

Colloids or artefacts? A TVO/SKB co-operation project in Olkiluoto, Finland

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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.

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Abstract (English)

TVO (Teollisuuden Voima Oy, Finland) initiated a co-operative task with SKB (Swedish Nuclear Fuel and Waste Management Co.) to critically evaluate colloid sampling methods at the test site in Olkiluoto, SW Finland. Three different colloid sampling methods were compared when sampling borehole OL-KR1 at 613-618m depth. One possible way to make a conservative in-situ colloid estimation is to omit the contribution from calcite precipitation which is considered to be the main artefact. When this is made the inorganic colloid content (size 1 - 1000 nm) in Olkiluoto is 184 ± 177 ppb consisting of clay minerals, silica, pyrite, goethite and magnesium oxide; the concentration of organic substances are around 10 ppb. The in-situ colloid concentration seems to be low which is in good agreement with experiences from years of sampling in similar environments and depths. The exercise shows the many difficulties encountered when sampling colloids. Small errors in the planning, pump-rate selection, a lack of precautionary measures, artefact sensitivity of the method etc. have a tendency to affect significantly the results on the measured ppb colloid level.

Abstract (Swedish)

TVO (Teollisuuden Voima Oy, Finland) etablerade ett samarbetsprojekt med SKB (Svensk Kärnbränslehantering AB) för att kritiskt granska kolloid provtagningsmetoder i Olkiluoto i sydvästra Finland. Tre olika provtagningsmetoder testades i ett av borrhålen (OL-KR1) på 613-618m djup. För att få ett konservativt mått på in-situ halten bör man räkna bort effekterna från kalsit utfällning som anses vara en av huvud artefakterna. När detta gjordes är den oorganiska kolloid halten (storleksområdet 1 - 1000 nm) i Olkiluoto 184 ± 177 ppb. Kolloiderna anses bestå av ler mineral, kisel, pyrit, goethit, magnesium oxid och organiska kolloider (ca. 10 ppb). In-situ kolloid halten tycks vara låg och stämmer med flera års erfarenheter från kolloid provtagningar i liknande miljö och djup. Försöket visar de många problem som man stöter på vid denna typ av provtagning. Små fel vid planering, valet av pumphastighet, otillräcklig provtagnings noggrannhet, metodens artefakt känslighet etc. har en tendens att påverka på ett avgörande sätt ppb halterna vid kolloid provtagning.

Summary

TVO (Teollisuuden Voima Oy, Finland) initiated a co-operative task with SKB (Swedish Nuclear Fuel and Waste Management Co.) to critically evaluate colloid sampling methods at the test site in Olkiluoto, SW Finland. Three different colloid sampling methods were compared when sampling borehole OL-KR1 at 613-618m depth. The colloid sampling consisted of *ordinary filtration* (cross-flow filtering, 20-450 nm) in open air, *inert filtration* (cross-flow filtering, prefilter = 2500 nm, separate filtration to three fractions 50, 200 and 400 nm) by using N₂ and *ultrafiltration* (tangential filtering, prefilter = 1000 nm, concentration to a single fraction 2-1000 nm) using positive N₂ pressure. Two samples per method were taken with an interval of three weeks for organic determination one sample was collected. Care was taken to avoid possible known artefacts in connection with the colloid sampling.

A pre-test showed that high pump extraction rates change the downhole groundwater chemistry and increase the colloid content. The groundwater chemistry was constant during the both sampling occasions due an optimum low pump rate. However, a low pump rate on the other hand may change the sample due to long transport and decompression times up to the surface prior to analysis. The master variables (Eh and pH) and hence the entire chemical system changed because of the different sampling times and chemical environments provided by the methods used. This in combination with analytical uncertainties and differences, made the comparison difficult and the results became conflicting. The colloid sampling in open air increased almost all the elements associated with colloids in the ordinary filtration, coprecipitation with calcite is suggested as a possible mechanism. The inert-filtration showed the lowest artefact contribution from calcite precipitation, despite the used cross-flow filtering technique. The advantage may be due to the used N₂-atmosphere in combination with short sampling time and small sampling volumes. The most detailed information was provided from the ultrafiltration but the long sampling and preparation time induced artefacts.

One possible way to make a conservative in-situ colloid estimation is to omit the contribution from calcite precipitation. When this is made the inorganic colloid content (size 1 - 1000 nm) in Olkiluoto is 184 ± 177 ppb consisting of clay minerals, silica, pyrite, goethite and magnesium oxide; the concentration of organic substances are around 10 ppb. The in-situ colloid concentration seems to be low which is in good agreement with experiences from years of sampling in similar environments and depths. The exercise shows the many difficulties encountered when sampling colloids. Small errors in the planning, pump-rate selection, a lack of precautionary measures, artefact sensitivity of the method etc. have a tendency to affect significantly the results on the measured ppb colloid level.

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1. Introduction and aim

Experience from laboratory studies, field investigations and performance assessment studies of high-level radioactive waste disposal points to the evaluation of colloidal particles in natural groundwater as being central to a realistic judgement of the relative importance of radionuclide migration. Colloids are usually defined as small particles in the range from roughly 1 nm to 1000 nm. Particles smaller than 1000 nm are not apt to sedimentate, thus the upper size limit considered for colloids is often 1000 nm.

The dispersed phase in natural groundwaters consists mainly of inorganic colloids (e.g. clays, metal oxides and hydroxides, metal carbonates), organic colloidal material (mainly humic substances) and microbial populations. These colloidal particles (commonly 20-450 nm) could be of importance for the migration of radionuclides from an underground repository for radioactive waste (SKB-91, 1992). The potential for transport is suggested because the nano-micrometer particles are far smaller than the pores in permeable and fractured media, and their large surface area per unit mass means that they will be effective sorption substrates remaining in suspension. The mobility and distribution of trace metals in the aqueous environment is naturally related to the hydrogeological and hydrochemical nature of the system.

The aim is to analyse those colloidal species which may play a role in the migration of radionuclides in the local scale (1 km) of the geosphere during thousands to hundreds of thousands of years. The colloids of interest must therefore be stable and not formed during or after sampling. The ultimate aim is not to describe the colloid concentration in the sample, but more how the sample can reflect the undisturbed in-situ conditions. Since the colloid concentration is at the ppb level, the contamination risk is obvious and the effect often dramatic. Induced particles can be generated by *in-situ*, *on-line*, *on-site* or *off-site* errors. These include excessively high or low pump rates, contamination from borehole activities, complex hydrological situations, contamination from tubes of varying compositions, atmospheric contamination of O₂ including losses or uptake of CO₂, coagulation effects, long storage times and contamination prior to analysis and the associated analytical errors etc. Colloids can form from different sources and be removed or stabilised by a number of different mechanism (Matthess and Harvey, 1982; Hem, 1989). The following processes may generate natural/unnatural colloids in the sample (after McCarthy and Degueldre, 1993):

Alteration: Fractures in crystalline rocks are often alteration zones which form pathways for the groundwater. Colloids are formed by two main mechanisms: microerosion of tectonically pre-crushed and hydrothermally altered primary minerals, and secondary mineral production caused by supersaturation of an element in the groundwater. These types of colloid formation are mainly natural but extensive pumping may stimulate an increase in the colloid formation.

Precipitation: Changes in pH, major element composition, redox potential and partial pressures of CO₂ can induce supersaturation and coprecipitation of colloidal particles.

The precipitates can include: major elements such as oxides of iron and manganese, calcium carbonates, iron sulphides and minor elements such as metals and radionuclides associated with carbonates and sulphides. These precipitates may be natural or caused by sampling.

Filtration: The filtration process generally used in colloid sampling especially cross-flow filtration can produce several types of artefacts. Seldom is there a total retention of colloids larger than the nominal pore size of the filter and no retention of smaller colloids are achieved (Danielsson, 1982). Other reactions such as straining filtration may occur between the colloids and the membranes (i.e. collection due to electrostatic or chemical interactions). Losses also occur due to weak adherence of the colloids on to the filter prior to analysis and sample preparation may alter the membrane or the colloids. In conclusion the size distribution derived solely from filtration data must often be viewed as semiquantitative.

Organics: Natural organic matter can be a critical factor for colloidal stability, especially for colloids with a net positive charge in generally negatively charged aquifers. Hydrous oxides of Fe, Al and Ti have been observed to be stabilised by coatings of organic carbon on the inorganic particles. Such coatings may become important in more shallow systems where contents of organic matter are generally high. Leaching of organic compounds from water tubing may also stabilise otherwise unstable colloids during sampling.

Dispersion: Colloidal particles can be dispersed and become mobile in aquifers as a result of changes in the groundwater chemistry i.e. decreases or changes in ionic composition from calcium- to sodium-dominated chemistry. Changes in groundwater chemistry can be caused by natural mixing or due to high extraction pump-rates.

Cementation: Colloids may become immobilised due to cementation by secondary mineral phases i.e. calcite. This types of cementation can be natural or induced by sampling artefacts such as changes in partial pressure of carbon dioxide.

Some of the above mentioned colloid formation processes are easily avoidable, others difficult or sometimes impossible. Some of these problems have been focused upon in order to improve techniques and the accuracy of the results within this co-operation project between TVO (Teollisuuden Voima OY) and SKB (Swedish Nuclear Fuel and Waste Management CO). The strategy was to; 1) try to minimise artefacts 2) compare sampling methods 3) estimate in-situ colloid concentration from the measured samples. The sampling was performed in a 1001 m deep borehole OL-KR1 in granitic bedrock (at a depth of 613-618 m) at the TVO research site in Olkiluoto, SW Finland (Figure 1-1).

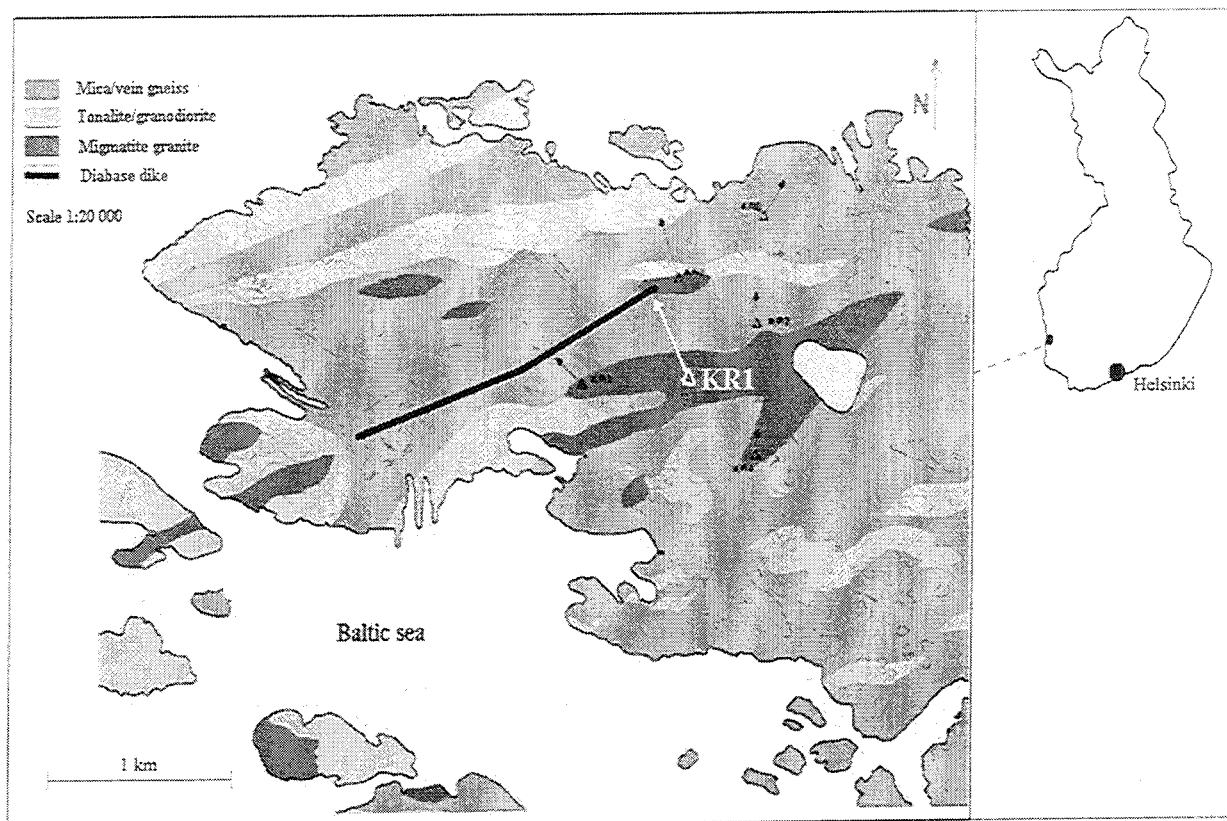


Figure 1-1. The location of the TVO test site at Olkiluoto in the SW part of Finland. The geological map shows the main rock types and the location of the investigated borehole OL-KR1 (after Pitkänen et al., 1992).

2. Sampling preparation

2.1. Borehole history

Borehole OL-KR1 was core drilled in the summer of 1989 to a depth of 1001m. After drilling a standard set of geophysical borehole measurements were carried out. Several groundwater samples were taken using double packers in the years 1989 to 1991. The sampling depths were 140-145m, 160.5 - 165.5 m, 613.5 - 618.5 m and 754-1001 m.

Hydraulic pumping tests were carried out in three phases between October 1991 and April 1992 using this borehole as a main well. The hydraulic head and groundwater table monitoring was performed in nearby shallow and deep boreholes. A preliminary colloid sampling optimisation test was made during the first pumping phase in section 592 - 622 m. Later, during installation of packer equipment, the equipment jammed at a depth of 600m. The borehole was re-opened by drilling and then flushed with water labelled with 12m^3 of uranine. The multi-packer equipment used for the colloid sampling was installed at a depth of 613 - 618 m in June 1992.

2.2. Field tests

In order to gauge how to minimise possible artefacts in connection with colloid sampling in OL-KR1, a field test was conducted. One of the most important sequence in field sampling is to avoid withdrawal of groundwater from other borehole sections or fractures with different groundwater compositions. Figure 2-1 clearly illustrates the structural complexity of OL-KR1. Several intersecting fracture planes are present which enhance the possibility of groundwater mixing from different sources. From one of the Swedish test sites Smellie (1983) has shown that an increase of the pump rate may withdraw groundwater from other more remote fractures and may result in short-circuiting around the packers.

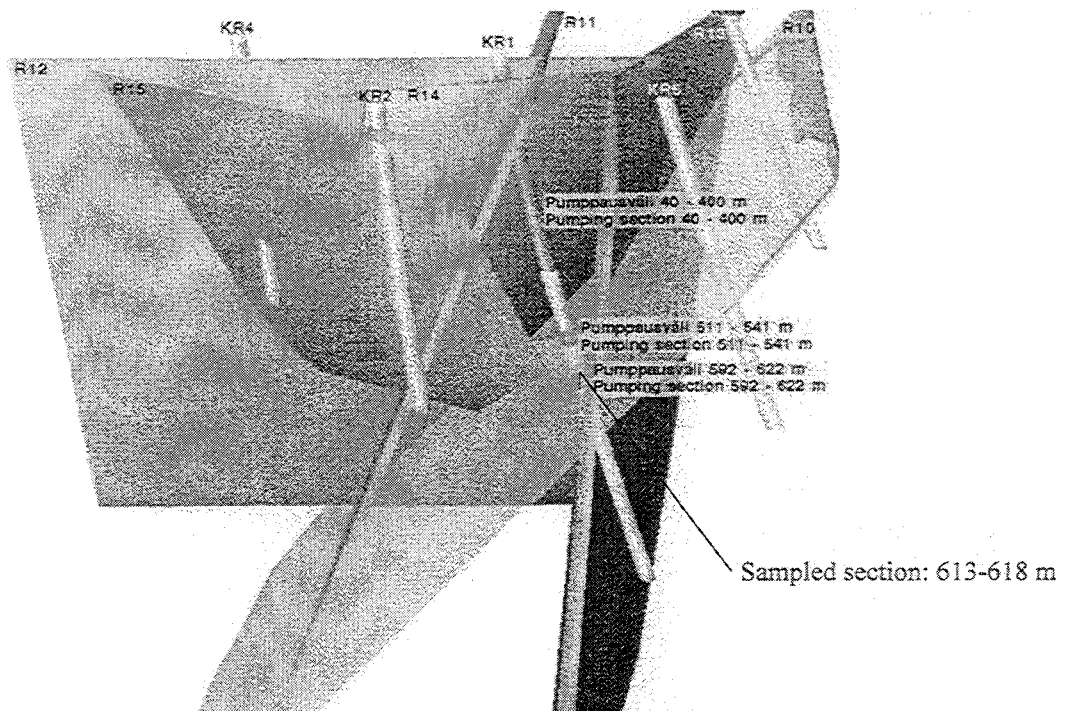


Figure 2-1. The many intersecting fractures and fracture systems may result in complex mixing of the sampled groundwater in OL-KR1. Based on an original CAD picture produced by Fintact (H. Ahokas pers. comm 1993).

Complex mixing, precipitation or dissolution reactions can change the colloid concentration. The character of the groundwater can be summarised using two important elements, Cl and HCO_3 . The Cl content can be used as an depth indicator while the HCO_3 is used as a shallow input indicator. Generally, the higher the Cl or the HCO_3 content, the larger is the proportion of the deep or shallow component found in the groundwater. The groundwater data sampled during different occasions at or close to the 613-618 m depth in OL-KR1 are plotted against the pump-rate in Figure 2-2 a and b.

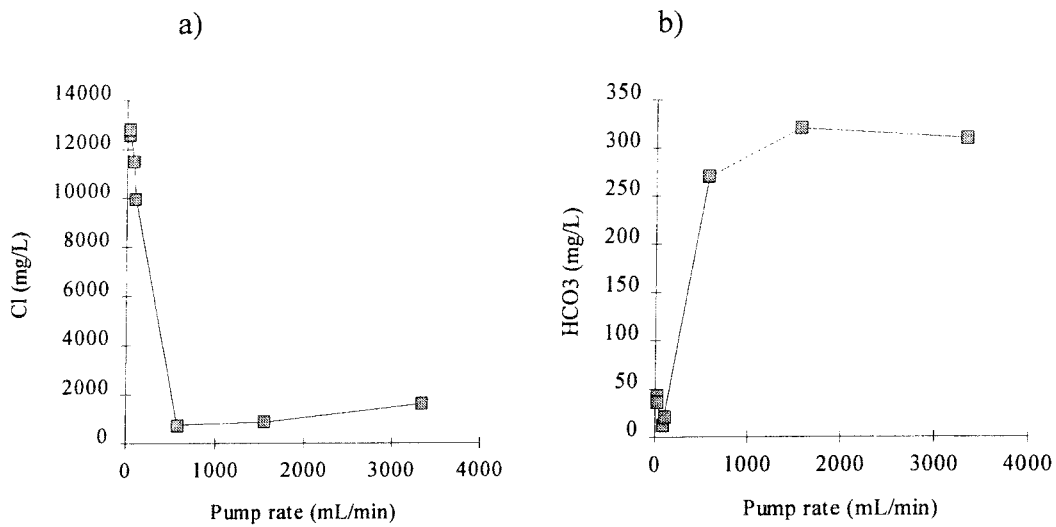


Figure 2-2. The a) Cl and b) HCO₃ content versus different pump rates used at the 600m level in borehole OL-KR1 (data from Pitkänen et. al., 1992).

The data show how the original groundwater composition can change with pump rate. In this particular case the higher the pump rate the higher the inflow of shallow groundwater.

An example of how mixing of oxygenated water (e.g. due to borehole activities) may affect the colloid concentration is given by Wikberg (1987). Native groundwater was pumped from a depth of 468 m to the surface where it was oxidised, tagged with uranine and re-injected. Groundwater sampling was then conducted with a constant pump-rate. The amount of tagged groundwater decreased rapidly in the studied section from 4% down to 0.2% within a few days. However, the measured Eh in the section rapidly levelled out at a value of -250 mV, indicating reducing conditions. The intrusion of oxygen had a dramatic effect on the concentration of colloids in the groundwater. The water was filtered and the filters analysed using energy dispersive X-ray fluorescence. Si and the Fe increased more than 6 times during the first day and then decreased to "initial" values after an additional two days. The sulphur content increased more than 20 times and was still 7 times higher than the initial value after four days. Al was constant and unaffected by the experiment.

In Olkiluoto we tested how different pump-rates may change the colloid concentration due to groundwater mixing and erosion in the sampling section. In November 1991 filtering, similar to the method described in the section 5.2, was conducted in section 591-621 m in the OL-KR1. The pump rate was fixed at three levels; 0.5 L/min for 9 days, 1.5 L/min. for 12 days and 3.3 L/min. for 9 days. The colloid filtering was performed at the beginning (when the dead volume of the tube was removed) and at the end of all the different rates of pumping (totally 6 samples). The results of the Al and Si values on the 400 nm filter (no pre-filter used) during the test are shown in Figure 2-3 a; Al and Si correlated with clay and silica (i.e. drilling debris?). The change in the Cl⁻ content of the groundwater during the same period is shown in Figure 2-3 b.

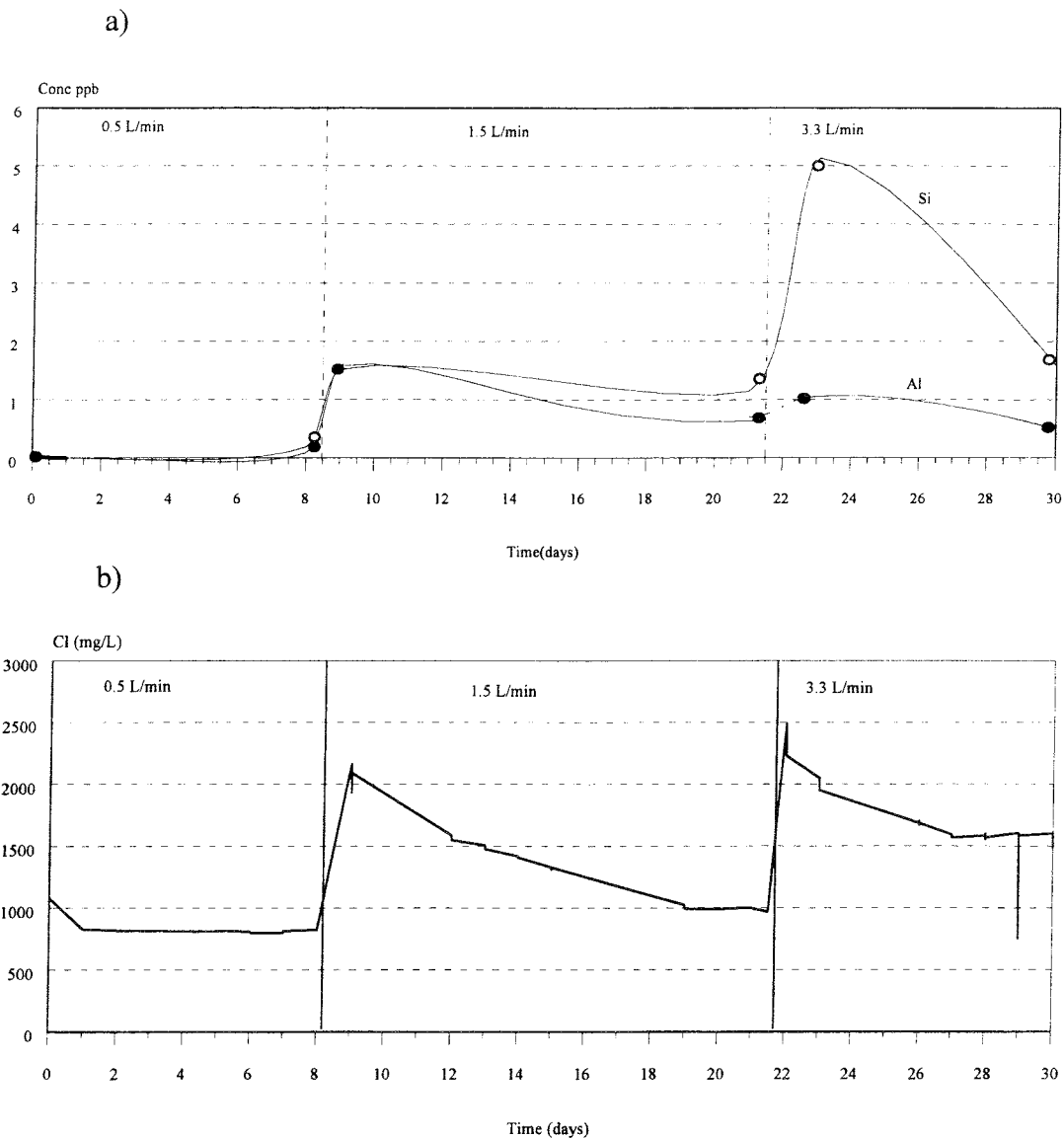


Figure 2-3 a) Al and Si content measured on the 400 nm filters; changes of pump rate are indicated for the respective period. b) The changes in Cl⁻ content of the groundwater is calculated from on-line continuous measurements of the electrical conductivity; changes of pump rate are indicated for the respective period.

The Al and Si contents increased, especially at the beginning of each pumping period. The largest Si content corresponded to the highest pump rate, while Al was greatest at the beginning of the second period. The other measured elements (S, Ca and Mn) were not affected by changes in the pump rate. The Fe content increased towards the end of the second period, which may indicate inflow of shallow groundwater due to a proven hydraulic connection to a higher level in a nearby borehole. The complex mixing situation is indicated by a sudden increase of the Cl⁻ content in the beginning of each period followed by a decrease. Interestingly, a strong pulse of shallow groundwater was detected on day 29 (Figure 2-3 b). This pulse was monitored with extra care using repeated off-line measurements to rule out possible instrument errors.

The test indicates the importance of knowing the hydraulic properties in the borehole. A general recommendation in this particular case was to use < 15% of the maximum pump capacity in order to try to minimise contamination from drilling debris, erosion and foreign water types. Fast and accurate sampling was performed at low flow in combination with a relatively long pumping period (weeks). This may on the other hand increase the up-lift time of the groundwater to the bedrock surface and may cause increased risk of precipitation/dissolution reactions in combination with air contamination prior to analysis.

2.3. Sampling protocol and precautionary measures

Originally one sampling event was planned where the pump rate would be systematically increased in three steps. At the commencement and end of every pumping period the section was to be sampled for colloids and groundwater. However, due to economic reasons, a simplified sampling programme was selected. The general plan of the sampling is shown in Figure 2-4. Originally a third sampling occasion was also planned, but due to a pump failure only two sampling occasions were actually conducted.

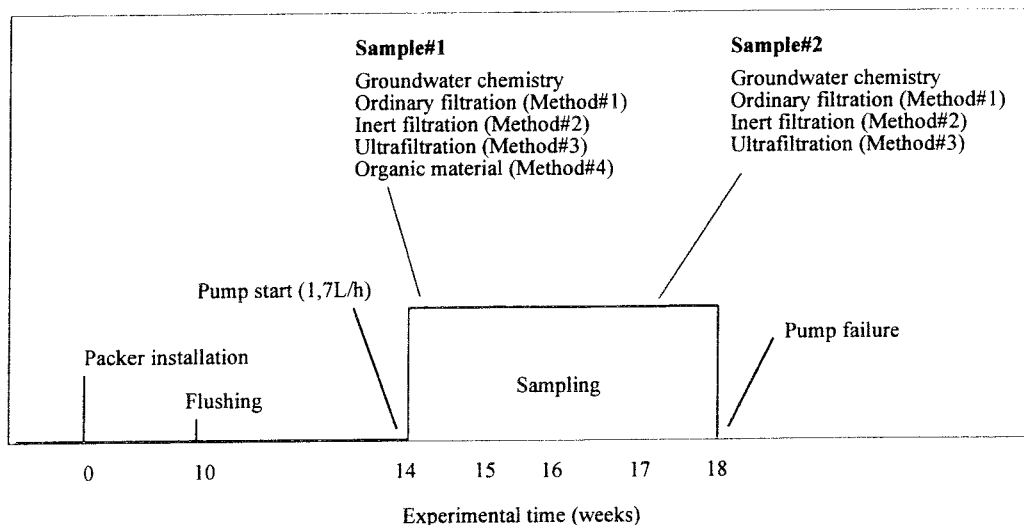


Figure 2-4. The sampling sequence in the OL-KR1 drillhole, showing the borehole and sampling activities during the experimental time.

In the following account the sampling occasions are referred to as sample#1 and sample#2. Sample#1 includes all the samples taken during the fourteenth experimental week (21-27 of September 1992). Sample#2 includes all the samples taken during the seventeenth experimental week (12-18 of October 1992).

In order to avoid possible contamination the following precautionary measures were taken:

- 1) After installation of the packer equipment the borehole was water flushed by pumping and then closed for 4 weeks to obtain natural flow conditions prior to sampling.
- 2) During sampling a low extraction flow-rate (the pulse pump gave two pulses per hour with 0.85 L per pulse; the total pump rate was 1.7 L/h) was established to avoid mixing of groundwaters and to ensure a representative sample from the section.
- 3) The low extraction rate causes long decompression times (up to 17 h) and therefore a possible contamination risk to the groundwater in the water outlet tube prior to analysis. In order to avoid air diffusion through the polyethylene water tube, the uppermost part of the tube was encased with an extra tube containing a positive N₂ (quality 5.0) pressure. One part of the tube (4.5 m) between the groundwater level and the bedrock surface was left without isolation due to technical reasons. This meant that 27% of the total length of the water outlet tube above the groundwater level was not isolated. Air diffusion through this part of the tube was therefore possible.
- 4) The mobile laboratory unit was vacuum cleaned rigorously prior to sampling to avoid possible particle contamination from the air.
- 5) In sampling methods using N₂ gas in direct contact with the groundwater (inert- and ultrafiltration) the highest quality (6.0) was used in purging and isolation.
- 6) Oxygen-, electrical conductivity- Eh- and pH measuring capability was available in the mobile field laboratory unit to be used for detection of contamination or changes in the sample chemistry.

3. Field equipment

3.1. Downhole unit

The downhole equipment consists of inflatable multipackers and a pump unit. The number of monitoring sections is seven; in addition five blind sections were installed to prevent vertical flow in the borehole. The colloid sampling was performed from the monitoring section 613-618 m (Figure 3-1). The changes in the natural hydraulic heads as well as in chemistry can be recorded from the monitoring levels. From each section a slim pipe is led to the uppermost part of the borehole which is of a greater diameter. Here the pressure transducers and the rubber membrane pump are located. Measurement of groundwater level changes were also performed on a regular basis in the upper part of the borehole. A detailed and comprehensive technical description of the units is given by Öhberg (1991).

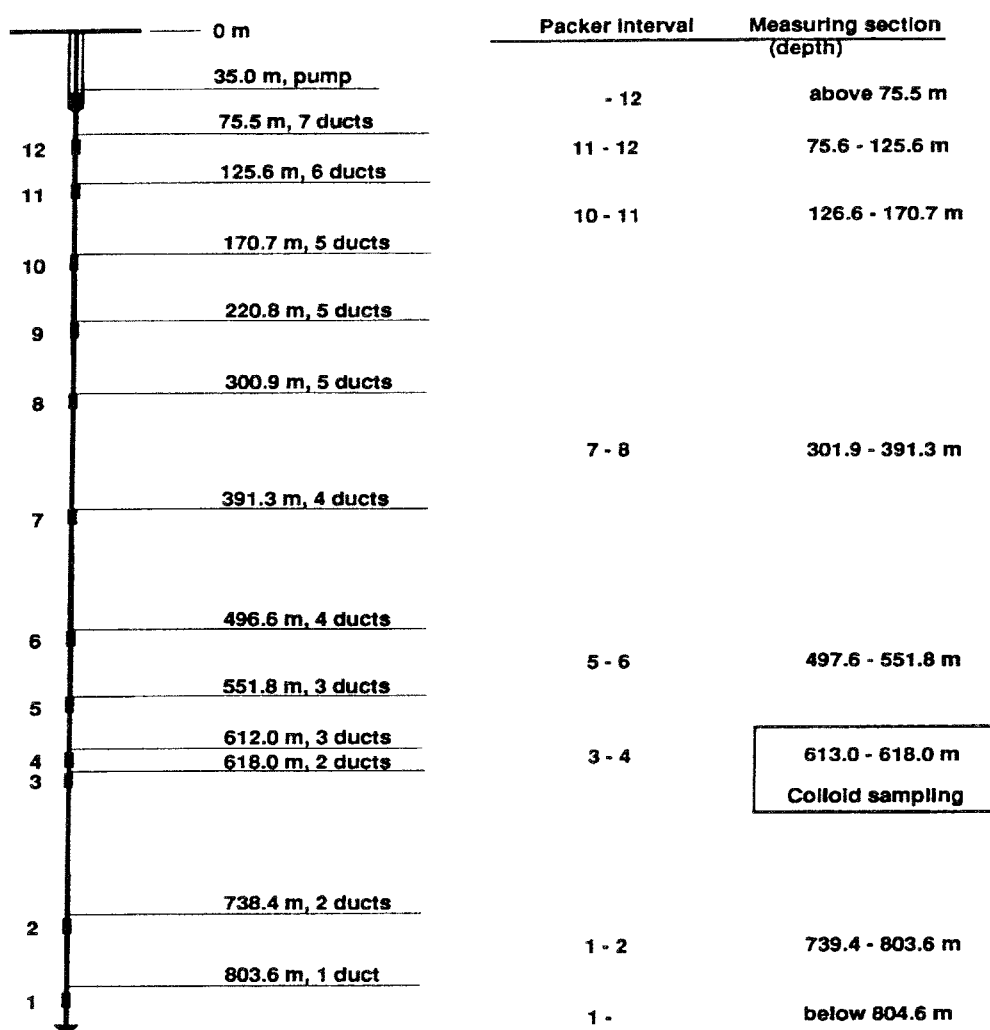


Fig. 3-1. The multipacker system installed in borehole OL-KR1. The colloid/groundwater sampling section 613-618m is framed.

3.2. Surface unit

The pump rate and packer inflation were regulated from the surface. The sampled groundwater was led to the mobile field laboratory unit (Figure 3-2) via a water tube which was isolated with N_2 over-pressure during the sampling. On-line measurements included electrical conductivity, dissolved oxygen and sulphide (pS), temperature, redox potential (Eh) and pH. The electrodes were placed in a flow-through cell, which was thermostated with a refrigerator and purged with N_2 gas to avoid chemical changes or interference from the atmosphere. The flow-through-cell also included a collector for gases released from the groundwater. Measurements carried out on-line and in the flow-through-cell were computer controlled. The computer registered the pumping operation in order to control pulse rates. The results were recorded and printed out in real time mode (for further details see Öhberg 1991).

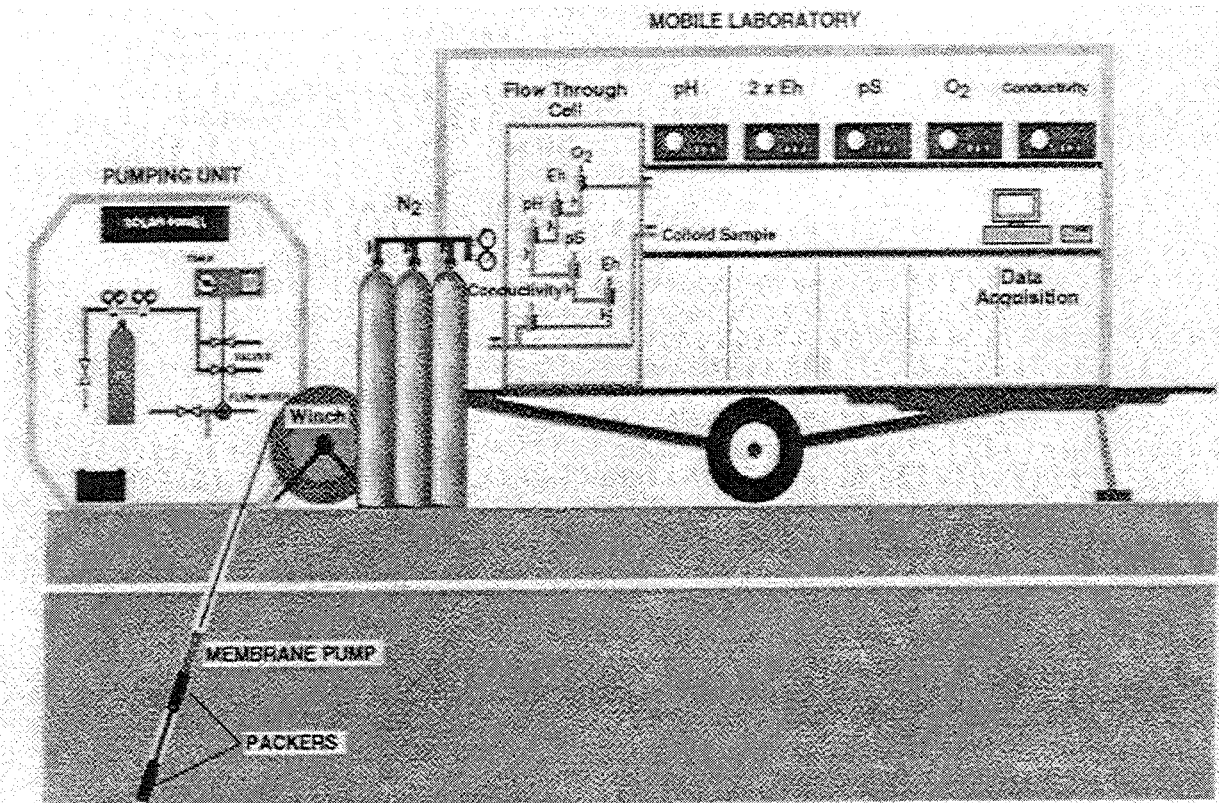


Fig. 3-2. Principle of the pump control unit and the mobile field equipment.

The flushing water used during drilling was labelled with uranine and sodium iodide which are analysed during groundwater sampling to trace any remaining drilling water components in the sample. Quantitative field determinations of uranine can be carried out using a visible light range absorption spectrophotometer or, alternatively, by fluorimetry down to a detection limit of 1 ng/L.

4. Groundwater chemistry

4.1. Method

Two main groundwater chemistry samples (sample#1-2) were taken during the experiment and analysed according to the protocol in Appendix#1. The analytical detection limits and instruments used are reported by Lampén and Snellman (1993).

4.2. Results

The main physico-chemical parameters obtained in sample#1 and sample#2 are presented in Table 4-1.

Table 4-1. Groundwater physico-chemical parameters, main cations and anions, isotopes and gases sampled from OL-KR1 within a two week interval. Analysed, but not found is denoted by (-). The automatic on-line measurements for S, E_h , pH O_2 and the electrical conductivity electrodes are shown in appendix#1.

Parameter	Sample#1	Sample#2
pH, field	8.42	8.61
Eh (Pt) (mV), field	-92.5	-64.2
Eh (C) (mV), field	140	177.8
conductivity (mS/m), field	3228	3229
O_2 (mg/l), field	0.34	0.07
alkalinity (meq/l), field	0.592	0.562
acidity (meq/l), field	-	-
$KMnO_4$ (mg/l)	61.6	61.3
Colour (mgPt/l)	118	124
Turbidity (FTU)	14	12.5
TOC (mg/l)	4.7	4.0
SiO_2 (mg/l)	1.6	2.9
Solid matter (mg/l)	3.8	2.4
TDS (mg/l)	20500	20300
Charge balance (%)	-1.082	-0.675
Ca (mg/l)	3510	3380
Na (mg/l)	4015	4100
Mg (mg/l)	58.2	58.5
K (mg/l)	21.5	21
Mn (mg/l)	0.52	0.62
Al (mg/l)	0.14	0.122
Fe tot (mg/l), field	1.90	1.95
Fe (II) mg/l, field	1.65	1.77
Fe tot (mg/l), laboratory	1.86	1.51
Cl (mg/l)	12800	12600
F (mg/l)	0.98	1.3
Br (mg/l)	104	96
I (mg/l)	1.75	1
NO_2 , NO_3 , NH_4 (mg/l)	<0.10	< 0.10
PO_4 , Ptot (mg/l)	<0.10	<0.10
SO_4 (mg/l)	1	2,3
HS- (mg/l)	0.2	0.12
S tot (mg/l)	0.5	1.5
H-3, TU	<8	<8
H-2, ‰ SMOW	-10.4	-10.6
O-18, ‰ SMOW	-78.5	-78.2
Ar, Vol.%	-	-
H_2 , Vol.%	0.01	-
He, Vol.%	0.74	1.1
N_2 , Vol.%	17.9	16.8
O_2 , Vol.%	0.66	0.46
CO_2 , Vol.%	-	0.004
CO, Vol.%	-	-
C_2H_4 , Vol.%	-	-
C_2H_2 , Vol.%	-	-
C_2H_6 , Vol.%	0.78	0.75
CH_4 , Vol. %	79.5	80.6
Uranine (%)	5.5	0.05

4.3. Conclusion

The groundwater samples represent saline Ca-Na-Cl waters after the classification of Davis (1964) and Davis & De Wiest (1967). According to the main cations and anions the groundwaters are similar to the waters sampled from the same depth conducted almost three years earlier (February 1990).

Both groundwater sample#1 and #2 are chemically similar, for example, the Cl concentration is 12800 mg/L and 12600 mg/L respectively. However, some small differences are evident; the alkalinity, calcium and sulphide values are somewhat lower and sodium, sulphate, manganese, silica and iron are somewhat higher in the second sample. The general homogeneity of the water chemistry is shown in the Piper diagram (Figure 4-1). These major features in combination with unchanged isotope and gas values, indicate stable groundwater conditions during the experiment. There is, however, a higher percentage of drilling water contamination of sample#1 (5%) than sample#2 (<0.05%).

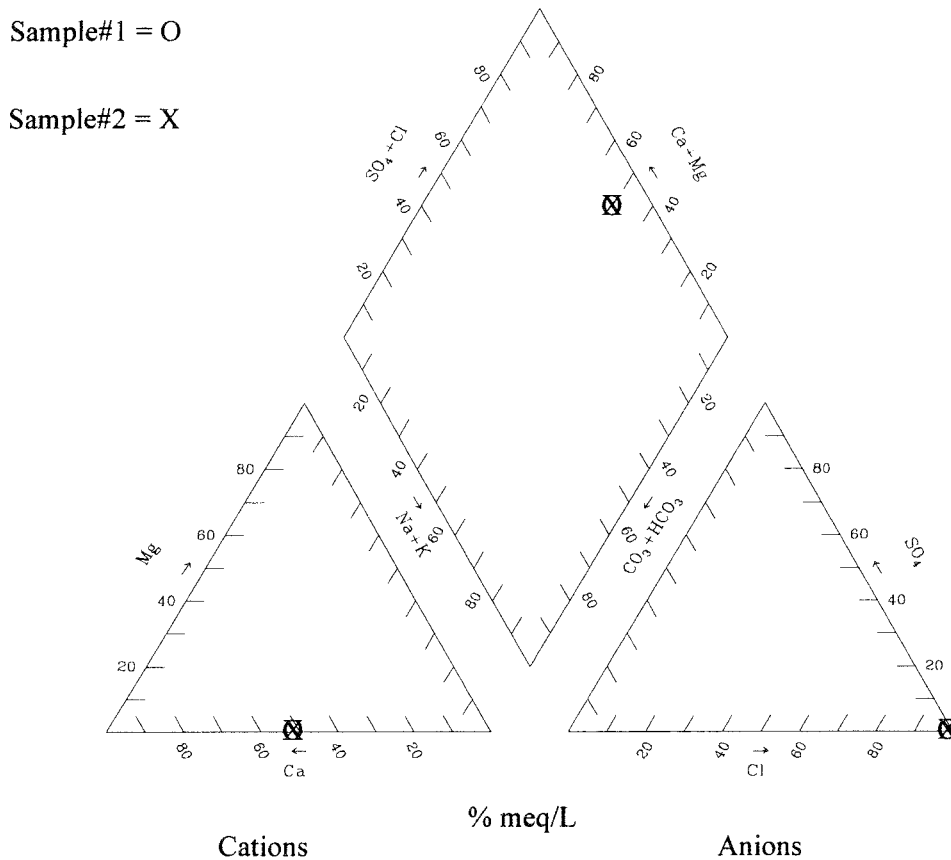


Figure 4-1. Piper diagram (Piper, 1953) of the major cations and anions for the sampled waters.

Compared to earlier sampling campaigns (Wickström and Helenius, 1990; Lampén and Snellman, 1993) a clear increase of the iron content was observed. Also a slight increase of alkalinity was found. The larger amounts of iron present might be due to contamination effects induced during the drilling and pumping activities in the borehole during the spring of 1992. The level of TOC has clearly decreased compared with the results from the earlier campaign. However, the still relatively high TOC content (4-4.7 mg/l) anyhow still points to possible contamination from an unknown source, or leaching from the relatively new nylon tubes in combination with the low pump rate. Possible analytical interference from the high Cl content in the

groundwater was tested by precipitating Cl. The treatment did not change the measured TOC content.

The groundwater is slightly reducing, the large amount of reducing gases, the Fe(II)/Fe_{tot} ratio (0.9) in combination with measurable amounts of sulphide, indicate lower redox conditions than the measured Eh (minimum -93 mV). Based on the pyrite/SO₄ equilibrium $\text{FeS}_2 + 8\text{H}_2\text{O} = \text{Fe}^{2+} + \text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^-$ (Stumm and Morgan 1981) the calculated redox values are -198 mV (Sample#1) and -210 mV (Sample#2). This is supported by the common occurrence of pyrite as a fracture mineral in the borehole. Possible reasons for the Eh discrepancy may include cell measurement disturbance caused by the newly installed valves/couplings. Also the long uplift time of the groundwater (17h) to the surface prior to analysis, may have promoted oxygen diffusion and leakage. In addition the calibrations carried out prior to sampling might have left traces of oxygen in the cell, which in fact was indicated by the large disturbances in the on-line measurements of oxygen. There is no doubt that pH has changed during up-lift of the groundwater and transportation to the laboratory due to CO₂ uptake (Pitkänen et. al. 1992).

5. Colloid sampling

Colloid sampling was performed by using four different methods; ordinary filtration, inert filtration, ultrafiltration and collection of organic material. The sampling procedures and results are discussed in this chapter.

5.1. Method#1; Ordinary filtration

5.1.1. Background and method

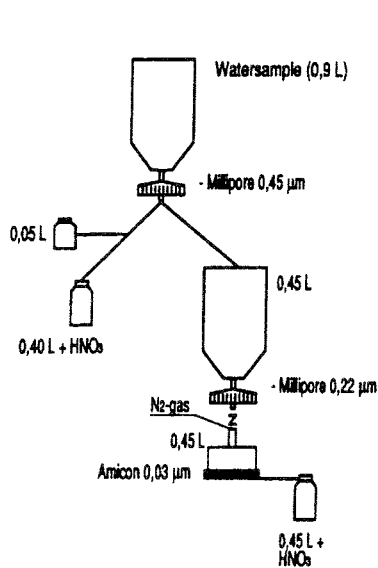
This so-called ordinary filtration of groundwaters has been used within the Finnish groundwater sampling programme from deep boreholes since 1989 (Lampén and Snellman, 1993). A total of 13 observations from five sites containing 8 deep boreholes (maximum depth 1000 m) have been sampled.

The method uses four membrane filters of different pore sizes; 450, 220, 30 and 20 nm. The first two filters are Millipore filters (Ø 45 mm) mounted in Swinnex Millipore filter clips. The 20 nm filter is a Whatman Anodisc (Ø 47 mm) membrane and the 30 nm filter is an Amicon Diaflo XM300 (Ø 75 mm) membrane. The last filtration is based on stirred-cell ultrafiltration using high purity nitrogen gas. All other filtrations were performed under atmospheric conditions using a vacuum pump.

Before starting the actual sampling the membranes were filtered using a minimum of 100 ml distilled water. Subsequent filtrations were performed with two parallel samples (Figure 5-1a and b), both involving three different steps. Both sample filtrations commenced by filtering groundwater (generally 1-2 L; here 0.9 L) through the 450 nm filter. In each case, half of the filtrate was retained for water analyses, of which one part (0.45 L) was acidified for subsequent trace metal analyses and the other part (0.05 L) was collected for sulphur analyses. The

remaining half of the filtrate was then put through the 220 nm filter. The third step differed in the parallel filtrations. The stirred-cell ultrafiltration unit using N_2 -gas pressure and a 30 nm filter membrane was used in one method (Figure 5-1 a) and an Anodisc 20 nm filter in the other (Figure 5-1 b). The filtrate (0.45 L) from the former filtration was collected and acidified for subsequent metal analyses. From the latter filtration, both the filter and filtrate were collected and specifically used for sulphur analyses.

a)



b)

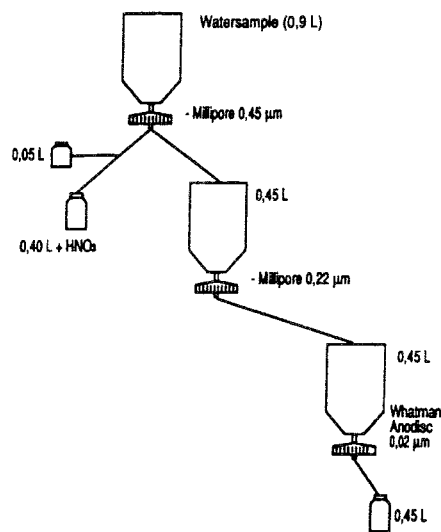


Figure 5-1a) Principle of the general filtering procedure b) A parallel sample is collected for sulphur analysis.

The elements analysed for in the filters were Al, Ca, Fe, Mg, Mn, Si and S. The analyses were performed with atom absorption spectrophotometry (AAS) except for SiO_2 which was analysed by spectrophotometry after wet digestion of the filters. The filter for S analyse was combusted at 1250°C using O_2 as a carrier gas to form SO_2 for gaschromatographic analyses. All values have been corrected against reference blank filters.

5.1.2. Results

Al, SiO_2 , S_{tot} , Ca, Mn, Fe and Mg from the filter analyses are recalculated in ppb considering the water flow through the filters and any additional to concentrations obtained from filtering the blanks. The results are shown in Table 5-1 and graphically in Figure 5-2 and 5-3; the results from the filtrate analyses are presented in appendix#3. The oxygen level and pH values on-line versus off-line are shown in Table 5-1b.

Table 5-1a. Element concentrations and size distribution of particles on filter sample#1 and #2. The elements analysed but not detected are denoted by (-).

Sample:no	Filter Size (nm)	Al (ppb)	SiO ₂ (ppb)	Stot (ppb)	Ca (ppb)	Mn (ppb)	Fe (ppb)	Mg (ppb)	Sum of all elements (ppb)
Sample#1	20	-	-	-	-	-	-	-	-
Sample#1	30	<1.2	30	<10	739	0.08	1.9	18	<800.2
Sample#1	220	0.7	<10	<10	1308	0.3	18.8	26	<1373.8
Sample#1	450	4.0	40	<10	699	0.4	210	15	<978.4
<i>Sum Sample#1</i>	<i>20+30+220+450</i>	<i><5.9</i>	<i><80</i>	<i><30</i>	<i>2746</i>	<i>0.78</i>	<i>230.7</i>	<i>59</i>	<i><3152.4</i>
Sample#2	20	-	-	-	-	-	-	-	-
Sample#2	30	<1.2	50	<10	722	0.03	<3.4	18	<804.6
Sample#2	220	<3.5	10	<10	1462	0.3	9.6	29	<1524.4
Sample#2	450	1.4	20	<10	754	0.2	54	16	<855.6
<i>Sum Sample#2</i>	<i>20+30+220+450</i>	<i><6.1</i>	<i>80</i>	<i><30</i>	<i>2938</i>	<i>0.53</i>	<i><67</i>	<i>63</i>	<i><3184.6</i>

Table 5-2 b. Sampling conditions on-line and off-line during the filtration of sample#1 and #2 from Olkiluoto. The off-line measurements are conducted after 5 min of filtering in open air. N/A indicates not measured due to practical or technical problems.

Sample	Filter Size (nm)	On-line O ₂ (mg/L)	Off-line Sample O ₂ (mg/L)	On-line pH (units)	Off-line pH (units) after filtration
Sample#1	20	0.34	N/A	8.42	N/A
Sample#1	30	0.34	N/A	8.42	N/A
Sample#1	220	0.34	N/A	8.42	N/A
Sample#1	450	0.34	9.4	8.42	7.55
Sample#2	20	0.07	N/A	8.61	N/A
Sample#2	30	0.07	N/A	8.61	N/A
Sample#2	220	0.07	N/A	8.61	N/A
Sample#2	450	0.07	N/A	8.61	N/A

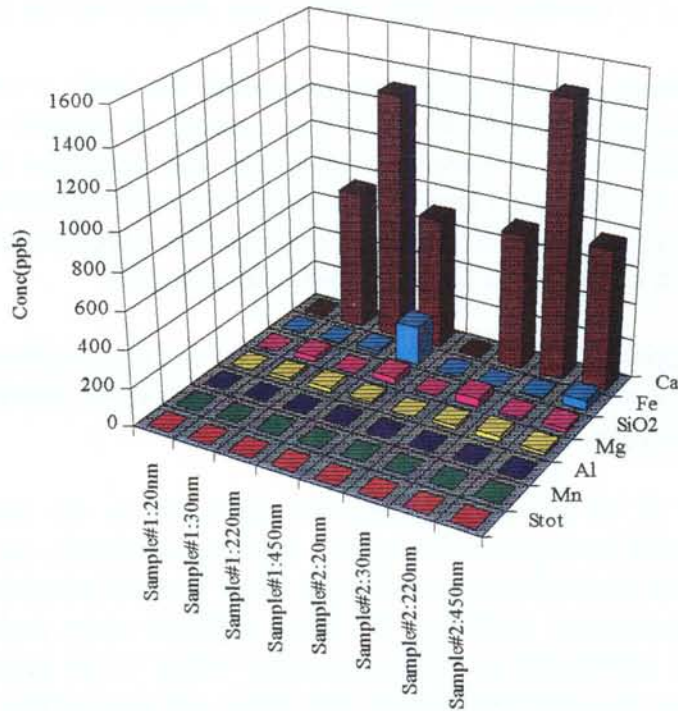


Figure 5-2. Element concentrations on filter sample#1 and #2 for different pore sizes.

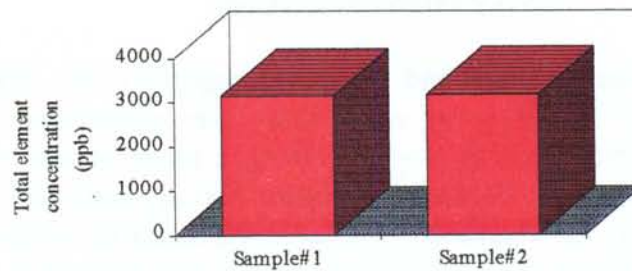


Figure 5-3. Total element concentrations on filter sample#1 and #2.

5.1.3. Conclusion

The element concentrations for Al and Fe were generally found to be higher on the largest pore size filters (450 nm) inferring that, these elements have probably formed larger particles. On the 220 nm size filter Ca and Mg were concentrated suggesting intermediate size aggregates. Most Si was found on both the 450 nm and the 30 nm filters; Mn was present on both the 450 nm and 220 nm filters. As no prefilter was used (as in inert filtration and ultrafiltration) the major fraction of the obtained elements on the 450 nm filters may also contain particles (>1000nm). Furthermore, the different filtering procedures used in this method might have influenced some results; e.g. the general decrease in colloid amounts on the 30 nm filter might have been influenced by the use of inert N₂-gas. The redox-sensitive

elements Fe and Mn might have been strongly effected, but even the Ca content measured on the 30 nm filter was also half of that obtained on the 220 nm filter.

In general however, the total element concentration was more or less constant (3.1 mg/L -3.2 mg/L) in both samples. The iron content, in contrast decreased from 0.23 mg/L to 0.07 mg/L in sample#2, indicating less oxidation problems in the second sample. Mn showed a similar behaviour. The increase due to oxidation and hence precipitation of these elements is supported by a higher value of dissolved oxygen (0.34 mg/L) measured in the groundwater sample#1.

The filtrate (Appendix 3) indicated similar values for almost all elements in both sample#1 and sample#2, although a slight decrease of Al, Ca and Fe was obtained for the second sample.

More than 98 % of the total element concentration in the samples was Ca, indicating probable precipitation of calcite. Calcium, therefore, can be considered mainly an artefact in combination with some of the iron and manganese aggregates. The filtering procedure, including the three different steps under atmospheric conditions, was performed as fast as possible within 15-20 minutes. However, oxidising effects, pH changes (seen in table 5-2b) and precipitation of calcite and the redox sensitive elements can all cause possible artefact material.

5.2. Method#2; Inert filtration

5.2.1. Background and method

The Swedish Nuclear Fuel and Waste Management Co. (SKB) has performed inorganic colloid sampling in connection with groundwater sampling in deep boreholes at different sites in Sweden, during a period of ten years. A total of 305 observations come from 22 deep (maximum 860 m) boreholes at 9 different study sites (Laaksoharju and Degueldre, 1994). In the sampling method used, the column contains of four filters of different sizes (50-450 nm) coupled in series. The sampled water is pressed through these filters with using an over-pressure of 2 bar. The advantage of this technique is that it is easily portable and simple which makes on-line measurements practical. Drawbacks may occur because a colloidal gel may develop on the first filter. The gel may deplete the concentrations in the later filters because of erroneous cut-off. Furthermore, the size distribution may be inaccurate, and iron hydroxide, calcite and salt might precipitate due to external influences or due to the filtering process.

To try to overcome these problems, a new filtering technique was suggested (Peter Wikberg pers. comm. 1992). Instead of filters coupled in series, each filter is used separately and the same volume of water is led through each filter. N₂-gas is used to minimise atmospheric contamination deionized water is used as a washing medium to avoid artefact precipitation (C. Degueldre pers. comm. 1991). This method is named "Inert Filtration".

The filters used were Polycarbonate in type (Nuclepore) of size 50, 200 and 400 nm. In order to avoid possible particle uptake from the air the filters were pre-assembled off-site and isolated with parafilm in a standard Millipore Sterifil Aseptic filter holder (\varnothing 47 mm) (Figure 5-4). One filter holder per filter size was used. The three filter holders were placed in a glove bag and left for minimum of 24h with constant N_2 -over-pressure (quality 6.0). The N_2 -gas was led through a flask containing ultra pure distilled water placed inside the glove bag to eliminate air traces. A water lock was used to avoid over-pressure build up in the glove bag when left unattended, and an oxygen meter inside the glove bag was used to detect possible air leakages. A pH meter was used to measure the pH in the sample prior to and after filtration. A prefilter (2500 nm) assembled at the filter holder gives the upper cut-off limit, and filters possible drilling debris from the groundwater. For the actual sampling procedure a constant volume of groundwater (500 ml) was filtered through each filter using a vacuum pump. The filters (not the prefilter) were then washed with 50 ml ultra pure deionized water. This step was used to avoid artefacts from salt and calcite precipitation. The last step included drying of the filter with N_2 -gas for 15-30min; this is important in order to avoid new reactions or precipitations from water droplets. The filter holders were then carefully removed from the glove bag and sent for analysis, in an upright position to avoid dislodgement of colloids from the filters. It is important to note that the filter was removed from the filter holder only shortly prior to analysis. The filters were analysed according to the SKB standard procedure i.e., Al, Si, S, Ca, Mn and Fe content were determined with energy dispersive XRF (X-ray fluorescence). The reported accuracy for this method is +/- 7% and the reproducibility is +/- 3%.

The element values from the filter analyses are recalculated in ppb ($\mu\text{g/l}$) considering the water flow through the filters. The final element concentration is corrected for any enhancement of a given element, obtained from running reference blank filters. The final calculated element concentrations used to obtain the right size and concentration distribution are obtained according to: for the 50 nm filter: $50\text{nm} = 50\text{nm}_r - 200\text{nm}_r - 400\text{nm}_r$; for the 200 nm filter: $200\text{nm} = 200\text{nm}_r - 400\text{nm}_r$ and for the 400 nm filter: $400\text{nm} = 400\text{nm}_r$, where r = results from the filter analyses.

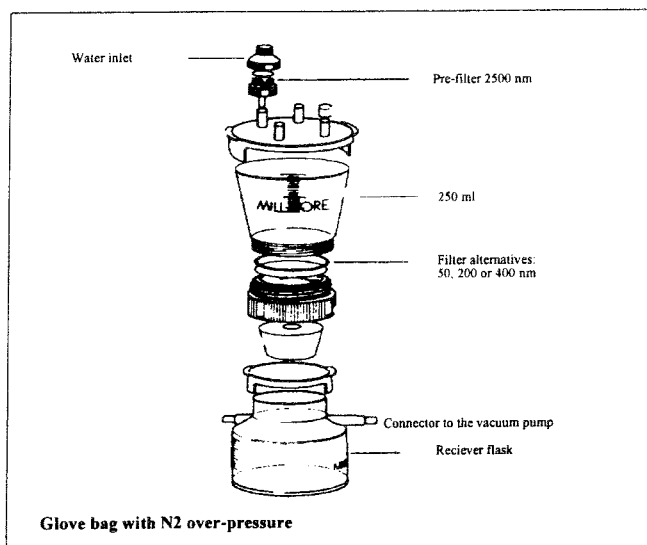


Figure 5-4. Principle drawing of the filter holder with enclosed in a glove bag with nitrogen over-pressure.

5.2.2. Results

The element values of Al, Ca, Fe, Mn, Si and S from the filter analyses are listed for deionized water, sample#1 and #2 in Table 5-2a, and shown graphically for sample#1 and #2 in Figure 5-5 and 5-6. The oxygen and pH values on-line versus in the glove bag are shown in Table 5-2b.

Table 5-2 a. Element concentrations and size distribution of particles from deionized water and sample#1 and #2 from Olkiluoto. Elements analysed but not detected (-).

Sample	Filter Size (nm)	Al (ppb)	Si (ppb)	S (ppb)	Ca (ppb)	Mn (ppb)	Fe (ppb)	Sum of all elements (ppb)
Deionized Water	50	-	-	-	-	-	0.4	0.4
Deionized Water	200	-	-	-	-	-	-	0.0
Deionized Water	400	1.3	18.5	3.2	3.2	-	1.2	27.4
<i>Sum: Deionized Water</i>	<i>50+200+400</i>	<i>1.3</i>	<i>18.5</i>	<i>3.2</i>	<i>3.2</i>		<i>1.6</i>	<i>27.8</i>
Sample#1	50	8.0	-	-	-	-	-	8.0
Sample#1	200	8.1	13.6	14.2	-	0.0	18.2	54.1
Sample#1	400	0.7	1.5	1.3	952.4	0.1	5.2	961.2
<i>Sum: Sample#1</i>	<i>50+200+400</i>	<i>16.8</i>	<i>15.1</i>	<i>15.5</i>	<i>952.4</i>	<i>0.1</i>	<i>23.3</i>	<i>1023.3</i>
Sample#2	50	1.6	-	-	-	-	-	1.6
Sample#2	200		5.5	-	-	0.0	4.0	9.6
Sample#2	400	0.2	4.2	5.7	460.8	0.1	1.3	472.3
<i>Sum: Sample#2</i>	<i>50+200+400</i>	<i>1.8</i>	<i>9.7</i>	<i>5.7</i>	<i>460.8</i>	<i>0.1</i>	<i>5.4</i>	<i>483.5</i>

Table 5-2 b. Sampling conditions on-line and in the glove bag during the filtration of the deionized water, sample#1 and #2 from Olkiluoto. The oxygen level is measured in the N₂-atmosphere; pH is measured prior and after filtration of the sample. N/A indicates not measured due to practical or technical problems.

Sample	Filter Size (nm)	On-line O ₂ (mg/L)	Glove bag O ₂ (mg/L)	Glove bag O ₂ (mg/L) in sample	On-line pH (units)	Glove bag pH (units) prior to filtration	Glove bag pH (units) after filtration
Deionized Water	50	N/A	0.1	N/A	N/A	N/A	N/A
Deionized Water	200	N/A	1.9	N/A	N/A	N/A	N/A
Deionized Water	400	N/A	1.8	N/A	N/A	N/A	N/A
Sample#1	50	0.34	1.3-0.2	0.3-0.1	8.42	8.75-8.83	8.73
Sample#1	200	0.34	0.0	0.0-0.1	8.42	8.85	8.88
Sample#1	400	0.34	1.8	0.4	8.42	8.80	8.80
Sample#2	50	0.07	1.4	N/A	8.61	N/A	N/A
Sample#2	200	0.07	0.2	0.2	8.61	N/A	N/A
Sample#2	400	0.07	0.1	0.1	8.61	N/A	N/A

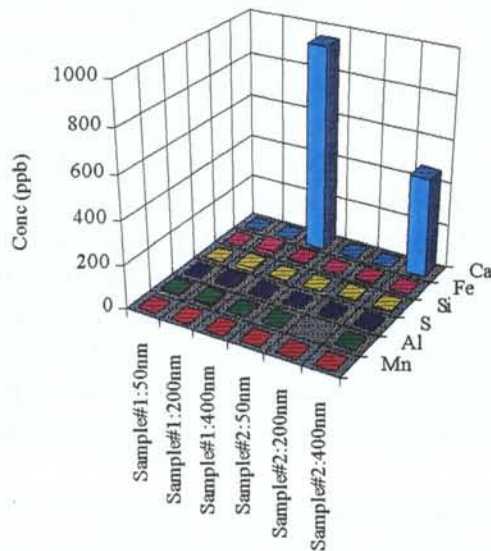


Figure 5-5. Element concentrations on filter sample#1 and #2 for the different pore sizes.

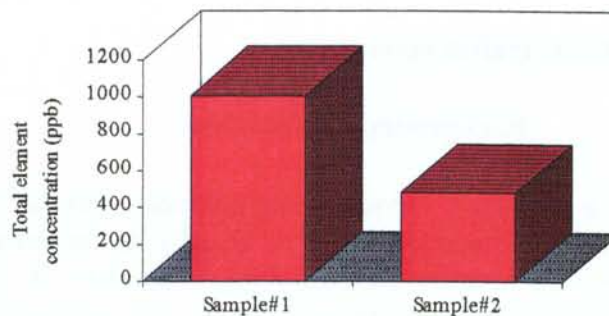


Figure 5-6. The total concentrations of filter sample#1 and #2

5.2.3. Conclusion

The deionized water contained large colloids of Al, Si, S Ca and Fe. When using this water for washing, the colloid content increases. The deionized water should therefore be ultrafiltered prior to use.

For sample#1 and #2 the element concentration for Al, Si, S seems to be generally higher on small and intermediate pore size filters (50-200nm). On larger and intermediate pore size filters (200-400nm) Ca, Mn and Fe dominate. The calcium may be due to insufficient washing.

The concentration of all elements is higher in the first sample. The total element concentration is decreased by 54% in the second sample compared to the first sample. In the groundwater analyses, only Ca is lower in the second sample. The other elements in the groundwater Si, S, Mn and Fe, do not correspond to the behaviour obtained on the filter analyses.

The following general conclusions may be made: 1) Al and Si is higher on filters with small pore size which may indicate possible small size clay particles, i.e. drilling debris. The clay forms small particles while calcite and the manganese oxides and iron hydroxides seem to form larger aggregates. Calcite is a possible artefact supported by a correlation with changes of Ca in the water, although the analytical precision of the analyses may also give this effect. Saturation index calculations of calcite also indicated a risk for calcite over saturation (+1.5) and hence precipitation especially in N₂-atmosphere (see Figure 6-3). The high manganese oxide and iron hydroxide content especially on the first sample may be due to sampling artefacts. In the first sample the filters were clogged, probably with clay particles, which caused long filtration times (>1h/filter). The clogging was followed by calcite precipitation and possible co-precipitation and oxidation of the Fe and Mn in the water. The oxygen meter mounted inside the glove box suggested oxygen leakage during sampling#1.

The second sampling carried out without clogging and under a shorter period of time (15min./filter). The oxygen meter indicated lower air contamination than for sample#1. The second sample is therefore regarded to be more representative for in-situ conditions than sample#1. The pre-filter used in the system was not analysed, so that the possible retention on the colloid concentration due to this filter is not known.

5.3. Method#3; Ultrafiltration

5.3.1. Background and Method

Ultrafiltration is a term used for separating colloidal material by filtration through microporous or semipermeable mediums. Usually the nominal pore sizes of the used membranes are smaller than 15 nm. A number of different techniques preventing concentration polarisation problems are commercially available e.g. tangential-flow, hollow fibre, cross-flow stirred-cell, and centrifugal ultrafiltration systems. Here tangential-flow and cross-flow (stirred-cell) techniques were used.

During the whole sampling procedure, and the different phases in sample treatment, nitrogen (quality 6.0) atmosphere with a small over-pressure was used to protect the colloid samples from atmospheric contamination. Since the sampling procedure with the various steps took about two days altogether, protection from atmospheric contamination was of utmost importance. The principle of the sampling set-up, the different steps undertaken and analyses connected with this sampling method, are shown in Figure 5-7. After fractionation, the concentrate and ultrafiltrate were treated similarly in order to detect possible artefact producing processes.

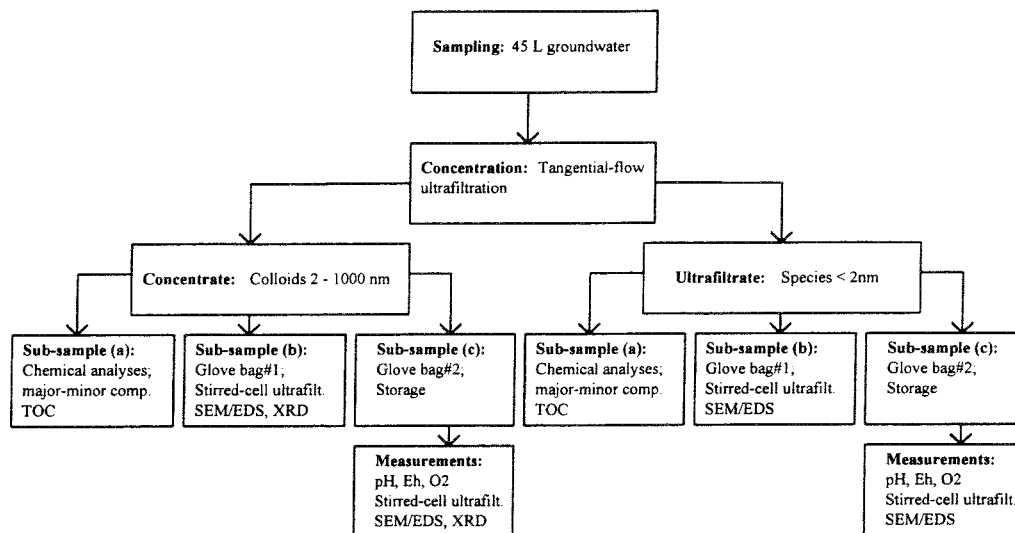


Figure 5-7. Ultrafiltration procedure for colloids sampling; nitrogen over-pressure was used to prevent air contamination.

Sampling

Two groundwater samples (sample#1 and sample#2), each about 44 L, were collected over a time interval of three weeks. As the groundwater pumping rate was low, collection of the large volume samples took about 24 h each. Sample collection was performed under anaerobic conditions using high purity nitrogen gas, for which an oxygen content of less than 0.1 ppm is guaranteed.

For sample collection a specially designed double container was used. The container consists of two separate polyethylene containers; the inner container is a 50 l bottle of polyethylene which is placed inside the outer one. The bottle is provided with necessary fittings allowing coupling to the lead-through connections of the outer container. The outer container is tightly closed with a plexi-lid which is fitted with lead-through pipes to which valves and tubes for water and gas flow are connected. As the inner container is of polyethylene, and thus permeable to atmospheric gases (O_2 , CO_2), the purpose of the outer container is to allow continuous gas (N_2) flow under slight over-pressure to prevent atmospheric contamination of the groundwater while the sample is collected, transported or concentrated. The same container is used first for collecting the entire groundwater

sample and then concentrating the sample by tangential-flow ultrafiltration in the laboratory.

Before starting sampling the container was carefully flushed with nitrogen under slight over-pressure over night. The groundwater was collected on site within the mobile laboratory and then transported to the nearby on-site laboratory for further treatment. While collecting the sample, the tubing leading from the refrigerator to the collection vessel was additionally protected with plastic lining allowing an nitrogen protection.

Concentration

Concentration of groundwater colloids by tangential-flow ultrafiltration was performed in order to obtain enough colloidal material for analysis. In the tangential-flow system the groundwater being concentrated sweeps tangentially the surface of the filter, and all colloids larger than the NMWC (Nominal Molecular Weight Cut-off) of the membrane are thus kept in dispersion preventing concentration polarisation. Only a part of the groundwater permeable to the membrane is forced through the filter (*ultrafiltrate*) by using low transmembrane pressure and the rest (retentate) is returned to the sample container with the dispersed material. Thus, after concentration, two solutions were obtained, the *concentrate* containing the colloids and the *ultrafiltrate* containing the soluble species. Concentration of the groundwater samples was performed with a system containing a pre-filter of 1000 nm, a pump of procon type and a Millipore Pellicon cassette for the tangential-flow filter with 10 000 NMWC, which corresponds to a pore size of about 2 nm. As the filters used in this study were not calibrated with particles of known size, the values of pore sizes refer to nominal pore sizes given by the manufacturers and, as such, are not precise.

In this study the colloids were only separated into a single fraction (2nm-1000 nm), thus the distribution of elements by size of the colloids was not obtained here, only elements present in the colloid *concentrate* and on the membrane filters. A diagram of the concentration system is shown in Fig. 5-8.

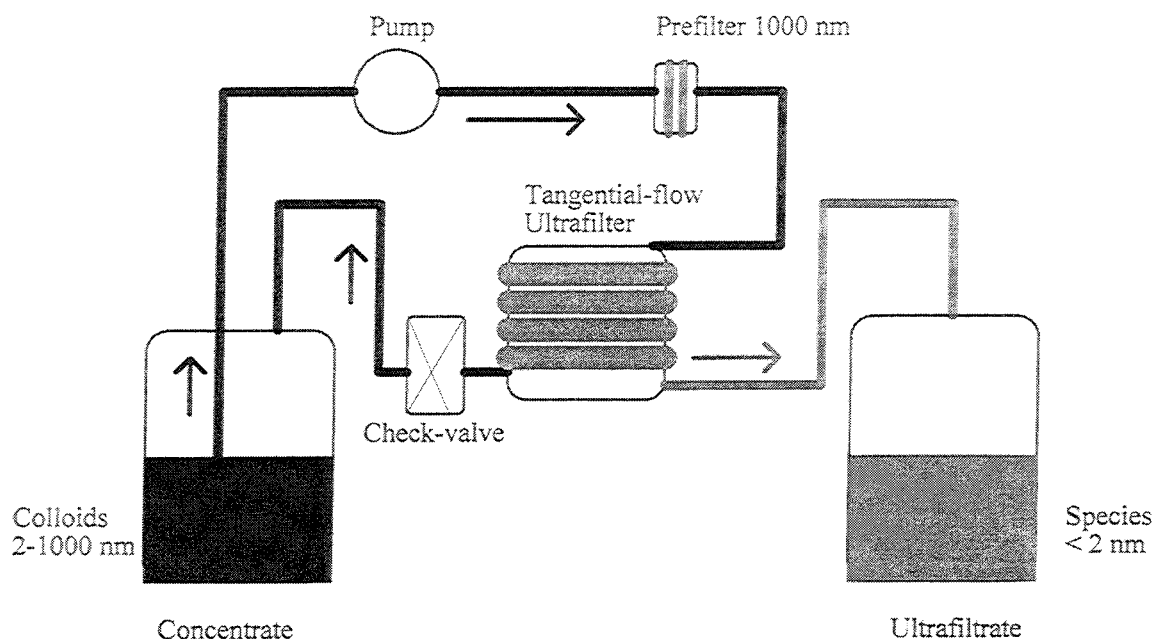


Figure 5-8. Diagram of the system used for concentration of the groundwater samples by tangential-flow ultrafiltration.

During concentration a low "transmembrane" pressure was used to reduce physical damage to colloidal particles, thus reducing salt retention, which can cause carbonate precipitation for certain groundwater compositions. Conductivity measurements of the concentrates and ultrafiltrates confirmed that no salt retention had occurred.

Before and after concentration the entire filtration system was thoroughly washed with 0.1 M NaOH and 0.01 M HNO₃ solutions. The washouts were not analysed for the particulate matter retained by the pre-filter. Before starting the concentration of the groundwater samples the system was first flushed with about 10 L of anaerobic deionized water. Separately collected anaerobic groundwater (about 5 L) was then used to treat the filter surfaces.

Sub-sampling and analyses

Separate sub-samples from both the *concentrate* and the *ultrafiltrate* were collected for different analysing purposes (see Fig. 5.7). The first Sub-samples (a) were used for chemical analysis of major and some minor components and TOC (Total Organic Carbon). TOC was analysed by Sybron/Barnstead Organic Carbon Analyzer. The ions Cl⁻, Br⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺ and Mg²⁺ were analysed with HPLC, the total elemental concentrations of Ba, B, Sr, Li, Mn, Rb with ICP-MS (mass-scan/single standard) and Na, K, Ca, Mg and Cu using atomic absorption spectroscopy, and Fe, Al, SiO₂ spectrophotometrically. As the sampled groundwater has high salinity ionpairing may be important in terms of speciation of elements and results on ionic species. In high salinity waters many ions e.g. Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻, HCO₃⁻, CO₃²⁻, OH⁻ and Cl⁻ can form ion pairs.

The second sub-samples (b) were used for cross flow (stirred-cell) ultrafiltration in order to obtain colloids on filter membranes for further analysis. In the stirred-cell a stirrer just above the surface of the membrane filter is used to prevent concentration polarisation. The membrane filters used were Amicon Diaflo XM50 (pore size 3 nm) and the filtration pressure was by using high purity nitrogen gas. Several membranes for further studies were produced. The filtered solution amount varied depending on the solution to be filtered, whether it was the *concentrate* or the *ultrafiltrate* and also, whether the membrane filter was to be examined by SEM/EDS (Scanning Electron Microscopy / Energy Dispersive Spectroscopy) or XRD (X-ray diffraction). SEM/EDS specimens were also prepared from the *ultrafiltrates* in order to discover possible artefacts due to concentration or cross flow filtration.

For SEM/EDS the filter membranes were mounted on a specimen holder and coated with a thin layer of carbon to obtain electrical conductivity. SEM was used to obtain micrographs of the retained colloidal material on filter membranes and EDS to obtain the elemental composition of the colloids. When using EDS it is necessary to bear in mind that the lightest elements cannot be measured and, those which can, can only give rise to very weak peaks, if present at all. Thus, carbon or oxygen are not usually detected. SEM suffers from a lack of resolution needed to detect the smallest colloids (below 50 nm - 100 nm) or colloid clusters. SEM micrographs are often used for counting colloidal particles on the membranes to obtain a measure for colloids per litre of groundwater. Such counting requires treating a substantial amount of micrographs to obtain statistically reliable results. It was not possible to include such counting in this work. With EDS it is possible to obtain elemental analysis of particles about 1000 nm in size. When smaller particles are analysed, the result will also include elements from the material in the surrounding of the measured particle. The membrane filter itself produced a very strong Cl peak and thus Cl was present in all the measured EDS spectra and made it difficult to distinguish whether additional Cl originating from the retained material on the filter was present, especially when small particles were analysed. Thus Cl is not mentioned in the following account when giving elemental composition of analysed particles unless Cl was evidently present in the analysed particle.

From the *concentrates* some membrane filters were produced for XRD examination to obtain information of the mineralogical character of the colloids. Difficulties in the analysis arose from the background caused by the membrane. The high background can conceal some of the peaks in the resulting spectra, especially here as small amounts of retained material were present.

The third sub-samples (c), first stored in a glove-bag with N₂-over-pressure, were taken into an off-site anaerobic glove-box (Mecaplex). The glove-box maintains a nitrogen atmosphere with an oxygen content normally less than 1 ppm. Usually the oxygen content (continuously measured) stays below 0.1 ppm, but may somewhat fluctuate when working with gloves. E_h (Pt electrode), pH and dissolved oxygen (trace oxygen analyser by Orbisphere) were measured in the glove-box for both *concentrates* and *ultrafiltrates*. These measurements were not possible on-site during concentration and glove-bag filtration.

5.3.2. Results

Chemical measurements and analyses of the concentrate and the ultrafiltrate

The results of chemical analysis of the *concentrates* and *ultrafiltrates* for sample#1 and sample#2 are given in Appendix 4, Table 13-1. Based on these results element enrichment in the *concentrate* fractions were obtained by subtracting the analysed values and calculated to give values in Table 5-4 by taking into account the concentration factors. These results can only be considered indicative and not quantitative. Because the concentration factors were rather low for both samples (8.8 for sample#1 *concentrate* and 12.2 for that of sample#2) the accuracy of the analysed concentrations is such that the results obtained by subtraction fall within the limits of precision. Thus the obtained calculated value can also be zero or negative. These calculated results given in Table 5-4 were needed for comparison of the results with the other two methods. Only the same elements which were determined in the other two methods were chosen and are graphically presented in Figures 5-9 and 5-10. The Ca results mask the real magnitude of Ca associated with the colloid phase since the element is a macro-component in the analysed solution. The Ca value is therefore indicated with a question mark (?) and is later omitted in the comparison (see chapter 6 and 7).

Table 5-3. Off-site (glove-box) measurements of E_h , pH and O_2 compared to those of on-line measurements. (n.m. = not measured due to technical problems). TOC results for the different samples are also included (off-site analysis).

Sample	E_h (mV)	pH	O_2 (ppm) Dissolved	TOC (mg/L)
Sample #1 -groundwater (on-line)	-93	8.42	0.34	4.7
-ultrafiltrate (off-site)	-170	6.97	0.07	0.5
-concentrate (off-site)	-190	6.89	0.03	0.5
Sample #2 -groundwater (on-line)	-64	8.61	0.07	4.0
-ultrafiltrate (off-site)	-180	7.02	n.m.	0.4
-concentrate (off-site)	-170	7.33	n.m.	0.4

Table 5-4. Calculated element concentrations (ppb) associated with the colloid fraction for sample #1 and #2, Ca included and omitted. The question mark (?) indicates the uncertainty concerning the Ca association with the colloid phase. The calculated element value was zero or negative are denoted by (-).

Sample:no	Ca	Mg	Si	Fe	Al	Mn	Sum	Sum omitting Ca
Sample #1	11400?	114	4.5	14.8	-	0.7	11534	134
Sample #2	8200?	82	4.1	5.7	4.9	0.7	8297	97

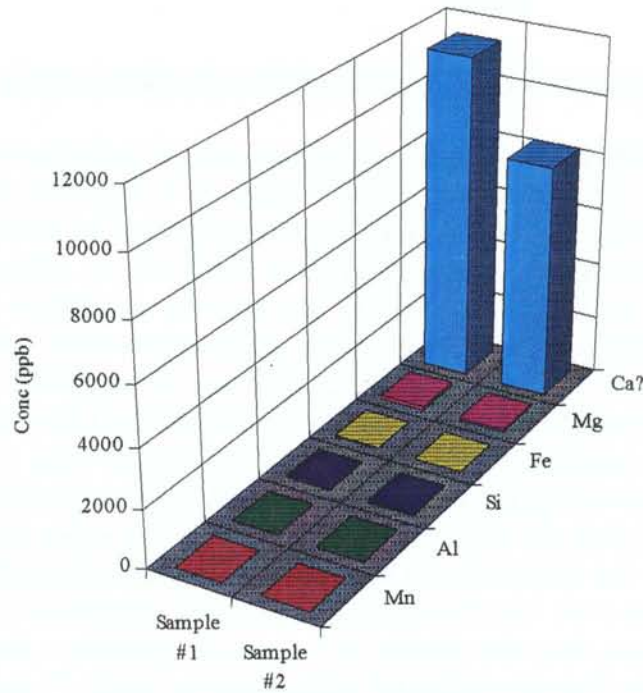


Figure 5-9. Element concentrations of colloid fractions in sample#1 and #2. The question mark (?) indicates the uncertainty concerning the Ca association with the colloid phase.

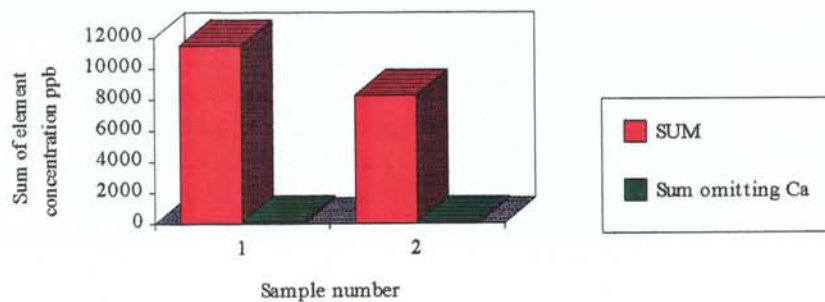


Figure 5-10. Total sum of the calculated elements associated with the colloids in sample#1 and #2. Ca included and omitted because of the uncertainty concerning the association with the colloid phase.

SEM/EDS and XRD

Filter membranes produced for both sample 1 and sample 2 colloid *concentrate* and *ultrafiltrate* were micrographed by SEM (Figures 5-11 - 5-14). The *concentrate* contained the 2-1000 nm colloid fraction and the *ultrafiltrate* contained species < 2 nm. One micrograph was also produced from a filtermembrane of the prefiltered groundwater. Micrographs of the *concentrate* filters were taken in order to visualise the colloids retained on the filters. The purpose of micrographing the *ultrafiltrate* membranes was also to learn about possible artefact effects of particle formation and aggregation etc. connected with the stirred-cell ultrafiltration.

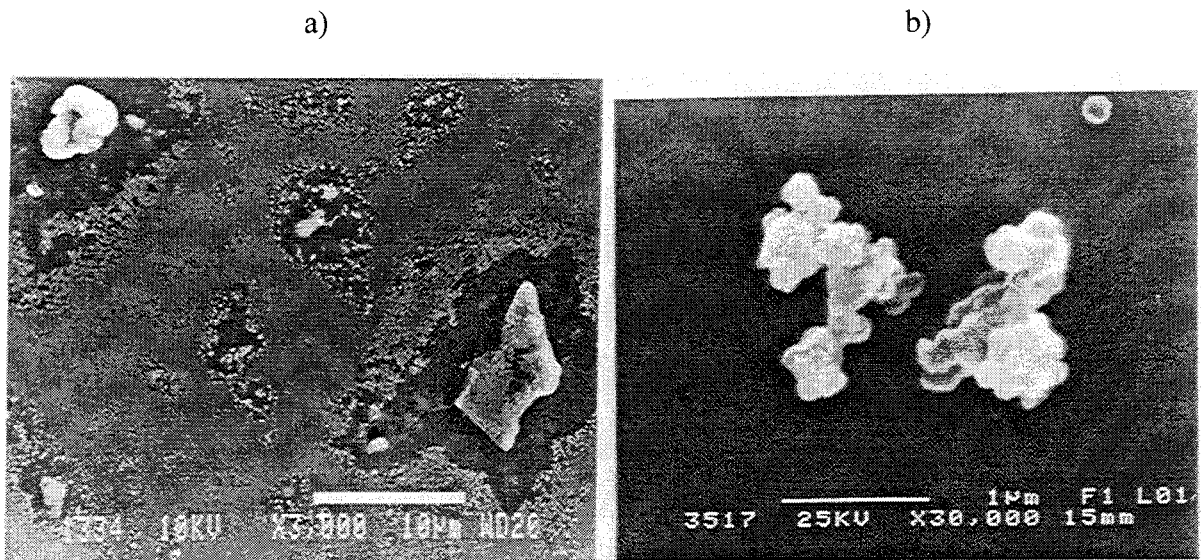


Figure 5-11. SEM micrographs of sample#1 colloid *concentrate* membrane filter. a) 3000 x magnification of fine material containing mainly Ca and little Si, (scale = 10 000 nm), b) 30 000 x magnification of an aggregation of smaller particles (350 nm) containing Ca and some Si, (scale = 1000 nm).

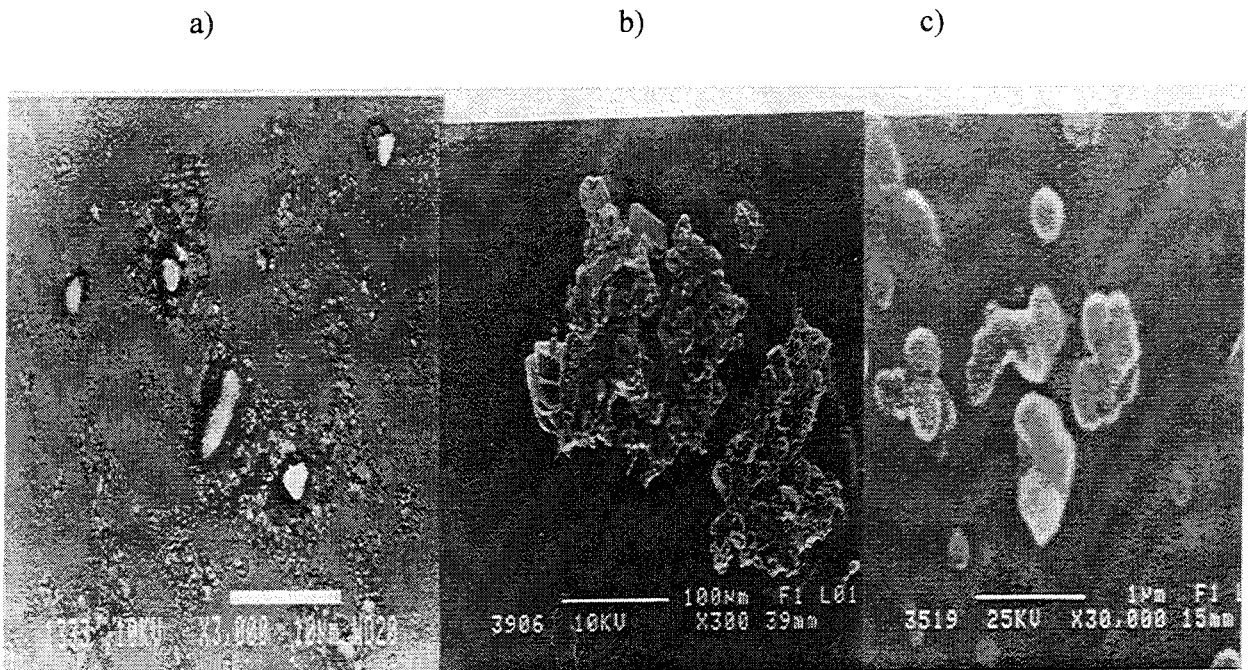


Figure 5-12. SEM micrographs of sample#1 *ultrafiltrate* membrane filter. a) 3000 x magnification of finely structured material containing mainly Ca and some Si, (scale = 10 000 nm), b) 300 x magnification of a larger aggregate (100 000 nm) consisting mainly of Ca and very little Si, (scale = 100 000 nm), c) 30 000 x magnification of small particles consisting of Si, (scale = 1000 nm).

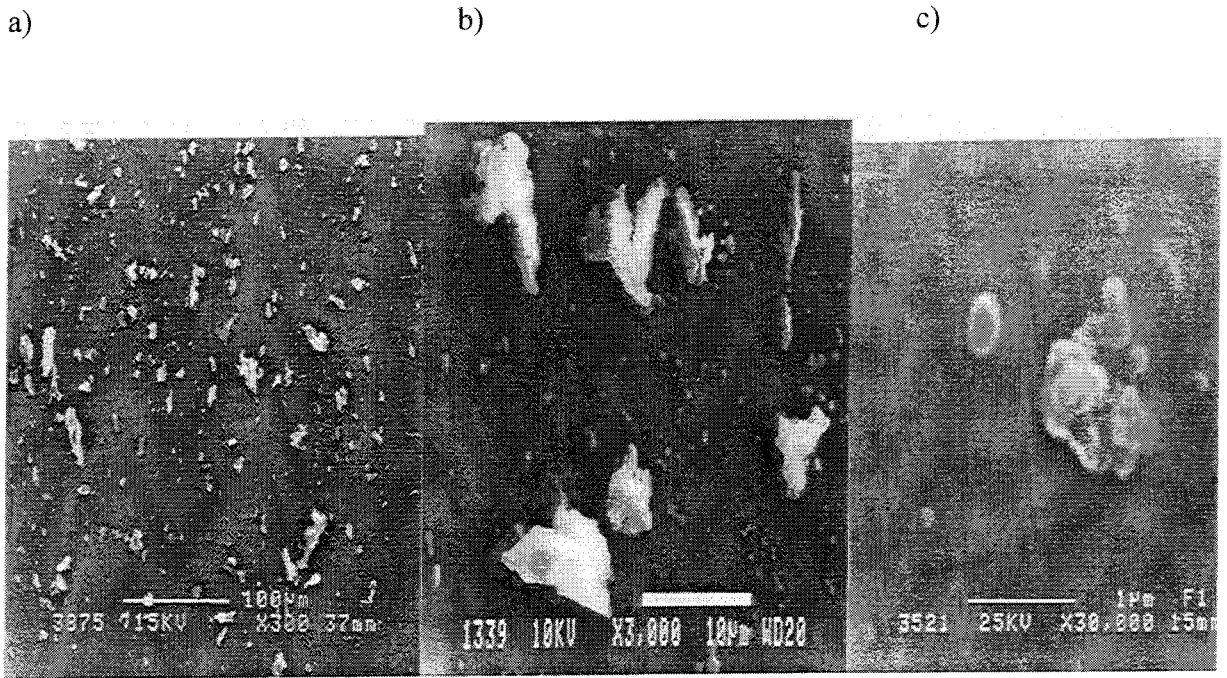


Figure 5-13. SEM micrographs of sample#2 colloid *concentrate* membrane filter. a) 100 x magnification, (scale = 100 000 nm) and b) 3000 x magnification of the fine and large particles (10 000 nm) containing mostly Si and Cl (scale = 10 000 nm), c) 30 000 x magnification of small Si particles (200 - 400nm) forming large aggregates (scale = 1000 nm).

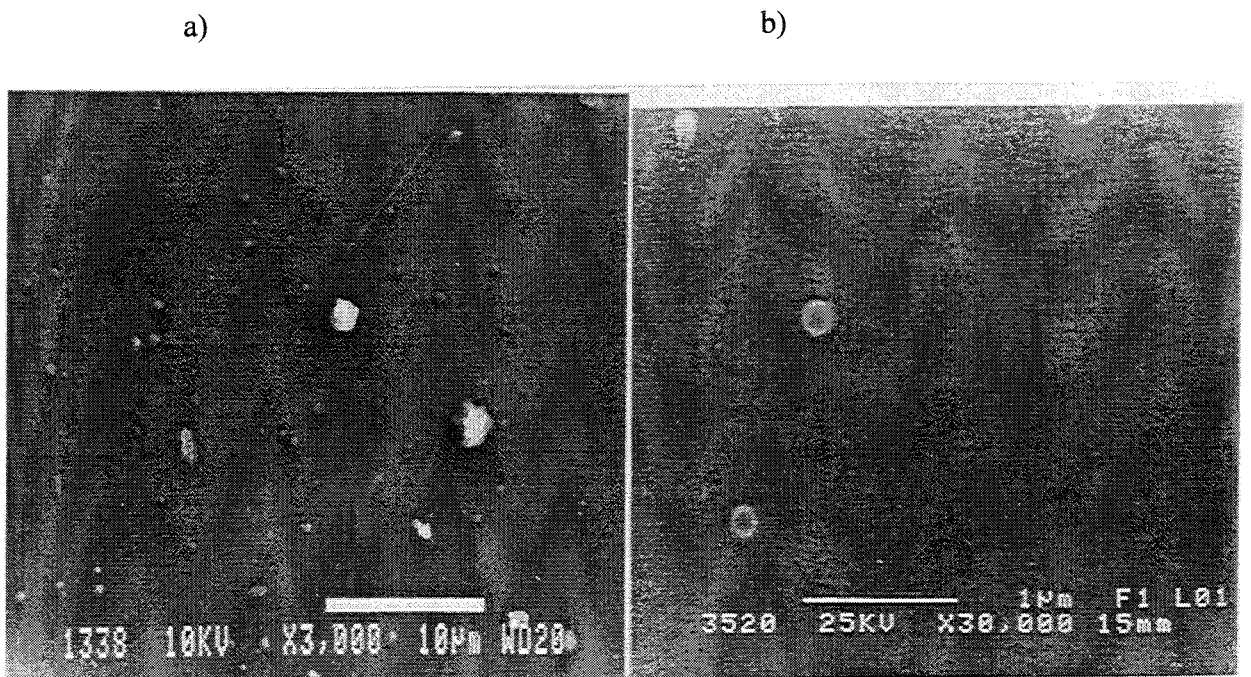


Figure 5-14. SEM micrographs of sample#2 *ultrafiltrate* membrane filter. a) 3000 x magnification of small Si particles and large Ca and Si particles; some large particles (10 000 nm) consisted of Na and Si, (scale = 10 000 nm) and b) 30 000 x magnification of small Si particles (scale = 1000 nm).

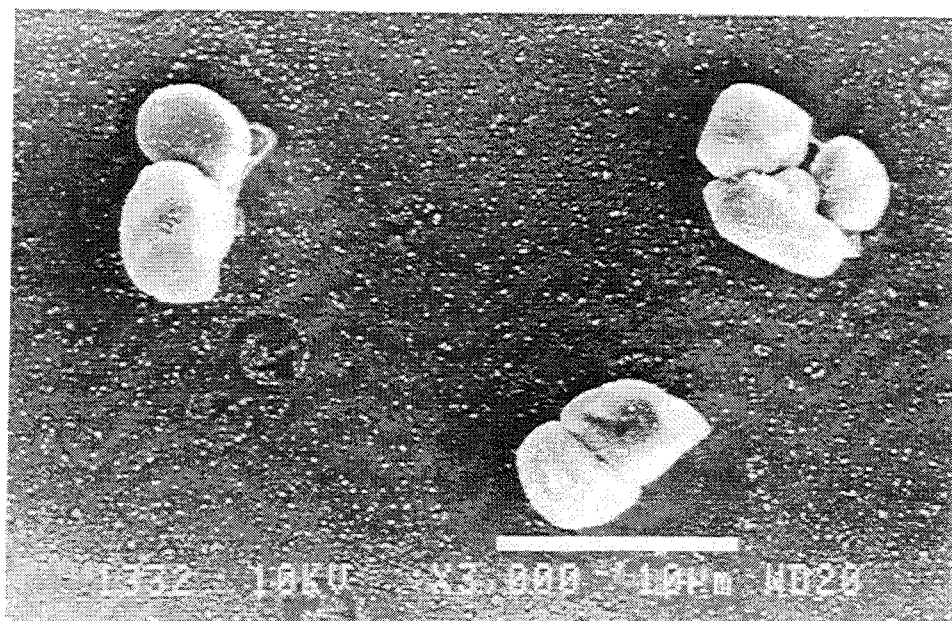


Figure 5-15. SEM micrographs of sample#1 pre-filtered groundwater membrane filter. The fine particles consist of Ca and Si, and the large ones, somewhat aggregated (4500 - 7500 nm), consist of NaCl (scale =10 000 nm).

Micrographs of the material retained on the sample#1 *concentrate* (Fig. 5-11) and *ultrafiltrate* (Fig. 5-12) membrane filters show both small and very large particles, as well as aggregates. EDS spectrum of the very finely structured material seen on both the *concentrate* and the *ultrafiltrate* micrographs (Fig. 5-11 a, Fig.5-12 a) showed only Ca with minor Si. This fine material, which is not seen on the sample#2 membranes, may have formed on the membrane due to too short a period of N₂ drying at the end of stirred-cell filtration leaving some solution to evaporate. The larger particles up to 10 000 nm in size found on the *concentrate* membrane filter generally contained either Ca and K or Ca, Al and Si or Ca, Si and K. Also on the *ultrafiltrate* membrane filter large particles up to several 1000 nm in size were found, as well as very large aggregates (Fig.5-12 b) some 100 000 nm in size. The EDS spectra for these particles showed only Ca peaks and a very tiny Si peak. The EDS spectrum obtained for the small particles in Fig.5-12 c gave just Si. The aggregated smaller particles about 350 nm in size in Fig.5-11 b contained mainly Ca with minor amounts of Si and K.

Micrographs of the material retained on the sample#2 *concentrate* (Fig. 5-13) and *ultrafiltrate* (Fig. 5-14) membrane filters show also the presence of both small and very large particles. The large particles, up to some 10 000 nm in size in Fig. 5-13 a and b, gave rise only to Si and Cl peaks in the EDS spectrum. As similar result was obtained for the smaller particles. Aggregation of smaller particles about 200-400 nm in size is shown in Fig. 5-13 c. According to the EDS, only Si was detected. Particle density on the *ultrafiltrate* membrane (Fig.5-14 a) was less and the size of particles smaller when compared to those of the *concentrate*. The large particles contained mainly Ca with minor Si, but also some needle-like 10 000 nm

long particles containing Na and Si were present. The small particles depicted in Fig.5-14 b contained Si, similar to those of the *concentrate* seen in Fig.5-13 c.

A micrograph, Figure 5-15, was also produced of the membrane filter produced of the prefiltered (1000 nm) groundwater (sample#1). Here the fine particles of about 200 nm in size contain only Ca and Si; the much larger aggregated ones from about 4500 nm to 7500 nm in size are NaCl particles. A few additional large particles containing Si and Mg with some Fe were also detected.

The large particles (1000-10 000 nm) in size found on the membranes prepared for SEM were additionally investigated with EDS. The results indicated a clear difference between the particles found on the membranes of the two groundwater samples. On the *concentrate* membrane of sample#1 the particles were composed mainly of Ca (ranging from about 70% to 80%) with some Si (ranging from 5% to 15%) and minor Al, Mg and Fe (ranging from 1% to 5%). On the *concentrate* membrane of sample#2 Si was the main component (90%) with minor Ca and Fe; occasionally Mg and Al were additionally present.

As the *ultrafiltrate* membranes also contained large particles, they were also examined using EDS. Similar differences to that found for the *concentrate* particle compositions were also evidenced for those found on the *ultrafiltrate* membranes, with the exception that the main components in sample#2 *ultrafiltrate* were somewhat changed; for Si from 70% to 85% and for Ca from 15% to 20%. Also, random particles containing Fe (40%-70%) and Si (15%-40%) as the main components with minor amounts of Ca, Al and Mg were present.

Two additional filter membranes were obtained for sample#1, one of the *concentrate* and one of the *ultrafiltrate*, both of which were washed with deionized water. These membranes were also investigated with SEM/EDS to analyse the large particles or aggregates found on the membranes. Results clearly showed that Ca was removed quite effectively. All the particles analysed on the *concentrate* membrane contained Si (23% - 77%) and minor amounts of Ca (1% - 16%). Additionally some Fe (0%-57%), Mg (0% - 65%) and Al (0% - 99%) was also present. Half of the analysed particles contained all 5 elements. Rather similar results were obtained for the *ultrafiltrate* membrane, except that Si was more clearly the main component in the analysed particles. The amount of Si ranged between 70% and 96%. Contents of the other elements ranged from 1% to about 25% for Al and Fe, and up to about 10% for Ca and Mg. Half of the analysed particles on this membrane also contained all 5 elements. (Note: The above given percentages are not exact values, but rather approximate to give some idea of the proportions of the elements present in the different particles.)

An association of small amounts of Cu with particles on the membranes could not be detected by SEM/EDS as the membranes were mounted on a holder containing Cu, which gave rise to background Cu peaks in every spectra measured. To compensate for this, additional filter membranes were prepared of both colloid *concentrates* in order to obtain more material on the membrane. These membranes were mounted on glass holders, thus allowing the detection of Cu, if present. The membranes were prepared by filtering 30 ml of *concentrate* and an equal amount of

deionized water. EDS revealed particles having the following compositions to be present on these membranes.

On the sample#1 *concentrate* membrane,

- Pure NaCl and CaCl₂ crystals and also NaCl crystals associated with Fe and Ca.
- Fairly pure grains containing Ca, Al, Si, and Mg were identified.
- Two kinds of mixed grains were present. One type consisting mainly Ca and Cl with minor S, Fe, Cu and Si, and another type having the same main components (Ca, Cl) with minor Fe, Cu, Si, and Al.
- Random particles giving rise to only Cu and sometimes to both Cu and minor Cl.

On the sample#2 *concentrate* membrane,

- Pure NaCl crystals as well as some associated with minor Ca.
- Random particles containing Fe with Ca and Cl, and another type containing mainly Si and Al with minor Ca and Cl.

For both *concentrates* one filter membrane (Amicon XM50) with the retained colloidal material was analysed by XRD to mineralogically characterise the colloids. Difficulties in the analysis arose from the background caused by the membrane which could conceal small peaks in the spectrum, especially when small amounts of material are present. Only halite (NaCl) crystals were detected, even though the membranes had been washed with deionized water when filtered. Two additional membrane filters, one for each *concentrate*, were prepared later with more material. These membranes were also washed with deionized water to remove soluble salts. On these membranes no halite was observed, the only crystalline material detected was cuprite (Cu₂O), which was present only on sample#1 *concentrate* filter.

5.3.3. Conclusion

E_h, pH and O₂: In the glove-box, measured E_h values were about 100 mV lower than the on-line values. In the glove-box measured dissolved oxygen values also show rather low oxygen content prevailed in the samples. Thus an indication of reducing conditions in the samples during filtration and transportation is obtained. The lower pH value (by 1.5 units) measured in the glove-box is due to the decrease in partial pressure of CO₂ in the groundwater, caused by the N₂-gas atmosphere, but contamination of atmospheric CO₂ may also be a cause and cannot be ruled out. Since the master variables have somewhat changed, artefacts due to on-site or off-site chemical reactions have most probably affected the original in-situ colloid content of the deep groundwater.

TOC: According to the TOC results (tables 4-1 and 5-3) the organic material present in the groundwater was either large or very small in size. The TOC results

of the *concentrates* and *ultrafiltrates* gives reason to believe that the majority of the organics proved to be either large in size or otherwise effectively retained by the 1000 nm pre-filter. Enrichment of organics in the size range of the colloid *concentrate* (2 nm-1000 nm) were not observed. This may be due to the small amounts of this organic size present in the groundwater, such that the precision of analytical method and the rather low organic concentration failed to show anything. The small-sized organics (< 2 nm) composed only about 10% of the total, but this value is in good agreement with that obtained for the analysed humic material (0.01-0.02 mg/L) in section 5.4.

Element concentrations: The calculated element concentrations obtained from the colloids for sample#1 and sample#2 (Table 5-4) can only give indication of possible enrichment. The concentration factors were rather low for both samples and the chemical analysis of different solution fractions do not give values accurate enough to obtain real enrichment, because calculated values fall within precision limits. These results were calculated for comparison purposes. To obtain quantitative results on elements associated with colloids the concentration factor should be increased, but care should be taken to avoid large concentration gradients. Sequential concentrations or dia-ultrafiltrations with simultaneous size fractionation could be applied. Also additional flat-bed membrane filters having differing pore sizes could be produced only for quantitative elemental analysis of the material retained on the filters.

SEM/EDS: SEM/EDS investigations were performed on specimens prepared of the membrane filters produced from both the *concentrates* and the *ultrafiltrates* of sample#1 and sample#2. Both small and large colloids were found on all the examined membrane filters, but the incidence of colloidal particles on the specimens for the *ultrafiltrates* was clearly less than on those of the *concentrates*. The specimens of both *concentrates* and *ultrafiltrates* could bear colloids as large as 10 000 nm and aggregates of 100 000 nm in size, and even a few larger ones. The analysed element compositions of the particles of the corresponding *concentrate* and *ultrafiltrate* specimens gave quite uniform results.

The large particles on the *concentrate* specimen of sample#1 contained about 70-80 % of Ca, 5-15 % of Si and occasionally some percent of Al, Mg or Fe. K was also detected in some particles. For the small sized colloids on the specimen only the major components, Ca and Si could be identified as the total amount of colloidal material on the specimen was quite small.

The *concentrate* specimen of sample#2 contained also large particles, which on analysis gave the main component to be Si (about 90%), associated with minor Ca, Fe, Cl and occasionally also Mg and Al. As the total amount of colloidal material also on this specimen was small, only the major component in the small sized colloids could be detected, giving merely Si.

The extended EDS investigation of additional filter membranes bearing more colloidal material revealed the presence of NaCl and CaCl₂ crystals, which upon more thorough washing with deionized water disappeared. Other types of grains found on the membrane specimen consisted of either fairly pure grains containing

Ca, Al, Si and Mg, or some type of mixed grains consisting Ca and Cl with some S, Fe, Cu, Si and Al, or occasional random particles containing merely Cu and sometimes additional Cl.

No evidence of distinct microbial populations was obtained from the SEM micrographs. A very rough estimate of the amount of colloidal particles in the sample#2 was obtained based on counting the colloidal particles on one micrograph. All particles greater than 1000 nm were omitted and only particles greater than about 200 nm could be counted. Thus obtained particle concentration in the groundwater was about $5 \cdot 10^8$ particles/L.

XRD: XRD of the membrane filters for both *concentrates* revealed presence of halite (NaCl) crystals only. All other material on the membrane filters appeared to be amorphous in nature. Two additional filter membranes, which were washed more thoroughly with deionized water, did not give any result of halite. The only crystalline material found was cuprite (CuO_2) and only on sample#1 concentrate.

General comments: The obtained results indicate that in the course of the first colloid sampling some oxygen contamination has probably taken place during groundwater pumping, collection or concentration. This is indicated by the low iron concentration obtained for the sample#1 *concentrate* and *ultrafiltrate* compared to that obtained for the original groundwater. The oxidised and precipitated iron has probably been retained by the pre-filter resulting in low iron content in the prefiltered sample and hence the obtained *concentrate* and *ultrafiltrate*. The large colloidal particles seen on the examined membrane filters for sample#1, mainly containing Ca, compared to those for sample#2, mainly containing Si, also suggest probable contamination from atmospheric gases. Generally the sampling conditions for the second sample are regarded more favourable and hence more representative.

The question of particle formation in the colloid samples cannot be ignored as the presence of oversized particles on both the *concentrate* and *ultrafiltrate* membrane filters were evidenced. The general mechanisms of colloid formation has already been discussed (section 1) but more detailed information is found in Loughnan, (1969); Yariv and Cross, (1979) and Brookins, (1987). The lack of crystallinity of the colloidal material found in the samples may suggest recent formation and may therefore also be an artefact. But on the other hand, amorphous phases are also present in the hydrospheric environment. Dissolved metallic cations occur in the hydrospheric constituents either in the form of hydrated charged ions or complexed with organic or inorganic ligands. An increase in the concentration of anions such as silica, phosphate, or carbonate or a change at the pH of the solution may result in the formation of insoluble species. A change in the Eh of the system may lead to the decomposition of the organic ligand and the oxidation of the metallic cation with the formation of an insoluble species. If the growth of crystalline particles is prevented a colloid dispersion may form.

The commonly found silica in the samples has a solubility which barely changes in the pH range 0-9 found in the groundwaters. There is almost no influence of pH, salinity or temperature on silica concentrations. The presence of certain metallic cations, such as Al^{3+} and Fe^{3+} , and organic ions, will affect Si solubility, as well as the presence of

F^- , which complex silicon by forming the soluble co-ordination ion SiF_2^{2-} . Colloidal silica is precipitated by evaporation, or by coprecipitation with other colloids, or by means of fairly concentrated solutions of electrolytes. The extreme insolubility of silica is well known (Figure 5-16a). Aluminium is also known to be very insoluble over much of the natural pH range (Figure 5-16b).

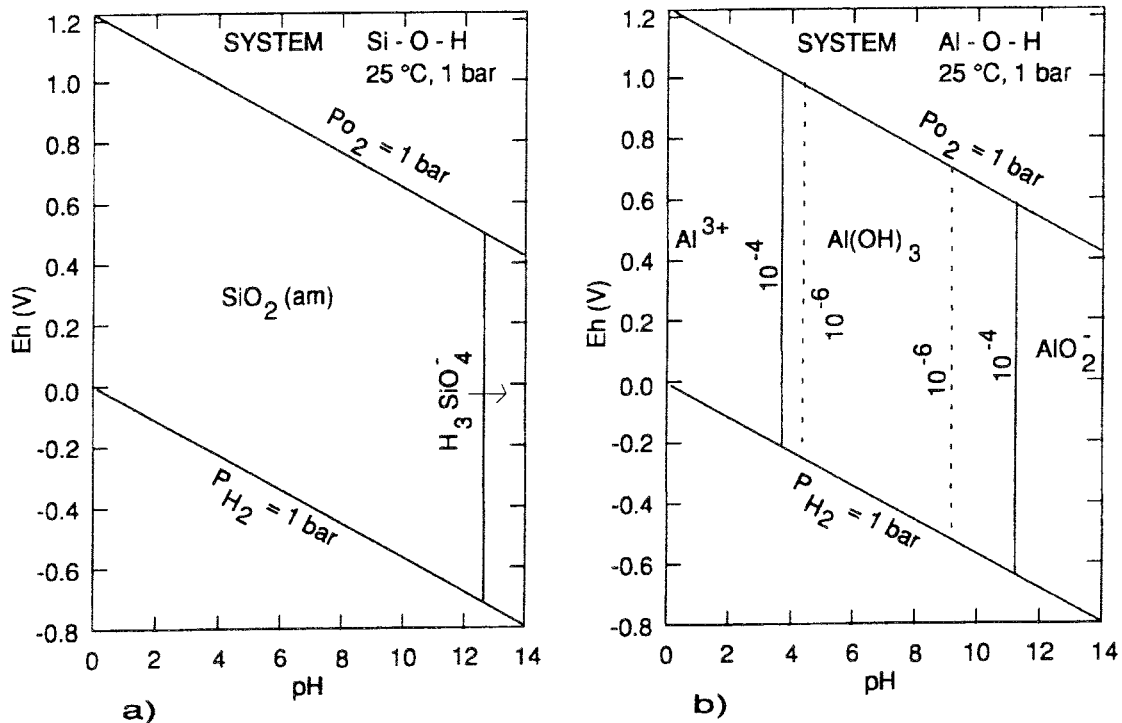


Figure 5-16. a) Eh-pH diagram for part of the Si-O-H system. The assumed activity of the dissolved $Si=10^{-3}$. b) Eh-pH diagram for part of the Al-O-H system. The assumed activity of the dissolved $Al=10^{-4}, -6$ (Brookins, 1987).

The transport of Al in natural waters (pH=4-9) occurs either as dissolved complexed ions or as colloid solutions and suspensions, e.g. gibbsite ($Al_2O_3 \cdot 3H_2O$) crystals near 100 nm in diameter have considerable physical and chemical stability. Hydroxide, phosphate and silicate anions are strong precipitating agents for aluminium. When silica is present at sufficient concentrations, aluminium solubility is generally considerably decreased owing to the accelerated polymerisation of aluminium hydroxide leading to rapid precipitation of poorly crystalline clay minerals. The presence of fluoride is strong complexes of aluminium and fluoride are formed. The complexing action of F is strong enough to have considerable influence on the form of dissolved Al even when very little F is present. In natural waters containing even tenths of a milligram per litre of F, Al would probably be complexed (AlF_2^+ , AlF_3), provided that the total Al is considerably less than the total F (Yariv and Cross 1979).

Cationic Mg (Mg^{2+}) will normally be the predominant form of magnesium in solution in natural water. The magnesium found in the samples may be strongly adsorbed by clay minerals and other surfaces having exchange sites. Coprecipitation of Mg with

calcite is easily occurred, since Mg^{2+} can fit into the calcite crystal structure. Due to the similar crystal systems of $MgCO_3$ and $CaCO_3$ they can form an isomorphous series of magnesian calcites, $(Mg_xCa_{1-x})CO_3$.

As a result of pressure change in the sampled groundwater, calcite precipitation due to the escape of dissolved CO_2 is unavoidable. In addition, contamination of atmospheric O_2 will oxidise iron and cause colloidal iron to be formed. Oxidation of iron is catalysed by clay minerals, but on the other hand organic materials that form stable complexes with Fe(II) may prevent the oxidation. Formation of calcite most probably induces coprecipitation of other phases and elements resulting in particles of mixed compositions. The cross-flow filtration procedures may also induce aggregation of polymerised material and hence coprecipitation with Ca resulting in formation of mixed particles.

Based on these considerations it seems quite probable that the oversized particles seen on the SEM micrographs are due to some artefact processes, which screen the original in-situ colloidal material. The existing in situ original colloids present in the deep groundwater may have become masked on the flat-bed membranes due to the promotion of particle formation or growth. Thus, the original colloids may have coprecipitated with the formed material leaving no evidence of their original character and composition. If in-situ colloids are considered, there is no exact way of estimating their concentration with the kind of groundwater pumping and sampling systems used in this study, especially, as the groundwater sample was withdrawn from a depth of more than 600m. The foremost problem is calcite formation, which most probably induces formation and aggregation of other particles, resulting in increased amounts of the measured colloids.

5.4. Method#4; Organic material

5.4.1. Background and method

Humic and fulvic acids, which could comprise up to 15% of the dissolved organic carbon in groundwater (Malcolm, 1991), generally form strong complexes with highly charged metal ions (e.g. the actinides). The formation of metal-humic complexes might increase the solubility of radionuclides, thus affecting their mobilisation. The "transporting capacity" has to be estimated from analysis of composition and concentrations of the organic material in the groundwater at the relevant repository depth.

The humic fraction of the dissolved organic carbon (DOC) in the groundwater from Olkiluoto was collected by the DEAE-method, previously used for isolation of aquatic humic substances from deep groundwater (Allard et al., 1990; Pettersson et al., 1990). The humic substances (HS) are adsorbed on a weak anion exchanger (DiEthylAminoEthyl-cellulose, DEAE-cellulose) without any pH adjustment or other conditioning of the groundwater sample. The procedure allows a collection on-line, without direct air contact (disturbance of changing Eh and pH conditions are avoided). The use of alternate methods (e.g. hydrophobic adsorption on XAD-8 at low pH) is difficult to

perform on-line in the field and would completely change the original character of the sample (acidification of the water to pH 2 is required).

The sampling column was installed during one sampling trip (September 25, 1992). The sampling was conducted by pumping water (750 l) through a filter with granulated DEAE-cellulose (Sample#1). Additional batch samples were taken (DEAE-cellulose added to 2.5 and 4 l of water, respectively).

5.4.2. Results

The amount of humic substances isolated was estimated by UV-measurement of the eluate from the DEAE-resin (at 250 and 365 nm). Only 7 mg humics were collected with the on-line procedure, despite the relatively high reported TOC-content in the groundwater (4- 4.7 mg/l) and the large water volume processed. The batch sampling resulted in minor amounts (not quantified).

The small amount isolated allowed only a few characterisation procedures. The UV-spectrum of the sample was typical of a humic substance (Figure 5-17).

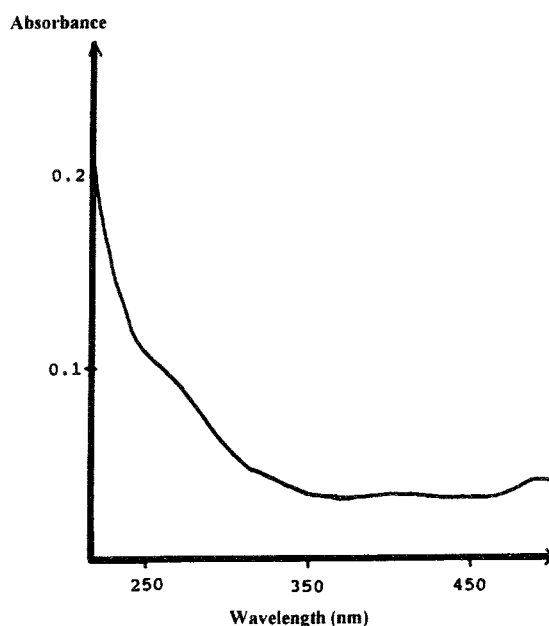


Figure 5-17. The UV-spectrum showing the absorbance of the humic fraction for Sample#1 at different wavelengths .

Gel filtration, in which the molecules are separated according to size, indicated a heterogeneous character of the sample. The retention time is inversely related to the size of the molecules. Thus, the larger -sized molecules will pass the column in a shorter time than will the smaller ones. A distinct peak indicating a low molecular weight fraction was observed. The molecular weight distribution of the sample#1 (Table 5-5) was calculated by using reference substances (polystyrene sulphonates) of known molecular weight. The average molecular weights (M_n and M_w) fall within the

range typical for groundwater humic substances, being largely fulvic acids (Pettersson, 1992).

Table 5-5. Molecular weight distribution (average molecular weights) for the humic fraction

M_n	M_w	M_w/M_n
900	1200	1.33

5.4.3. Conclusion

The isolation of humic substances from the groundwater resulted in a minor amount of humics, corresponding to a original concentration of the order 0.01-0.02 mg/l (10-20 ppb) of HA (7 mg from 750 l). Groundwaters often have a humic fraction corresponding to 5-15 % of the DOC (see e.g. Malcolm, 1991). Thus, a DOC-concentration in the range 0.04-0.4 mg/l would be expected (humic substances contain 50 % C) rather than the high TOC values of 4.0 and 4.7 mg/L reported for analyses of the groundwater (see Table 4-1).

The small yield could be explained in several ways:

- o The groundwater volume passing the filter was overestimated due to clogging of the filter.
- o The efficiency in the first recovery step adsorption on DEAE-cellulose was considerably less than expected (generally above 50 %; usually around 90-95 %). The DEAE-cellulose in the filter tube contained a large amount of iron; this might have disturbed the adsorption of humics to the resin, thus resulting in a reduced efficiency
- o The reported TOC-value may be overestimated (due to artefacts discussed in section 4.3 since deep groundwater often has a TOC concentration of less than 2 mg/L (e.g. Pettersson et al., 1990).

6. Comparison of results from the different techniques

6.1. Methods

To compare the results from the different methods becomes a complex task despite the fact that the sampled groundwaters were the same, the colloid sampling methods, method of analysis, the sampling conditions and, cut off-limits etc. differ (Table 6-1).

Table 6-1. Comparison of the three colloid sampling methods.

	Method#1 Ordinary filtration	Method#2 Inert filtration	Method#3 Ultrafiltration
Condition for filtering	- on-site - atmospheric	- on-site - N ₂ atmosphere	- on-site/off-site - N ₂ atmosphere
Filtering system	Fig. 5-1 - consecutive flat-bed filters (450 nm, 220 nm, 30 nm or 20 nm)	Fig. 5-4 - prefilter + individual flat-bed filters (2500 nm, 400 nm, 200 nm, 50 nm)	Fig. 5-8 - prefilter + tangential-flow filter (1000 nm, 2 nm)
Prefilter	none	2500 nm flat-bed filter	1000 nm Millipore Cartridge
Particle fraction > 1000 nm	collected on the first 450 nm filter (with larger colloids 450nm - 1000 nm) - analysed	collected on the 2500 nm prefilter and partly on the 400 nm filter (with larger colloids) - 2500 nm not analysed - 400 nm analysed	retained by the 1000 nm prefilter - not analysed
Colloid fractions: (not size calibrated)	20 nm - >450 nm	50 nm - 2500 nm	2 nm - 1000 nm
- Collection of colloids on filters	yes	yes	no (colloids in concentrate)
- Collection of filtrates	yes	no	yes
Additional steps			Filtration of colloid concentrate and ultrafiltrate on flat-bed filters (3 nm)

But since one of the main tasks of this project was to compare the results from the different methods, the following strategy was established:

- a) Establish *cut off-limits* for the different methods
- b) Calculate the *phases* associated with the measured elements
- c) *Comparison* of the results
- d) Estimate the *precision* and *accuracy* of the sampling methods

Cut off-limits: The maximum cut-off limit using inert filtration and ultrafiltration is defined by the largest filter (2500nm respective 1000nm). For ordinary filtration, as no prefilter was used, the largest filter 450nm is therefore regarded as a "prefilter" and a maximum cut-off limit for the method. The element analyses of this filter are omitted in further comparison.

Phase calculations: The measured elements are assumed to be associated with the following mineral phases which have been identified or calculated to be in equilibrium with the groundwater in the borehole OL-KR1 (Pitkänen et al. 1992); Ca with calcite (calcium carbonate), Fe with goethite (iron hydroxide), S with pyrite (iron sulfide), Si with chalcedony (silica oxide), Mn with pyrolusite (manganese oxide; so far none has been observed in the borehole) and Al with K-Mg-illite (clay mineral). The SEM/EDS measurements often indicated the colloids to contain a mixture of different elements associated with Ca and Si. Here the chosen mineral phases were, however, the best approximates until further detailed data on the mineral phases of the colloids are available.

Comparison: In order to be able to compare the results a normalisation of the results of each individual methods must be performed so that the results reflect the colloid concentration in the range 1 - 1000nm. For normalisation of the results the following equation is used:

$$\text{Eq\#1: } [Coll] = \frac{PhaseSum(ppb)}{(Max - Min)FilterPoreSize(nm)} \bullet (1000 - 1)nm$$

Precision and accuracy: The reliability of the sampling methods may be evaluated in terms of precision and accuracy. Precision is a measure of the reproducibility of replicated determinations without regard to how close their average is to true value. Accuracy deals with closeness of the measured value to a true value (Rose et al. 1991). The few observations in combination with no separate test of the precision or accuracy of the individual methods make this comparison extremely difficult. By definition, when the precision is higher, the less the difference is between sample#1 and sample#2. The true colloid content is not known but it is believed to be low. By definition the lower the value the better the accuracy. Knowing these limitations, the following equations which express the deviation (Dev) of precision and accuracy may be written:

$$\text{Eq\#2: } PrecisionDev = AbsoluteValue ([Coll]Sample\#1 - [Coll]Sample\#2)$$

$$\text{Eq\#3: } AccuracyDev = \frac{[Coll]Sample\#1 + [Coll]Sample\#2}{2}$$

6.2. Results

Table 6-2 gives the gathered results of the element analysis (Al, Ca, Fe, Mn, Si and S) and the calculated colloid concentrations assuming association of a distinct phase with each element. The normalised results by application of Equation#1 permits a certain kind of comparison of the different methods in a range 1-1000nm. For the ultrafiltration the results are uncertain as discussed earlier (5.3.2). Especially for Ca, as the result is based on analysis of macro amounts in solution and the analysis results in the solution can only be given with a precision of 100 ppm. For methods#1 and #2 where micro amounts of material on the filters have been analysed this kind of calculations will reflect the differences of the methods. Despite the problems discussed above a systematic treatment of the results have been applied. The results of the calculated colloid concentrations for all the methods including calcite are shown graphically in Figure 6-1. The results of the precision and accuracy calculations including calcite are shown in Figure 6-2. The calculated colloid results omitting calcite for all of the methods are given in the last row of Table 6-2 and discussed in more detail in chapter 6.3 and 7.

Table 6-2. The results of the element analyses (Al, Ca, Fe, Mn, Si and S) and the calculated colloid concentrations assuming the colloids form distinct phases. The colloid concentrations are compared by using Equation#1. The results are shown for: Method#1 = Ordinary filtration, Method#2 = Inert filtration and Method#3 = Ultrafiltration. The question mark (?) indicates the uncertainty concerning the Ca association with colloidal calcite. The (-) indicates that the value was not taken into account. The n.a. indicates that the element was not analysed. The detection limit of a particular element in the tables (5-1a, 5-2a and 5-4) has been used as a lower value for that element.

Filter analyses:	Method#1 <i>Ordinary filtration</i> Sample#1 (ppb)	Method#1 <i>Ordinary filtration</i> Sample#2 (ppb)	Method#2 <i>Inert filtration</i> Sample#1 (ppb)	Method#2 <i>Inert filtration</i> Sample#2 (ppb)	Method#3 <i>Ultra- filtration</i> Sample#1 (ppb)	Method#3 <i>Ultra- filtration</i> Sample#2 (ppb)
Filter Pore Size nm	20 - 450	20 - 450	50 - 2500	50 - 2500	2 - 1000	2-1000
Element analysis:						
Al	1.9	4.7	16.8	1.8	-	4.9
Ca	2047	2184	952.4	460.8	11400?	8200?
Fe	20.7	13	23.4	5.4	14.8	5.7
Mn	0.38	0.3	0.1	0.1	0.7	0.7
Si	18.7	27.9	15.1	9.7	4.5	4.1
S	20	20	15.5	5.7	n.a.	n.a.
<i>Sum</i>	<i>2108.7</i>	<i>2249.9</i>	<i>1023.3</i>	<i>483.5</i>	<i>11420?</i>	<i>8215.4?</i>
Calculated colloid phases:						
Ca, Calcite CaCO_3	5110	5452	2378	1150	28460?	20471?
Fe, amorphous Goethite Fe(OH)_3	40	25	45	10	28	11
S, Pyrite FeS_2	43	43	33	12	n.a.	n.a.
Si, Chalcedony SiO_2	40	60	32	21	10	9
Mn Pyrolusite MnO_2	0.6	0.5	0.2	0.2	1.1	1.1
Al, K-Mg-Illite (Clay) $\text{K}_0.6\text{Mg}_0.25\text{Al}_2.3\text{Si}_3.5\text{O}_{10}(\text{OH})_2$	27	67	239	26	-	70
<i>Phase Sum</i>	<i>5261</i>	<i>5647</i>	<i>2727</i>	<i>1219</i>	<i>28499?</i>	<i>20562?</i>
Comparison: [Coll] size 1-1000nm Eq#1:						
Ca, Calcite CaCO_3	11872	12666	970	469	28460?	20471?
Fe, amorphous Goethite Fe(OH)_3	93	58	18	4	28	11
S, Pyrite FeS_2	100	100	13	5	n.a.	n.a.
Si, Chalcedony SiO_2	93	139	13	9	10	9
Mn Pyrolusite MnO_2	1.4	1.2	0.1	0.1	1.1	1.1
Al, K-Mg-Illite (Clay) $\text{K}_0.6\text{Mg}_0.25\text{Al}_2.3\text{Si}_3.5\text{O}_{10}(\text{OH})_2$	63	156	97	11	-	70
<i>Sum</i>	<i>12223</i>	<i>13119</i>	<i>1112</i>	<i>497</i>	<i>28499?</i>	<i>20562?</i>
Sum omitting Calcite precipitation	350	454	142	28	39	91

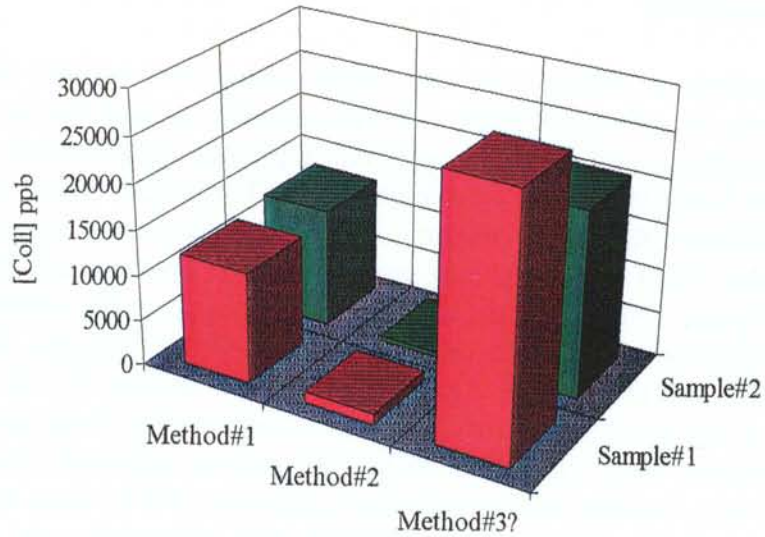


Figure 6-1. The results of the calculated colloid concentrations (Sum in table 6-2) including the contribution from calcite for sample#1 and #2 for the different methods: Method#1 = Ordinary filtration, Method#2 = Inert filtration and Method#3 = Ultrafiltration. The question mark (?) indicates the uncertainty concerning the Ca association with colloidal calcite in Ultrafiltration.

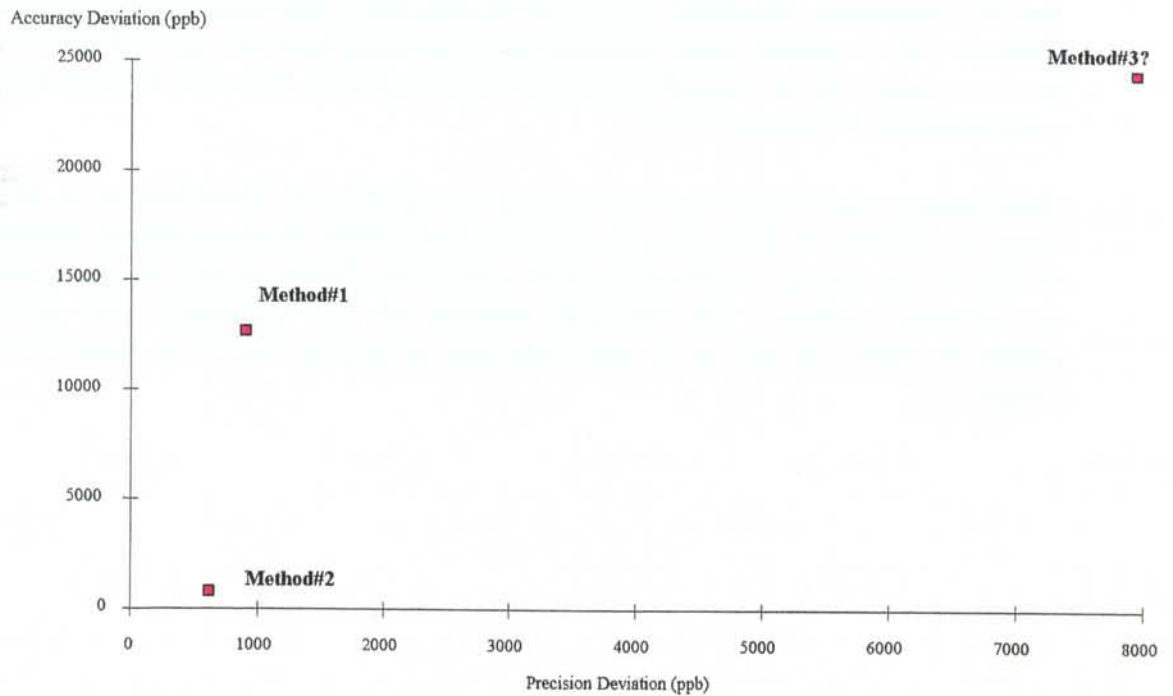


Figure 6-2. The results of precision- and accuracy-deviation calculations (Equation#2 and#3) for the different methods: Method#1 = Ordinary filtration, Method#2 = Inert filtration and Method#3 = Ultrafiltration. The higher the value the lower the accuracy or precision. The question mark (?) indicates the uncertainty concerning the Ca association with colloidal calcite in Ultrafiltration.

6.3. Conclusion

The comparison in Table 6-2 showed a high loading from colloids containing Ca and Fe, especially in ordinary filtration. The risk of calcite precipitation in connection with colloid sampling is well known from Swedish granitic ground waters containing high TDS (Total Dissolved Solids) (Laaksoharju and Degueldre, 1994). Smaller pore size filters < 200 nm often show clogging tendencies during the sampling. An attempt to minimise the risk of calcite and iron precipitation was tried in inert- and ultra-filtration by using N₂-gas. The calcite and iron precipitation is generally a factor 7 lower in the inert filtration compared to the ordinary filtration without N₂-gas. The effect is also seen in ultra-filtration which show a lower iron content in the second sample compared to the result from inert-filtration. The exact effect from calcite precipitation in ultra-filtration is not known but SEM/EDS analyses indicated calcite formation on the membranes. On-line measurements by Ledin et al. (1993) using the PCS-technique (Photon correlation spectroscopy) indicated that particulate iron phases are also formed relatively fast in groundwater samples in contact with N₂-atmosphere. The small amount of oxygen resulting from diffusion and leakage seemed to be sufficient to oxidise the iron. The N₂-atmosphere only seem to slow down the reactions but cannot prevent oxidation during a longer period of time. This may be a risk in ultra-filtration which may had oxygen diffusion despite the used ultra pure (quality 6.0) N₂-gas for several days and the measured reducing redox potentials. The results indicate that iron hydroxide and calcite formation was not totally prevented in any of the used methods. The Fe results show that there was an overall trend of a general decrease in the iron content for the second sampling, which may have been due to lower oxygen contamination of the groundwater.

Geochemical modelling using the computer code PHREEQE (Parkhurst et. al. 1986) using the CHEMVAL2 database to simulate the different chemical systems obtained during in-situ, at-line, on-site and off-site conditions during colloid sampling using the different methods. The indicated changes of iron hydroxide- and calcite-saturation indexes as well as the partial pressure of carbon dioxide are demonstrated (Figure 6-3).

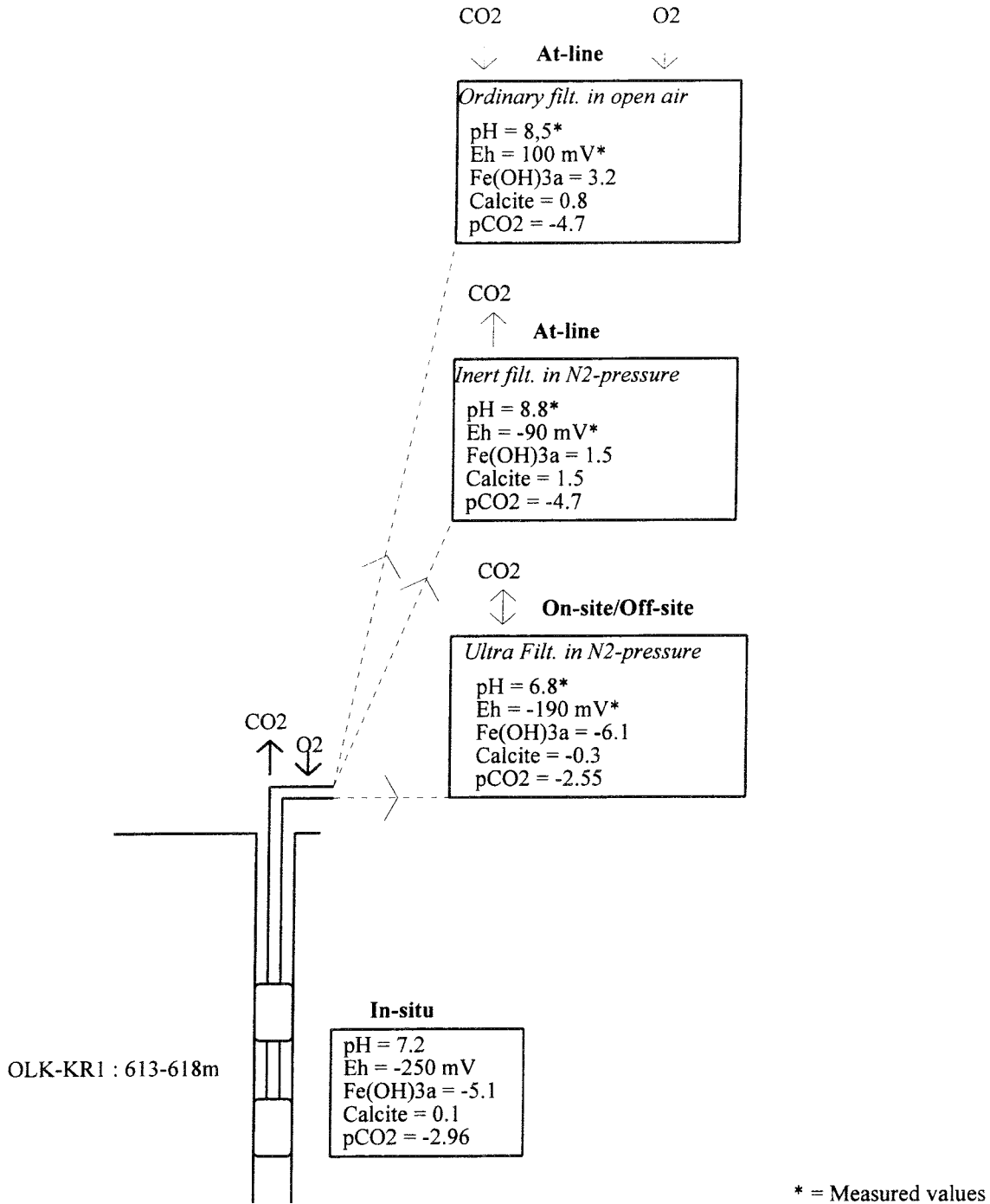


Figure 6-3. Modelling simulations (PHREEQE) of the different chemical systems obtained during colloid sampling during; in-situ, at-line, on-site and off-site conditions for the water samples. The chemical system is constantly changing, depending on de-compression, loss or uptake of carbon dioxide and oxygen contamination. The calculations are only indicative. The assumed in-situ conditions are; Eh = -200 mV and saturation index for calcite = 0. Other assumptions give different results (see Pitkänen et. al., 1992). The measured on-line conditions (flow trough cell) are; Eh = -90...-65 mV and pH= 8.4...8.6. Positive values for the saturation indexes (SI) indicate risk for precipitation, negative values indicate possible dissolution. Fe(OH)_{3a} = amorphous iron hydroxide, pCO₂ = partial pressure of carbon dioxide (log bar).

In the sampling procedure the chemical master variables Eh and pH change and hence affect the overall chemical system and causing precipitation (positive saturation indexes) or dissolution (negative saturation indexes) for different phases. The calculations indicate a risk of calcite precipitation as well as iron precipitation in ordinary- and the inert filtration. In the ultra-filtration the risk is lower. The calculations are in good agreement with the observed results except for the results for ultrafiltration since calcite precipitants were observed. The long sampling time may have change the system gradually and in a different way than modelled. The risk of calcite precipitation in the inert- and ultrafiltration methods could have been further minimised if a mixture of CO₂ and N₂ had been used to simulate the prevailing in-situ partial pressure of carbon dioxide. The calculations demonstrate once again the difficulties in colloid sampling since small changes in the chemical system are strongly affecting the colloid concentration ppb levels.

The element analyses and hence the amount of calculated Si, Al and S containing colloids (Table 6-2) is somewhat higher the ordinary filtration compared with inert filtration. Indications of sulphur association with the colloidal material were also obtained from EDS results in the ultrafiltration method. High fluctuations were observed for the aluminium and silica content, which might have been due to both contamination or analytical problems. High contents could be seen especially for silica, SiO₂, using the ordinary filtration method, as well as for aluminium using the inert filtration method in sample#1. The high silica for the ordinary filtration method might be due to contamination effects from deionized water used to wet the filters prior to filtration. According to analyses performed in connection with the inert filtration method, the amounts of silica from distilled water could be as high as 0.04 mg/L (chalcedony, SiO₂) and thus some 0.008 mg/L (0.1 L/filter) could have been added to the filters. The results may have been affected by some other silica source or by possible analytical uncertainties. The high aluminium content for samples in the inert filtration method may well be from analytical uncertainties known for that element when using X-ray fluorescence. The overall content of Mn in the colloid fractions was low for all filtration methods.

The calculated colloid concentration in Table 6-2 for ordinary filtration showed the highest colloid concentrations but little difference between the first and the second sample (~12000 - 13000 ppb). The inert filtration gave higher colloid content in the first sample than in the second sample (~1000 - 500 ppb). The ordinary filtration suggests a possible higher value in the first sample than in the second sample (~29000? - 21000? ppb). The results are therefore inconsistent, one method suggests stable, the other two decreasing colloid content during the sampling period. It is important to note that the methods suggest a maximum difference by a factor of 58 in colloid concentration measured on a similar groundwater. The inert-filtration method showed a considerable lower colloid content compared to the other methods. This is believed to be due to the N₂-gas used in combination with a short sampling time. Since almost all the elements associated with colloids were increased in the ordinary filtration, coprecipitation with calcite is suggested as a possible mechanism. The general variation is probably due to many reasons; different artefact sensibility of the different methods and different resolution of the chemical analyses etc. The result for the ultrafiltration is questionable because of the discussed uncertainty of the Ca

analysis. The accuracy and the precision test results showed in Figure 6-2 is highest for inert filtration. Ordinary filtration showed high precision but low accuracy. The results from the precision and accuracy test is only approximate since only two samples per method were considered.

7. Calculated in-situ colloid concentrations

The in-situ colloid concentration is not known, but may be estimated and calculated from the results. As the many possible artefacts discussed in the previous chapter may mask or bias the original in-situ colloid content, this effect must therefore be considered. The major artefact is calcite precipitation which may cause coprecipitation of other elements. The degree of this process is unknown, as well as the effect from changes in the redox system. The only straight-forward way to make a conservative in-situ colloid estimation is to omit the colloid loading resulting from calcite precipitation. This calculated effect is shown in Table 6-2 and in Figure 7-1.

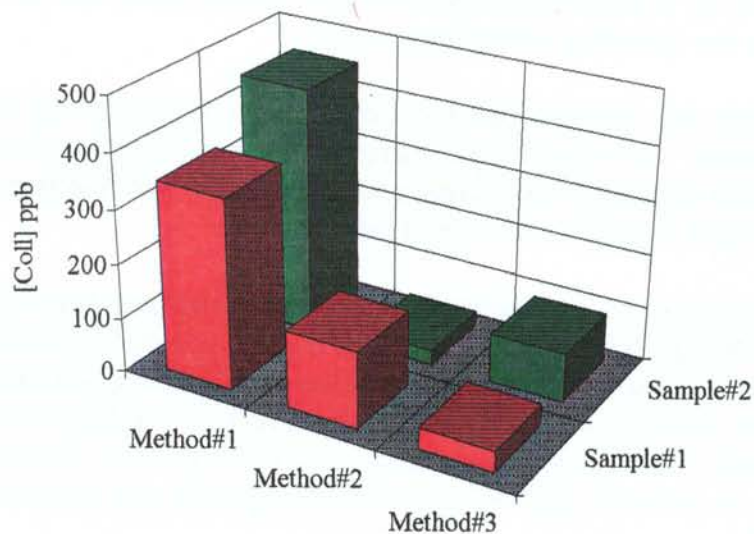


Figure 7-1. The results of the calculated colloid concentrations omitting the effect from calcite precipitation for sample#1 and #2 for the different methods: Method#1 = Ordinary filtration, Method#2 = Inert filtration and Method#3 = Ultra-filtration.

Based on the chosen inorganic phases (clay minerals, silica, goethite and magnesium oxide) the estimated inorganic colloid content in the size range 1-1000 nm in Olkiluoto groundwater is 184 ± 177 ppb. The organic substances were analysed to give a concentration around 10 ppb. The bacterial content was not measured, but no distinct evidence of bacterial population was observed on the SEM micrographs, giving reason to believe that their concentration is low.

Some similarities can be found with the Grimsel colloid experiment (Degueudre et al. 1990) and this experiment. In Grimsel experiment various colloid sampling methods

were used: Cross-flow ultrafiltration, Tangential ultrafiltration in combination with filtrates and unfiltered water were sent to different laboratories for characterisation. The isolated colloids were characterised with several different methods: scanning electron microscopy, gravimetry, chemical analysis, micro/ultrafiltration, transmission single particle counting, transmission electron microscopy, static and dynamic light scattering and laser-induced photoacoustic spectroscopy. The various methods gave rather different results and the reported concentrations range over one order of magnitude. The final colloid concentration was 200 ± 100 ppb which is similar to the concentration obtained from Olkiluoto.

8. Conclusions and recommendations

The aim of the exercise in the borehole OL-KR1 in Olkiluoto, Finland was to compare the results from three different colloid sampling methods: ordinary- inert- and ultrafiltration to sample organics, and to estimate by calculation the possible in-situ colloid concentration of deep saline groundwater. Two sampling campaigns were arranged with an interval of three weeks and care was taken to avoid known artefacts. During the exercise the following were demonstrated:

1) High pump rate changes the downhole groundwater chemistry and increases the colloid content. Low pump rate changes the sample due to long transport and decompression time up to the surface prior to analyses. The selection of the pump rate is thus crucial to maintain a balance of priorities.

2) The major artefact process interfering colloid sampling were calcite and iron hydroxide precipitation. Short sampling time in combination with N_2 -atmosphere seems to be an advantage in this respect since the N_2 -atmosphere seems only to be able to slow down the reactions but cannot prevent the oxidation occurring over a longer period of time, despite measured reducing conditions. Cross-flow filtration procedures in particular may promoted particle growth and formation, as well as aggregation.

3) Strong potential of particle formation was indicated by the SEM micrographs of the ultrafiltrates, because some very large particles (up to 10000 nm) could be observed where the particle size should have been only < 2 nm. By XRD the examined particle material was amorphous in nature except for the crystalline phases $NaCl_2$ and $CaCl_2$. The salt crystals are surely artefacts, but the amorphous phases can also partly contain original colloidal phases.

4) Due to the selected low pump rate the groundwater chemistry was constant during the both sampling campaigns. The master variables (Eh and pH) and hence the entire chemical system changed because of the different sampling methods used. These, in combination with analytical uncertainties, gave conflicting results. The comparison of the results is therefore difficult especially with ultrafiltration since the difference of the method. The ordinary filtration method suggested consistent colloid content, inert filtration and ultrafiltration showed decreasing colloid content. The methods

suggested a maximum difference by a factor of 58 in colloid concentration measured on the same groundwater. The inert- and ultra-filtration methods, where nitrogen with a positive pressure were used, showed generally a lower content for most of the elements compared with ordinary filtration. Since almost all the elements associated with colloids increased during ordinary filtration, coprecipitation with calcite is suggested as a possible mechanism. The accuracy and precision is highest for inert filtration. The results from the precision and accuracy test is only approximative since only two samples per method are considered.

5) The in-situ colloid concentration of this deep groundwater can be considered to be low. Such a conclusion can be drawn when the obtained results are considered without the major artefact process, calcite precipitation, which manifolds the concentration of colloids. Omitting the load of calcite precipitation from colloid results, gives one possibility to estimate the conservative in-situ colloid concentration. The obtained inorganic colloid concentration in Olkiluoto groundwater (in size range 1-1000 nm) is 184 ± 177 when the colloids are considered to be formed of clay minerals, silica, pyrite, goethite and magnesium oxide. The concentration of organic substances is about 10 ppb. The microbial population is believed to be small.

Recommendations for future work:

- a) Colloid filtration in open air is not recommended since the high risk of precipitation and coprecipitation.
- b) Ultrafiltration method containing several investigations steps and phases can give detailed information of the colloidal phase and also possible artefact phenomena encountered. Care should be taken to use concentration factors high enough for detecting actual enrichment of colloids. The long sampling should be reduced, which is quite feasible by decreasing the sample size. Further characterisation of colloids from the concentrate by some alternative methods than cross-flow filtration should be considered. Nitrogen gas containing CO₂ in the right proportion to simulate the in-situ partial pressure of CO₂ is recommended as a working atmosphere.
- c) Inert filtration seems to be a relatively simple and reliable method to get a conservative colloid sample. Increased accuracy may be achieved by decreasing the sampling volume (e.g. 250ml) and thus reducing the sampling time when filtering. The information value may be increased by including more elements and by using SEM/EDS. The vacuum pump used may change the partial pressures and hence increase the risk for calcite precipitation. Nitrogen gas to press the water through the filters is recommended in combination with CO₂ gas to simulate the in-situ partial pressure.
- d) Chemical composition of colloids by size fractions can possibly give some information on their origin, formation, ageing, stability and mobility. The information by size fractions should preferably be obtained without fractionating by cross-flow filtrations. Alternative methods avoiding filtering should be tested. On-line

measurements using dilution to stabilise the colloids in combination with particle counting may result in more reliable information concerning the size and concentration of the colloids (C. Degueldre pers. comm. 1992).

e) The possible microbial population should be investigated.

f) The colloids reflect a laser beam, a hand held laser is therefore useful to check the quality of the deionized water (C. Degueldre pers. comm. 1993).

The large risk of artefact processes due to the mere pumping process of groundwater from great depths to the ground level strongly speaks in favour of in-situ sampling of colloids. If at-line measurements are used, a small sampling volume and a short sampling time in inert atmosphere may provide useful colloid information. Otherwise money and effort may be wasted on careful investigations of sampling artefacts.

9. Acknowledgements

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11. Appendix#1

Table 10-1. Analytical protocol of the groundwater samples. The analytical methods are standard analytical methods according to Finnish SFS standards, or generally used methods for analyses of water (Standard Methods for the examination of water and waste water, 1981). The analyses for main cations and anions as well as gases were performed at the IVO Chemistry laboratory, isotopes H⁻²/O⁻¹⁸ at Institutt for Energiteknikk Norway, H⁻³ at the University of Helsinki, Department of Radiochemistry, and TOC at the Helsinki City Energy Laboratory.

Sample	Species/Element	Container	Volume	Preservative	Analytical Methods
Anions	HCO ₃	PE	1 L	-	titrimetry, IC, spectrom.
	SO ₄ , PO ₄ , NO ₂ , NO ₃ , Br, Cl, I, F S ²⁻	glass	0,1 L x 3 Winkler= (124.61- 118.98 ml)	0,5 ml 1M Zn(Ac)+ 0,5 ml 1m NaOH	turbidimetry, potent. nefelom. spectrom.
Cations	Na, K, Ca, Mg Al, Fe, Si, Sr Fe, Fe ²⁺	HDPE	0,5 L	5 ml HNO ₃	AAS spectrom., ferrozine
Others	pH, cond., tot. hardn. colour, turb.	HDPE	1 L x 2		potent. conduct., titr. spectr., turbid., nefelom.
	Ntot, Stot, NH ₄	PE	0,5 L	5 ml 4M H ₂ SO ₄	titrim. instrum.
	Ptot, KMnO ₄	PE	1 L		filtering
	solid.mat.	PE	0,3 L x 2		instrum. Carbon
TOC	PE	0,3 L x 2	analyzer		
Isotopes	H-2, O-18	glass	0,3 L		MS
	H-3	glass	1 L		liq.scintillation
Gases	N ₂ , O ₂ , CO ₂ , CO, H ₂ , Ar	alum.bag	0,2 L		GC
	He, CH ₄ , C ₄ H ₄ , C ₄ H ₈ C ₂ H ₂		0,1 L		

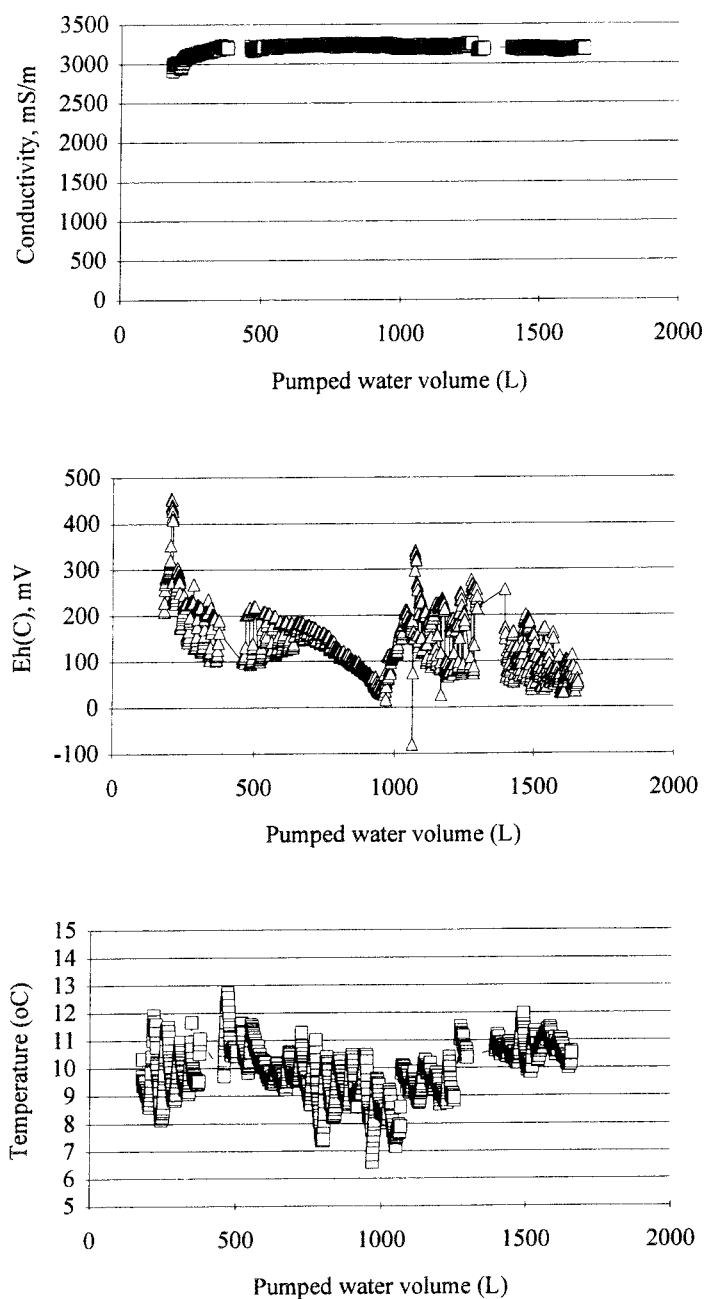
12. Appendix#2

Figure 11-1. The results of the automatic on-line measurements in OL-KR1 613-618 m. In the upper most Figure the electrical conductivity (mS/m) and in the middle Figure Eh (mV, carbon electrode) are shown as a function of the pumped water volume in the section. In the lowest Figure the temperature (C) are shown as a function of the pumped water volume in the section. The disturbance in the measurements around 1000 L is due to reduced flow caused by clogging of the organic matter sampler. Sample#1 was taken at 400 L and sample#2 at 1300 L.

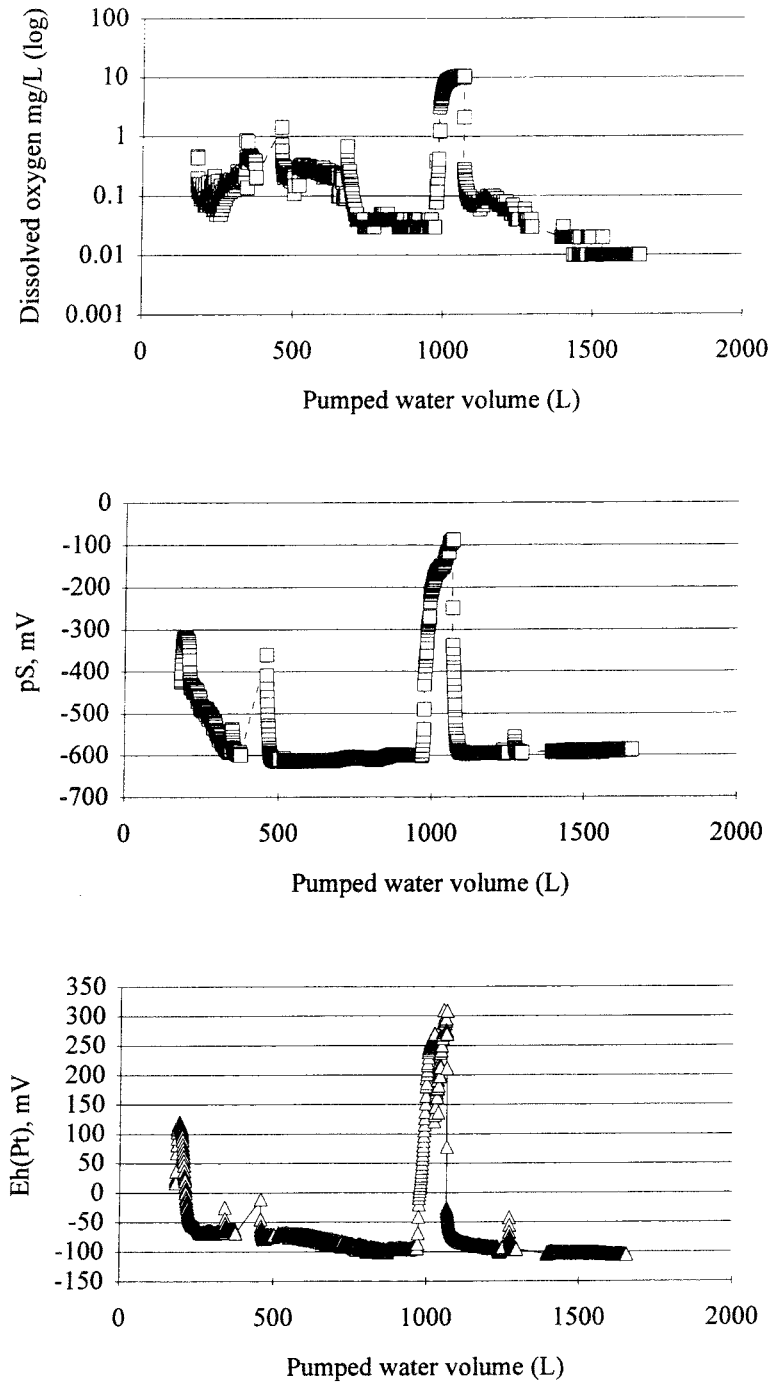


Figure 11-2. The results of the automatic on-line measurements in OL-KR1 613-618 m. In the upper Figure the dissolved oxygen (mg/L) is shown as a function of the pumped water volume in the section. In the middle Figure the sulphide (mV) and in the lower Figure Eh (mV, platinum electrode) are shown as a function of the pumped water volume in the section. The disturbance in the measurements around 1000 L is due to reduced flow caused by clogging of the organic matter sampler. Sample#1 was taken at 400 L and sample#2 at 1300 L.

13. Appendix#3

Table 12-1. The analytical results of filtrates using ordinary filtration in Olkiluoto, borehole OL-KR1, 613-618 m, date; 22 of September 1992 (sample#1) and 12 of November 1992 (sample#2). The line (-) indicates that the element is analysed but not detected

Sample#1:	Al(mg/L)	Ca(mg/L)	Fe(mg/L)	Mg(mg/L)	Mn(mg/L)	SiO ₂ (mg/L)
OL-KR1, 0,45 µm	0.13	3520	1.9	58.1	-	1.8
OL-KR1, 0,03 µm	0.12	3230	1.85	58.7	-	1.9
Sample#2:						
OL-KR1, 0,45 µm	0.101	3380	1.58	58.5	-	3
OL-KR1, 0,03 µm	0.102	3430	1.57	57.8	-	3

13. Appendix#4

Table 13-1. Analyses of the elemental concentrations for sample#1 (concentration factor 8.8) and sample#2 (concentration factor 12.2) concentrate (2nm -1000 nm) and ultrafiltrate (<2nm) (n.d. = not detected).

Element	Sample #1				Sample #2			
	concentrate mg/l		ultrafiltrate mg/l		concentrate mg/l		ultrafiltrate mg/l	
	AAS ICP-MS	HPLC	AAS ICP-MS	HPLC	AAS ICP-MS	HPLC	AAS ICP-MS	HPLC
Cl/Cl ⁻		12200		12200		12600		12600
Br/Br ⁻		71.9		66.9		70.9		74.1
SO ₄ ²⁻		n.d.		n.d.		n.d.		n.d.
Na/Na ⁺	4400	4380	4400	4360	4700	4380	4800	4460
K/K ⁺	22	26.9	22	22.2	22	27.5	22	20.4
Ca/Ca ²⁺	3400	3310	3300	3310	3400	3170	3300	3150
Mg/Mg ²⁺	58	59.7	57	59.5	60	59.0	59	59.8
SiO ₂ /Si	1.8 / 0.84		1.7 / 0.80		2.9 / 1.36			2.8 / 1.31
Fe	1.07		0.94		2.02			1.95
Ba	0.805		0.787		0.802			0.742
B	0.509		0.493		0.557			0.495
Al	0.13		0.19		0.17			0.11
Cu	0.08		0.08		0.08			0.09
Sr	31.9		32.3		31.9			31.5
Li	0.015		0.016		0.016			0.016
Mn	0.502		0.496		0.493			0.485
Rb	0.030		0.029		0.030			0.027

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R Pusch¹, O Karnland¹, A Lajudie², J Lechelle², A Bouchet³

¹ Clay Technology AB, Sweden

² CEA, France

³ Etude Recherche Materiaux (ERM), France
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R Pusch¹, O Karnland¹, A Lajudie², A Decarreau³,

¹ Clay Technology AB, Sweden

² CEA, France

³ Univ. de Poitiers, France
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Fredrik Brandberg¹, Bertil Grundfelt¹,

Lars Olof Höglund¹, Fred Karlsson²,

Kristina Skagius¹, John Smellie³

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Thomas Eliasson

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L Romero, L Moreno, I Neretnieks

Department of Chemical Engineering,

Royal Institute of Technology, Stockholm, Sweden

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Joel Geier

Golder Geosystem AB, Uppsala

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Clay Technology AB, Lund, Sweden

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Roy Stanfors (ed.)¹, Lars O Ericsson (ed.)²

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Department of Geology, Chalmers University of Technology and University of Göteborg

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Robert Muir Wood

EQE International Ltd, Warrington, Cheshire, England

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G S Boulton, A Payne

Department of Geology and Geophysics,
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Kemakta Konsult AB

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MBT Tecnologia Ambiental, Cerdanyola, Spain

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Janusz Janeczek, Rodney C Ewing
Department of Earth & Planetary Science, University
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Trygve E Eriksen¹, Pierre Ndalamba¹, Daqing Cui¹,
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Bengt Leijon
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Catharina Bäverman

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Susanne Ekendahl, Johanna Arlinger, Fredrik Ståhl,
Karsten Pedersen

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University of Göteborg, Göteborg, Sweden

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Geosigma AB, Uppsala, Sweden

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Geosigma AB, Uppsala, Sweden

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