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Forsmark site investigation

**Granitic groundwater colloids
sampling and characterisation**

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August 2007

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Colloid characterisation.

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

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Abstract

Natural ground water colloids were sampled by micro-filtration of water samples collected from a granitic groundwater and maintained at the in situ thermodynamic conditions. The methodology avoids the generation of artefacts produced by pH changes due to CO₂ exchange, yielding potential carbonate precipitation, or by O₂ contaminations yielding oxidized insoluble phases. The enhanced pressure and the anoxic conditions are maintained also through the filtering procedure. In situ groundwater sampling followed by micro-filtration of the colloids were carried out after a period of regular sampling of groundwater pumped to the ground surface and continuous on-line long-term measurements (weeks, months) of chemical and physical parameters in the unbroken sample water both at the ground surface and at depth down-hole. Colloid samples were characterized by scanning electron microscopy. At deep granitic groundwater conditions, natural colloids occur sparsely. The colloid concentration was determined $C_{col} \sim 1 \mu\text{g}\cdot\text{L}^{-1}$ for sizes ranging from 50 to 500 nm or $N_{col} \sim 10^8 \text{ L}^{-1}$ for sizes larger than 100 nm. These colloids are clay with an average size smaller than 200 nm. For the Na-Ca-Cl groundwater (pH 7.53, ionic strength $\sim 10^{-1}\text{M}$), the colloid concentration values are comparable with values reported earlier in the literature.

Sammanfattning

Kolloidprov från naturligt granitiskt grundvatten erhöles genom mikrofiltrering av grundvattenprov. Vattenprovet bibehöll sitt in situ termodynamiska tillstånd under provtagningen. Med den använda metoden kan man undvika bildandet av artefakter orsakade av syreinträngning eller pH-förändring (beroende på utbyte av CO_2). En ändring av pH-värdet kan ge utfällning av karbonater medan O_2 föroreningar orsakar utfällning av olösliga oxider. Tryckförhöjningen liksom det anoxiska tillståndet bibehölls även under filtreringsförfarandet. Provtagning av in situ grundvatten åtföljd av mikro-filtrering av kolloider genomfördes efter en mät- och provtagningsperiod på tre–fyra veckor. Under den perioden gjordes regelbundna uttag av vattenprov på det uppumpade grundvattnet och kontinuerliga långtidsmätningar on-line av kemiska och fysikaliska parametrar i flödesceller vid markytan och i borrhålssektionen. Kolloidproven analyserades med svepelektronmikroskopi. I djupa granitiska grundvatten är förekomsten av naturliga kolloider sparsam. Kolloidkoncentrationen uppmättes till $C_{col} \sim 1 \mu\text{g}\cdot\text{L}^{-1}$ i området mellan 50 och 500 nm eller $N_{col} \sim 10^{-8} \text{L}^{-1}$ över 100 nm. Kolloiderna bestod av lera med en genomsnittlig storlek på mindre än 200 nm. Kolloidkoncentrationen i Na-Ca-Cl grundvattnet (pH 7,53, jonkoncentration $\sim 10^{-1}\text{M}$) befanns vara jämförbar med de värden som tidigare rapporterats i litteraturen.

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1 Introduction

Colloids are present in all groundwaters /Degueldre et al. 2000/. Trace element properties in water may be affected by their association with colloids. These colloids are defined as particles of size ranging from 1 to 1,000 nm /Stumm and Morgan 1996, Degueldre et al. 1996a/. To evaluate the impact of contaminant transport by colloids, information on colloid concentrations, size distribution and chemical nature is needed. Effective studies on groundwater colloids require very careful sampling /McCarthy and Degueldre 1993, Backhus et al. 1992/ and characterisation of the colloids as well as accurate analysis of the groundwater.

This document reports the colloid results gained by microscopic investigation of colloids on filters, which is an activity that was performed only once within the site investigation at Forsmark. The work was carried out in accordance with the complementary addition 2007-03-21 to the Activity Plan AP PF 400-07-004 concerning hydrochemical characterisation in borehole KFM11A. A general overview over the site investigation area and the location of the borehole KFM11A is shown in Figure 1-1.

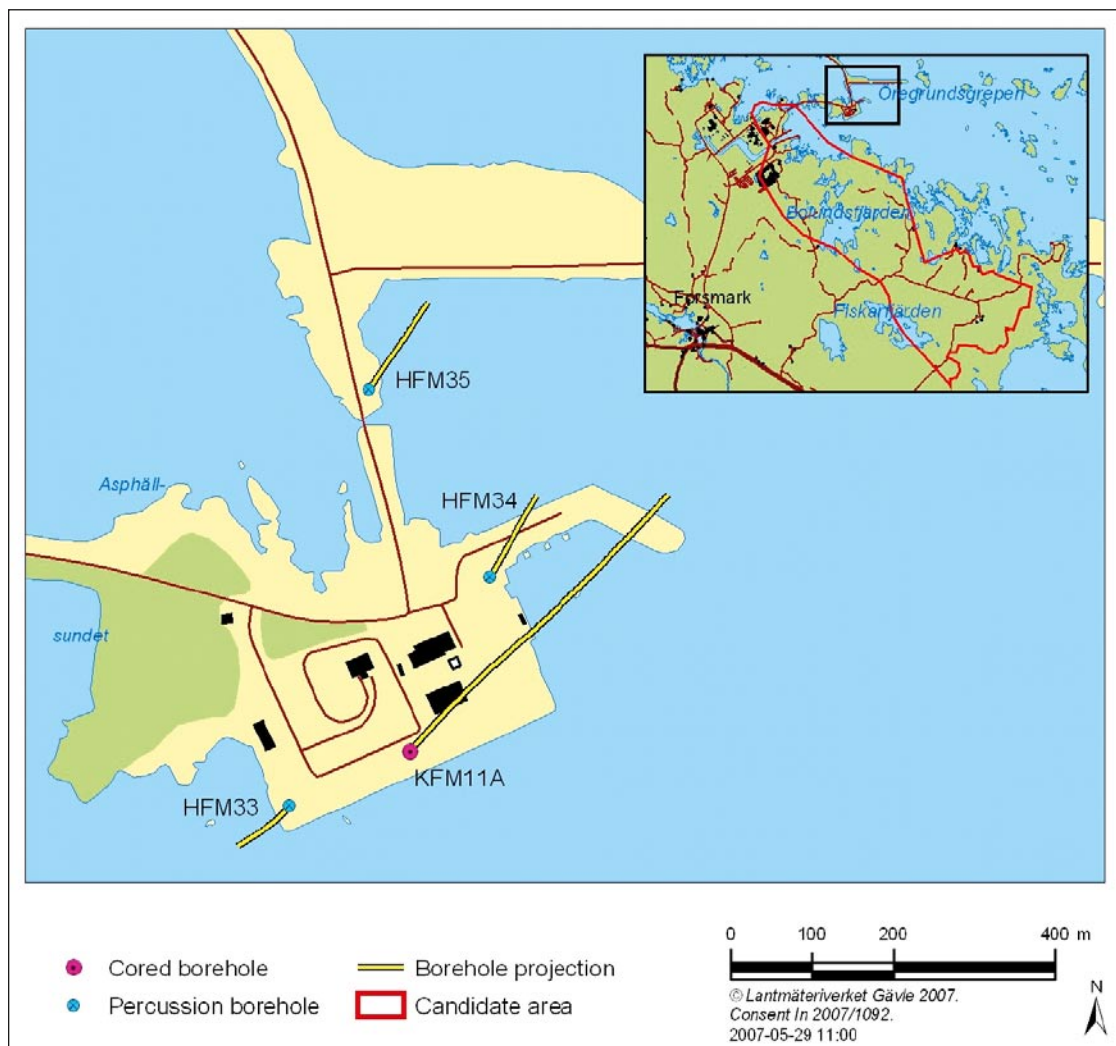


Figure 1-1. Location and projection on the horizontal plane of the telescopic borehole KFM11A and the percussion boreholes HFM33, HFM34 and HFM35 at drill site DS11. The location of DS11 within the Forsmark candidate area is displayed on the map in the upper corner.

The site for the present colloid study is located in the granite Scandinavian mole. At this location the cooperative for the nuclear waste management in Sweden (SKB) is investigating a potential site for a deep repository for spent nuclear fuel. The host rock is metamorphosed granite /SKB 2005/ where water-bearing fracture zones or single fractures occur relatively scarcely. The site investigation implies, among other things, drilling of boreholes in order to study the geological and hydrogeological conditions and especially the properties of the few larger zones.

The borehole selected for the colloid study, KFM11A, intersects a major deformation zone starting at approximately 500 m borehole length. However, water for this study was sampled from a flow anomaly at 452.7 m borehole length (391.0 m vertical depth) in a fractured part of the bedrock adjacent to this zone. Water sampling for colloid studies was carried out in situ in a borehole section delimited by double-packers. The enclosed water sample in its container was lifted to the surface where it was filtered in a closed system. The entire procedure was performed under argon atmosphere and at maintained pressure from the borehole section /Nilsson et al. 2007/.

This paper presents and discusses the granite groundwater colloids sampling and characterisation from the borehole test KFM11A-44T.

2 Background

Since colloids are present in all waters, consequently groundwater colloids are taken into account in the performance assessment studies. Colloid facilitated transport mechanisms are evaluated considering the geosphere as a source of colloids with constant concentration in the groundwater. Their presence is a consequence of solid-water interaction, and they are generated when rocks interact with the groundwater. An attempt to correlate their concentration and their stability is currently in progress a decade ago /e.g. Degueldre 1997/. These studies are difficult because colloid sampling is not always properly carried out and because the uncontaminated colloid concentration obtained may also be a function of the history of the aquifer prior to sampling /McCarthy and Degueldre 1993/. Numerous colloid data are systematically affected by interfering phases such as precipitates which are generated during sample preparation or additional components induced by perturbation in the aquifer during water collection. These perturbing phases are often erroneously measured as colloids and thereby increase the concentration recorded. They are called artefacts.

Colloid sampling and characterization was recently reviewed by /McCarthy and Degueldre 1993/. It was pointed out that sampling must be optimized in all cases prior to characterization. Today various techniques (including single particle counting to colloid bulk analysis) are available involving on-site sampling and characterisation on-line or off-line. For example, samples can be taken on site and characterised directly at the site by light scattering. Or alternatively, samples can be separated by filtration and filters can be sent for characterisation. In all cases artefact tracking is required (see also /Degueldre et al. 1996a/), e.g. assess the enhancement of the colloid amount by increasing the volume of the groundwater sample. However, this work requires resources that are not always available.

The colloid concentration of deep groundwaters is usually around the $\mu\text{g}\cdot\text{l}^{-1}$ level and thus the contamination risks are obvious during water sampling and colloid sample preparation. Colloidal particles can be generated as artefact, even proceeding to on-line sample preparation. The sampling errors are due to: excessively high or low pump rates, contamination from borehole activities, complex hydrological situations, contamination from tubes varying the composition of the groundwater, air contamination (O_2 uptake), losses or uptake of CO_2 , aggregation-coagulation effects, long storage times prior to analyses, analytical errors etc. Some errors in the sampling and analysis of colloids are easy to avoid, others are difficult or impossible to evaluate. These problems have been addressed among others by /Laaksoharju et al. 1994/.

3 Hydrogeochemical system and water analysis

Borehole KFM11A is a 851.2 m long telescopic borehole and the first 71 m were percussion drilled /e.g. Claesson et al. 2007/, whereas the 71–851.2 m interval was drilled with a conventional rotary core drilling system. The drilling was completed at a vertical depth of 713.2 m in November 2006. Rock around the interval from where the water is collected consists of granite which is composed of muscovite / biotite, feldspar, quartz and clay components such as chlorite and illite.

Differential flow logging revealed several water bearing fractures along the borehole e.g. /Pöllänen and Sokolnicki 2007/. A flow anomaly at 452.7 m (391.0 m vertical depth) was selected for investigation due to a suitable hydraulic transmissivity and its location above a major deformation zone that may act as a hydraulic borderline for groundwater flow. A down-hole equipment, consisting of from the top; umbilical hose, length mark detector, measurement cell for in situ measurements, upper packer, borehole pump, in situ water sampler and lower packer, was installed in the borehole on 14 February 2007 and a section at 447.5–454.6 m borehole length was isolated by the packers. Water samples were collected regularly at the ground surface during the four week long pumping and measurement period, which was completed on 13 March 2007. Prior to lifting the equipment the valves to the in situ sampling containers were opened from the surface in order to rinse the system and fill the containers. After some hours the valves were closed and the water sample portions for analyses of colloids, dissolved gases and microbes were secured. Following stopping of the borehole pump and deflation of the packers, the equipment was lifted and the different down-hole units were dismantled.

Prior to the investigation period, nitrogen flushing was performed several times from the bottom of the borehole and contemporaneous efficient pumping was maintained from the top of the borehole. In this way a water volume close to 1,000 m³ was exchanged in order to reduce the content of remaining flushing water from drilling of the borehole. At the start of the investigation period in the sampling section, the drilling water content was still 6.6%. Due to the continuous pumping at a flow rate of about 150 mL min⁻¹ for regular water sampling from the section, this content was reduced to 5.7% at the time of the in situ water sampling for colloid filtration.

Regular water sampling was performed from pumped water and filtration of sample portions for chemical analyses was carried out by connecting the filter holders directly to the outlet tubing made by polyamide. Field-pH was measured on-line in the unbroken water line with glass- and Ag/AgCl reference electrodes in measurement cells down-hole in the borehole section as well as at the ground surface. Laboratory pH was measured in batch samples at 25°C using a combined electrode. The pH was measured to ± 0.02 units after careful standardisation with buffers (4, 7 and 10).

Analyses of Fe(II), alkalinity, ammonium, lab-pH and electrical conductivity were performed immediately after each sampling at the site. The other analyses were performed by several consulted laboratories and the water was analysed for its dissolved and suspended solid contents. Mohr titration (chloride) and ion chromatography (Dionex 120) was utilised for assaying major anions. Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) were determined using a carbon analyser, Shimadzu TOC-5000. ICP-AES and ICP-MS techniques were used for minor and minor elements.

Careful sampling and analysis of the water must be performed during borehole flushing in order to ensure correct colloid results.

4 Colloid analysis methodology

4.1 Colloid sampling

The in situ groundwater samples were lifted to the ground surface at maintained pressure from the borehole section. One of these samples was used to obtain colloid samples on filters. The colloid filtering system allowed micro-filtering of groundwater followed by rinsing with a small volume of de-oxygenised, de-ionised water through five connected filters in a closed system under argon atmosphere. The membranes of diameter 47 mm are mounted with a 1.8 mm O-ring in the filtration cell and the volume of water V was 140 ml. The system was kept at 9.8°C in isotherm and isobar conditions, and maintained in the in situ conditions for filtration. The filtering was performed at a pressure similar to that of the groundwater in the borehole section and five filters in the pore size order 2, 2, 0.4, 0.2 and 0.05 μm were used. The two first filters were used to prevent clogging. The filters were stored under argon in welded plastic bags in the fridge. The SEM investigations were carried out on 0.2 and 0.05 μm pore size membranes.

4.2 Colloid analysis

Particle analysis was carried out at by SEM/EDS. The scanning electron microscopy (SEM) investigations were performed with a Zeiss DSM 962 unit under 30 kV. SEM investigations were earlier tested with the gold colloids as recently reported by /Degueldre et al. 2005/. For the present tests the filter membranes were coated with 15 nm Pt layer by Magnetron sputtering prior to microscopic investigation. The energy dispersive spectroscopy (EDS) analysis was performed using the Zeiss unit. This single particle monitoring allows specific counting of 3 size classes from 50 to 100, 100 to 200 and 200 to 500 nm.

4.3 Colloid data handling

The number of colloid n detected on a micrography (surface s) of the membrane of surface S may be translated in number of particle N_{col} in volume of filtered water V . The colloid number concentration N_{col} is simply given by:

$$N_{col} = \frac{n \cdot S}{V \cdot s} \quad (1)$$

The colloid number concentration N_{col} may be modelled as a function of their size d using a power law size distribution:

$$\frac{\Delta N_{col}}{\Delta d} = A \cdot d^{-b} \quad (2)$$

where A and b are constant for given size ranges.

The colloid mass concentration C_{col} may be calculated assuming spherical colloids of density ρ :

$$\frac{\Delta C_{col}}{\Delta d} = \frac{\pi \cdot A \cdot \rho}{6} \cdot d^{3-b} \quad (3)$$

Concentration can be calculated for size range $d_{min} - d_{Max}$ by integrating the concentration over the size interval. Calculations could be done utilising the COLIAT code based on particle size distribution including shape hypothesis /see Degueldre et al. 1996, 1999/ when the number of colloid is large enough and when colloids present aggregates, or, simple calculation may be carried out size class wise.

5 Results and discussion

5.1 Ground water colloid characterisation

The groundwater chemistry is given in Table 5-1. The granitic water is of Na-Ca-Cl type, with an Eh of -203 ± 2 mV and a pH of 7.53.

The analysis of the colloid by scanning electron microscopy on the prepared membranes reveals colloids of various sizes, shapes and morphologies as it can be seen in Figures 5-1 and 5-2. Figure 5-1 presents typical micrographies taken for ground water colloid sample KFM11A-44T-35 on the 0.2 μm membrane. The 0.2–0.3 μm colloid number n on the membrane is very low. Occasionally a larger particle is found on the 10–30 micrograph field of magnification 10,000.

Figure 5-2 presents typical micrographies taken for ground water colloid sample KFM11A-44T-36 on a 0.05 μm membrane. The colloid number n on the membrane is low. It must be noted that these colloids attach on the membrane and do not clog pores. Some pores seem to be apparently larger than 0.05 μm , however their structures below the membrane surface respect the cut off. The low magnification picture reveals the presence of two active areas on the membrane: one active for filtration and one less active (above the filter support). Both surfaces are covered with colloids, however, the density is somewhat larger on the active surfaces.

Table 5-1. Element/species concentrations (C, in mass or M, molality) in the studied granitic groundwater. The water conductivity is 1,220 $\text{mS}\cdot\text{m}^{-1}$ and its pH 7.58. The charge balance is -0.24% . Temperature T 9.8°C, Eh -0.203 V.

Concentration Element/species	C ($\text{mg}\cdot\text{L}^{-1}$)	M (M)
Li	0.047	6.820×10^{-6}
Na	1250	5.475×10^{-2}
K	5.930	1.527×10^{-4}
Mg	37.50	1.543×10^{-3}
Ca	1280	3.216×10^{-2}
Sr	17.10	1.965×10^{-4}
Al	0.027	1.008×10^{-6}
Si	5.960	9.989×10^{-5}
Mn	0.123	2.255×10^{-6}
Fe	0.246	4.400×10^{-6}
Fe(II)	0.24	4.327×10^{-6}
Cl ⁻	4210	1.196×10^{-1}
Br ⁻	16.6	2.092×10^{-4}
HCO ₃ ⁻	23.9	3.944×10^{-4}
SO ₄ ²⁻	95.0	9.958×10^{-4}
TOC	1.10	9.166×10^{-4}

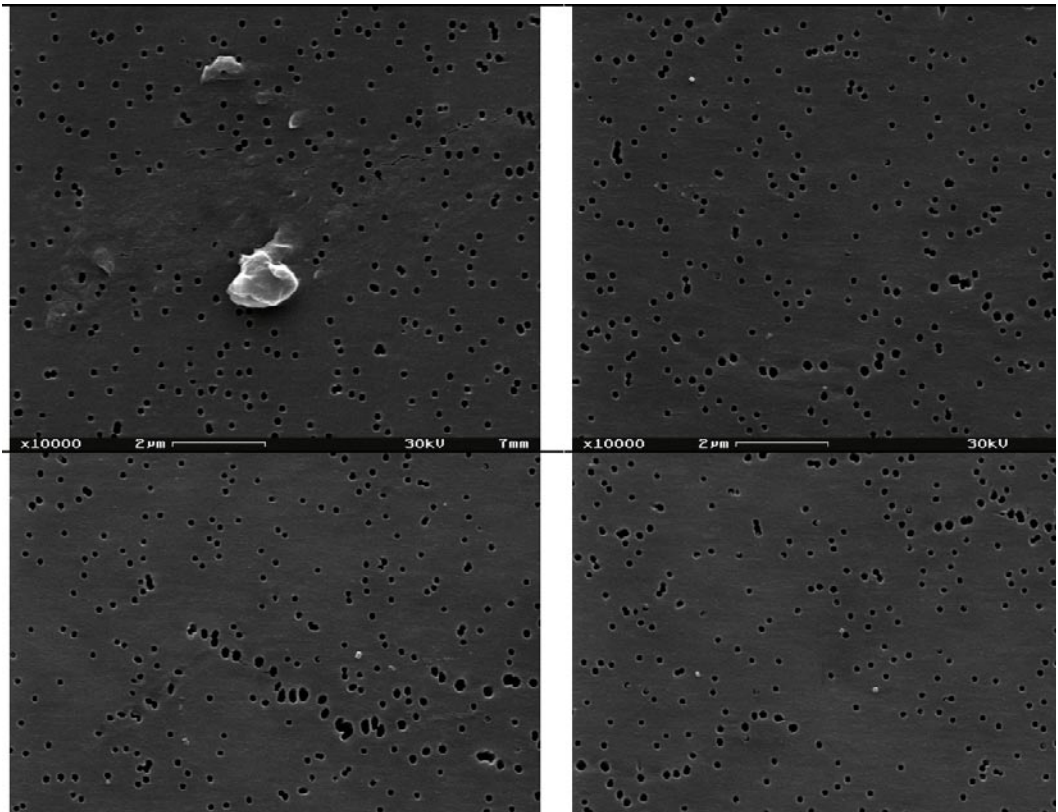


Figure 5-1. SEM micrographs of the ground water colloids (KFM11A-44T-35).

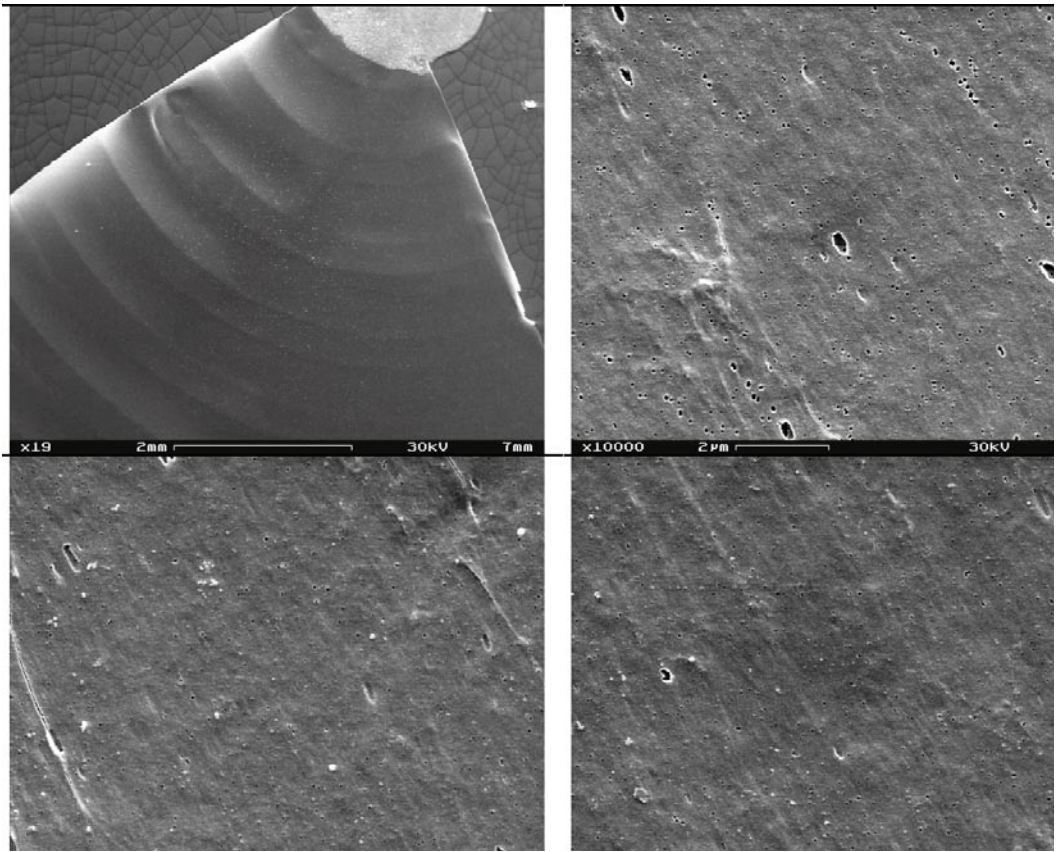


Figure 5-2. SEM micrographs of the ground water colloids (KFM11A-44T-36).

The counting of the colloids was carried out systematically. Table 5-2 gives details about the colloid concentration for the investigated sizes. The colloid size distribution is shown in Figure 5-3.

Based on SEM micrographs, colloid morphology indicates a composition of mostly clay particles. However, Al and Si are not detectable by EDS, the colloid size being too small to allow analysis. X-ray diffraction XRD analysis of colloids from 0.10–1.00 μm collected on membrane filters should be tempted to analyse their clay nature. These particles are expected from the rock mineralogy described in Section 2.1. The colloid concentration C_{col} in the marl water is $0.0018 \text{ mg}\cdot\text{L}^{-1}$ for the 50–500 nm size range and a colloid density of $2 \text{ g}\cdot\text{cm}^{-3}$.

5.2 Assessing the colloid data

In order to assess the quality of the colloid data, it is imperative to understand if the water quality is affected or not by the borehole construction and packer installation. In principle the artefacts from borehole construction and packer installation have been purged out and discarded by dilution during the week flush out. Micro-filtration of the colloids is carried out after on-line long-term measurements (weeks, months) of chemical and physical parameters in the unbroken sample water line both at the surface and at depth down-hole.

Table 5-2. Quantification of the colloid specific size distribution. Conditions: for the colloid size d on the basis of the number of colloids n on the micrograph the colloid number concentration N_{col} is calculated on the basis of the active membrane size and the filtered volume. For the average colloid size d_{av} , of volume V_{av} or mass m_{av} (estimated for a density of $2 \text{ g}\cdot\text{cm}^{-3}$ and for $d_{max} \approx 2 \times d_{min}$) the colloid concentration C_{col} is calculated.

Size d / nm	50	100	200	50–500
Colloid data				
n / –	30	3	(0.3)	33.3
N_{col} / L^{-1}	36×10^8	3×10^8	0.3×10^8	33.3×10^8
d_{av} / nm	60	120	240	
V_{av} / cm^3	0.2×10^{-15}	1.7×10^{-15}	1.4×10^{-14}	
m_{av} / g	0.4×10^{-15}	3.4×10^{-15}	2.8×10^{-14}	
C_{col} / $\text{mg}\cdot\text{L}^{-1}$	0.00014	0.00090	(0.0008)	0.0018

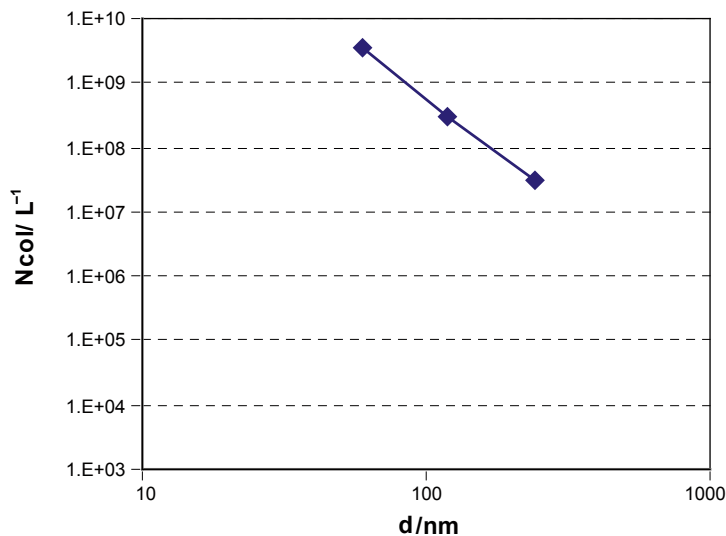


Figure 5-3. Colloid size distribution estimated from data reported in Table 5-2.

On site, colloid transit during pumping in the borehole line creates a cut-off (balance between transport upward and sedimentation). The particle of size d acquires in the borehole a constant settling velocity v which is given by Stoke's law: $v = 0.05556 g d^2 (\rho - \rho_w) \eta^{-1}$ with g the gravity acceleration ($981 \text{ cm}\cdot\text{s}^{-2}$), ρ_w the water density and η is the fluid viscosity (1.4 cPoise or $\cdot 10^{-3} \text{ Pa}\cdot\text{s}$ at 9°C). For a colloid density of $2 \text{ g}\cdot\text{cm}^{-3}$ the corresponding maximum size that transit from the interval to the container must be determined. Large colloids may concentrate in the interval while small are extracted.

Residence time in the interval from the water bearing zone to the container aperture is also important. During this period, the aggregation of the colloids in the size range considered should not be significant. The aggregation half-time has to be estimated for a colloid concentration level of 1 ppm or 1 ppb and for attachment coefficients of the order of 10^{-1} (corresponding to the Ca, Mg, Na and K concentration) and size 100 nm, /see Degueldre et al. 1996b/.

From the chemistry point of view the question is: are colloids affected by any carbonate or oxy-hydroxyde precipitation? The generation of artefacts produced by pH changes due to CO_2 exchange, yielding potential carbonate precipitation, or by O_2 contaminations yielding oxidised insoluble phases was evaluated running the code PHREEQ for the data reported in Table 5-1. The results are given in Table 5-3.

Table 5-3. PHREEQ indicative results obtained for the water chemistry given in Table 5-1. Conditions: Electrical balance = 5.83×10^{-04} eq, error: $100(\text{Cat}-|\text{An}|)/(\text{Cat}+|\text{An}|) = 0.24\%$, Iterations = 7.

Parameter Phase	SI	log IAP	log KT	Formula
Al(OH) ₃ (a)	-1.16	10.69	11.84	Al(OH) ₃ (a)
Albite	-0.43	4.89	5.32	NaAlSi ₃ O ₈
Alunite	-2.50	-1.92	0.58	KAl ₃ (SO ₄) ₂ (OH) ₆
Anhydrite	-1.34	-5.67	-4.34	CaSO ₄
Anorthite	-1.99	26.52	28.51	CaAl ₂ Si ₂ O ₈
Aragonite	-0.26	-8.51	-8.25	CaCO ₃
Calcite	-0.10	-8.51	-8.41	CaCO ₃
Celestite	-1.25	-7.88	-6.63	SrSO ₄
Chalcedony	-0.25	-3.98	-3.74	SiO ₂
Chlorite(14A)	-5.85	68.50	74.35	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₆
Chrysotile	-6.71	27.48	34.18	Mg ₃ Si ₂ O ₅ (OH) ₄
Carbon dioxide(g)	-3.40	-21.62	-18.22	CO ₂ (g)
Dolomite	-1.60	-18.32	-16.72	CaMg(CO ₃) ₂
Iron trihydroxide(a)	-4.86	13.44	18.29	Fe(OH) ₃
Gibbsite	1.68	10.69	9.01	Al(OH) ₃
Goethite	0.47	13.44	12.97	FeOOH
Gypsum	-1.08	-5.68	-4.59	CaSO ₄ ·2H ₂ O
Hausmannite	-29.89	35.11	64.99	Mn ₃ O ₄
Hematite	2.87	26.88	24.01	Fe ₂ O ₃
Illite	2.18	15.74	13.56	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂
K-feldspar	-0.24	2.32	2.55	KAlSi ₃ O ₈
Kaolinite	4.58	13.41	8.82	Al ₂ Si ₂ O ₅ (OH) ₄
Pyrochroite	-6.31	8.89	15.20	Mn(OH) ₂
Pyrolusite	-26.61	17.33	43.94	MnO ₂
Quartz	0.23	-3.98	-4.22	SiO ₂
Rhodochrosite	-1.66	-12.73	-11.07	MnCO ₃
Sepiolite	-4.51	11.68	16.18	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O
Siderite	-1.61	-12.40	-10.79	FeCO ₃
Silica(a)	-1.14	-3.98	-2.84	SiO ₂
Strontianite	-1.43	-10.72	-9.29	SrCO ₃

For pH 7.53 as well as for the concentrations of bicarbonate, calculations show that the carbonates of Ca, Mg, Sr, Fe, and Mn are undersaturated and that the partial pressure of CO₂ is 10^{-3.4} Atm. The water could expurge slightly its CO₂ increasing slightly its pH. The oxy-hydroxydes are undersaturated or very slightly saturated e.g. Al, Fe, Mn and Si. As an example, and as usual, Fe(OH)₃ is undersaturated, goethite is saturated and Fe₂O₃ is slightly over-saturated. Finally, some of the clay minerals are slightly oversaturated as well as gibbsite suggesting presence of Al/clay colloids in the analysed phases. The on-line procedure allows to working at the well head at *T* and *P* conditions similar to the in-situ conditions, i.e. artefact free. This methodology avoids the generation of artefacts produced by pH changes due to CO₂ exchange, yielding potential carbonate precipitation, or by O₂ contaminations yielding oxidised insoluble phases. The on-line procedure allows to working at the well head artefact free.

The colloid concentration was determined $C_{col} \sim 1 \mu\text{g}\cdot\text{L}^{-1}$ for sizes ranging from 50 to 500 nm or $N_{col} \sim 10^{-8} \text{L}^{-1}$ for sizes larger than 100 nm. These colloids are clay. The concentrations are indicative since they concern a single filtration campaign, but the results make sense.

6 Summary

Samples of natural groundwater colloids were produced by micro-filtration on-line from a granitic groundwater at the well head in the in situ T and P conditions. This methodology avoids the generation of artefacts produced by pH changes due to CO_2 exchanges, yielding potential carbonate particles, or by O_2 contaminations yielding oxy-hydroxyde colloids. The on-line procedure allows to working at the well head artefact free. Micro-filtration of the colloids is carried out after on-line long-term measurements (weeks, months) of chemical and physical parameters in the unbroken sample water line both at the surface and at depth down-hole. Colloid samples were characterised by scanning electron microscopy. In the deep granitic groundwater conditions, natural colloids occur. The colloid concentration was determined $C_{col} \sim 1 \mu\text{g}\cdot\text{L}^{-1}$ for sizes ranging from 50 to 500 nm or $N_{col} \sim 10^8 \text{L}^{-1}$ for sizes larger than 100 nm. These colloids are clay with an average size smaller than 200 nm. For the Na-Ca-Cl groundwater (pH 7.53, ionic strength $\sim 10^{-1} \text{M}$), the colloid concentration values are comparable with values reported earlier in the literature.

Acknowledgements

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