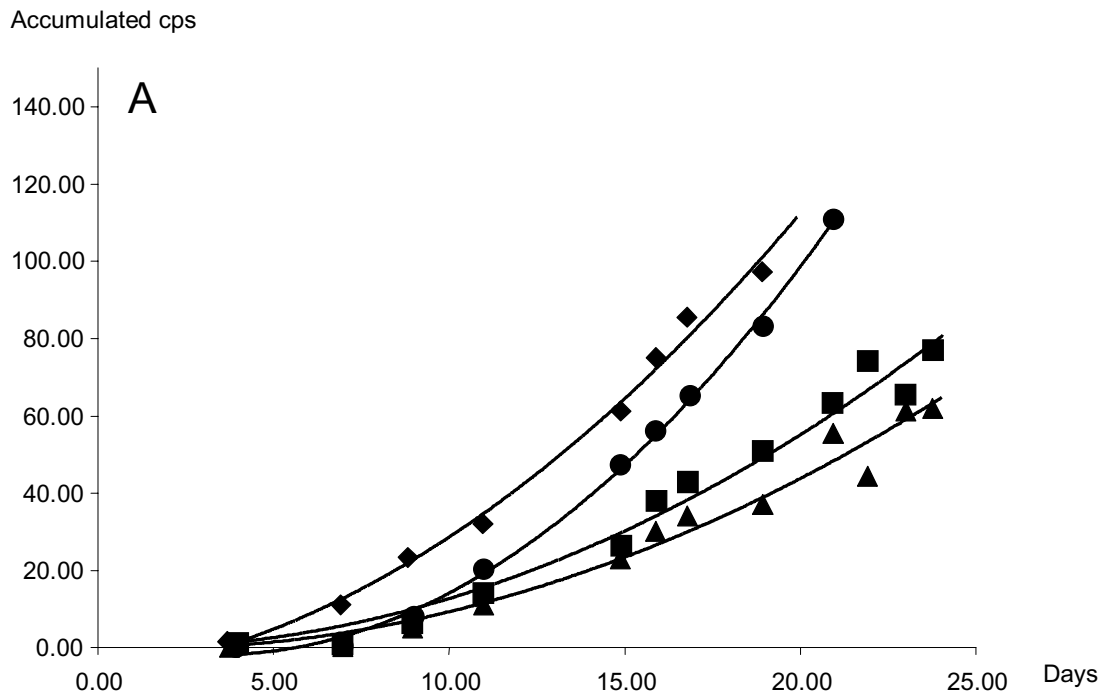


Figure 14 A, B. Representative examples of breakthrough curves for strontium with (A) and without (B) HA in the system. The points represent the experimental data, and the straight lines the modeled data. As can be seen the breakthrough curves in A and in B can not be separated from each other; they are in the same variance area.

The results from the experiments were statistically treated with MLR. The flux is given as the slope of the experimental breakthrough curves (see column 6), Accprof represents the activity in the plug (see column 7), see Table 7. Profin denotes the percentage of the activity in the outlet at the end of experiment of the inlet solutions at start (see column 8), Table 7, which are all used as responses and with the factors initial pH, Sr^{2+} -concentration and HA content.

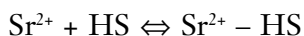
The MLR analysis shows no clear tendency, which confirm the trends identified from the breakthrough curves and the activity profiles, namely that the presence of HA in the inlet solutions has not affected the diffusion behavior by Sr^{2+} in this system.

5 Conclusion and discussion

Organic colloids like HA and LS diffuse through bentonite with time. At low ionic strength (0.01 M NaClO₄) α -values of LS and AQS are in the same range as for Cl⁻ and I⁻, see Table 9. At higher ionic strength the α -values are even higher for LS and HS than for Cl⁻ and I⁻. This is unexpected, since the LS and HS colloids are large in molecular size and are dense negatively charged. It should, however, be pointed out that the size distributions are broad. Small size fractions will diffuse faster and leave the larger size fractions of the distribution behind. It is very difficult to determine the size of the diffused colloids since the colloids in the outlet solution will be a mixture of inorganic colloids leached from the bentonite and organic colloids. In diffusion studies of LS through bentonite by Eriksen [23] the size of the diffused LS was calculated to 4 nm. Even if high uncertainties are attached to diffusion data, it can be seen that transport capacity increase considerably with increasing ionic strength. The high capacity factors for the organic colloids can be explained by the following:

The geometrical porosity of bentonite is pretty low for organic colloids at low ionic strength. The colloids are stretched out and the negative charges are exposed which leads to ion exclusion in the pore space of bentonite. At high ionic strength the colloids coil and decrease in size, see results of size measurements in Table 8. The charged sites of the colloids are shielded and the surface charge is low. Probably the colloids also bind Na⁺ provided by the electrolyte. Strontium binds poorly to HA at high ionic strength, which indicates that the negative sites of the HA are not available, Figure 9. It also indicates that HA is coiled and not fragmented, because if fragmentation was an important process at high ionic strength there should be more sites available for complexation. Titrations performed in this study show that the HA used has a higher charge than LS. This explains the higher α -value in HA as compared to LS solutions with 0.1 M NaClO₄ electrolyte. Ionic strength has a big impact on the coiling process for polyelectrolytes, and the higher the charge initially the higher the impact.

Strontium form complexes with fulvo acids with log β_{overall} -values of 2–6 [24] and is therefore expected to complex with HA as well. Strontium clearly forms complexes with HA in 0.01 M NaClO₄ solution, but not to any larger extent in 0.1 M NaClO₄ according to this study, Figure 9. Complexation is possible when the colloids are in “linear” form when the charged sites are available. Diffusion of strontium is not affected by the presence of HA in 0.1 M NaClO₄ solutions since complexes are not formed to any greater extent. Another reason why the diffusion is not affected can be that complexes form and diffuse into the bentonite but as the HA concentration is lower in the bentonite Sr²⁺ is released from the complexes due to the generalized equilibrium below.



The diffusion of radionuclides like strontium which sorbs on bentonite by cationic exchange and forms relatively weak complexes with HA is probably not affected substantially by the presence of HA. Therefore it should be of interest to study the effect HA on diffusion of Eu³⁺ since Eu³⁺ is known to form strong complexes with HA. The Co²⁺, which sorb strongly on bentonite, is interesting too since the competition between sorption on bentonite and complexation with HA can be studied in this case. The Tc^(IV) should be studied because of its low solubility, which may increase if strong complexes are formed with HA.

6 References

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