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# **Forsmark site investigation**

# Hydrochemical characterisation in borehole KFM10A

Results from three investigated borehole sections: 298.0–305.1 m, 436.9–437.9 m, 478.0–487.5 m

Anette Bergelin, Anna Lindquist, Kersti Nilsson ÅF Process AB/Geosigma AB

Ann-Chatrin Nilsson, Geosigma AB

June 2007

#### Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel and Waste Management Co Box 5864 SE-102 40 Stockholm Sweden Tel 08-459 84 00 +46 8 459 84 00 Fax 08-661 57 19 +46 8 661 57 19



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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 authors and do not necessarily coincide with those of the client.

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# Abstract

Complete chemical characterisation is the most extensive chemical investigation method performed in core drilled boreholes. The method entails pumping, measurements on-line and regular water sampling for chemical analyses in isolated borehole sections during approximately three weeks per section at a flow rate of between 50 and 200 mL/min.

The method has been used in two sections from borehole KFM10A at 298.0–305.1 m borehole length (vertical depth 215 m) and 478.0–487.5 m borehole length (vertical depth 328 m). The results include on-line measurements of redox potential, pH, dissolved oxygen, electrical conductivity and water temperature in the borehole section, together with chemical analyses of major constituents, trace metals and isotopes as well as gas content and composition. Furthermore, inorganic and organic colloids (humic and fulvic acids) were investigated by fractionation. In water samples from section 478.0–487.5 m, laser-induced breakdown colloid detection (LIBD) was also performed.

In addition, one fracture with low transmissivity  $(1E-9 \le T < 1E-8 \text{ m}^2/\text{s})$  was sampled using special Sampling equipment for Low-Transmissive fractures (SLT). The section was at 436.9–437.9 m borehole length (vertical depth 301 m), and the collected water sample was analysed according to SKB class 3 including isotope options and uranium.

The groundwater in section 298.0–305.1 m showed a slightly increasing salinity trend with time during the investigation period, while in section 478.0–487.5 m the salinity first increased and then decreased again, and the last sample in the series showed the lowest chloride concentration. The chloride concentrations in selected samples amounted to 4,050 mg/L and 4,340 mg/L while the flushing water contents were 1% and 4% in sections 298.0–305.1 m and 478.0–487.5 m, respectively. The redox potential measurements were successful and stabilised at approximately –281 mV (298.0–305.1 m) and –258 mV (478.0–487.5 m). The colloid content measured by Laser-Induced Breakdown Detection (LIBD) amounted to 30–50 µg/L in section 478.0–487.5 m. The organic constituents were present mainly as low molecular weight acids < 1,000 D. However, presence of the larger sized fractions between 1,000 D and 5,000 D as well as > 5,000 D were observed in section 478.0–487.5 m.

The groundwater composition in the deepest investigated borehole section at 478.0–487.5 m assigned to deformation zone ZFMA2, indicates mainly Littorina origin of the groundwater. The Littorina character of the groundwater in section 436.9–437.9 m is less pronounced while the more shallow section at 298.0–305.1 m shows non-marine origin and reveals a strong glacial signature.

# Sammanfattning

Fullständig kemikkarakterisering är den mest omfattande kemiska undersökningsmetoden för kärnborrhål. Metoden innebär pumpning, mätning on-line och regelbunden vattenprovtagning för kemiska analyser i avgränsade borrhålssektioner under cirka tre veckor per sektion med ett pumpflöde på mellan 50 och 200 mL/min.

Metoden har utförts i två sektioner av borrhålet KFM10A vid 298,0–305,1 m borrhålslängd (vertikalt djup 215 m) och vid 478,0–487,5 m borrhålslängd (vertikalt djup 328 m). Resultaten omfattar mätningar on-line av redoxpotential, pH, löst syre, elektrisk konduktivitet och vattentemperatur i borrhålssektionen liksom kemiska analyser av huvudkomponenter, spårelement, isotoper samt bestämning av gasinnehåll och sammansättning. Vidare undersöktes oorganiska och organiska kolloider (humus och fulvosyror) med fraktioneringsteknik och från sektion 478,0–487,5 m utfördes också detektering genom laserinducerad nedbrytning (LIBD).

Dessutom togs ytterligare ett prov från en spricka med låg transmissivitet ( $1E-9 \le T < 1E-8 \text{ m}^2/\text{s}$ ). För det senare provet användes en specialutrustning för provtagning av sprickor med låg hydraulisk transmissivitet, Sampling equipment for Low-Transmissive fractures (SLT). Sektionen omfattade 436,9–437,9 m borrhålslängd (vertikaldjup 301 m) och det uttagna vattenprovet analyserades enligt SKB klass 3 med tillval av isotoper och uran.

Grundvattnet i sektionen 298,0–305,1 m visade en trend med något ökande salinitet under undersökningsperioden, medan den först ökade för att sedan gå ner igen i sektionen vid 478,0–487,5 m. Kloridkoncentrationerna i de sista proven uppgick till 4 050 mg/l och 4 340 mg/l medan spolvattenhalterna var 1 % och 4 % i sektion 298,0–305,1 m respektive 478,0–487,5 m. Redoxpotentialmätningarna var lyckade och stabiliserade sig på –281 mV (298,0–305,1 m) och –258 mV (478,0–487,5 m). Kolloidkoncentrationen mätt med Laser Induced Breakdown Detection (LIBD) uppgick till 30–50 µg/L i sektionen 478,0–487,5 m. De organiska komponenterna förekom huvudsakligen som lågmolekylära syror < 1 000 D. Även om förekomst av fraktioner med större molekyler, dvs mellan 1 000 D och 5 000 D samt > 5 000 D, kunde observeras i sektionen 478,0–487,5 m.

Grundvattensammansättningen i den djupaste borrhålssektionen vid 478,0–487,5 m som tillskrivs deformationszonen ZFMA2, indikerar att grundvattnet huvudsakligen har Littorina ursprung. Littorinakaraktären hos grundvattnet i sektionen vid 436,9–437.9 m är mindre uttalad medan den övre sektionen vid 298,0–305,1 m visar på icke-marint ursprung och avslöjar en tydlig glacial signatur.

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# 1 Introduction

This document reports performance and results of the activity Complete Chemical Characterisation in borehole KFM10A within the site investigation programme at Forsmark /1/. The work was conducted according to the activity plan AP PF 400-06-095. The report presents hydrogeochemical data from field work carried out during October to November 2006. Besides sampling for complete chemical characterisation in two borehole sections, sampling using the Sampling equipment for Low-Transmissive fracture (SLT) was also performed.

The controlling documents for the activity are listed in Table 1-1. The activity plan, the method description and the measurement system descriptions constitute SKB's internal controlling documents. Original data from the reported activity are stored in the primary database Sicada. Data are traceable in Sicada by the Activity Plan number (AP PF 400-06-095). Only data in databases are accepted for further interpretation and modelling. The data presented in this report are regarded as copies of the original data. Data in the databases may be revised, if needed. However, such revision of the database will not necessarily result in a revision of this report, although the normal procedure is that major data revisions entail a revision of the P-report. Minor revisions are normally presented as supplements available at www.skb.se.

Sampling for microbe studies, based on the activity plan AP PF 400-05-66, was also performed within the present activity. The microbe investigations will be reported in a separate primary data report /2/.

Borehole KFM10A is a telescopic borehole /3/ and its location together with other current deep telescopic and conventional core-drilled boreholes within the investigation area are shown in Figure 1-1. Figure 1-2 presents a detailed map of drill site DS10 with KFM10A and nearby situated percussion drilled boreholes indicated. KFM10A is inclined at 50°, dipping north-northeast. The borehole section between 0–60.7 m is percussion drilled and has a stainless steel casing with an internal diameter of 200 mm, whereas the 60.7–500.2 m interval is core drilled with a diameter of 75.8 mm. The design of the borehole is presented in Appendix 1. The borehole is of the so-called SKB chemical-type; see the SKB method descriptions MD 620.003 (Method description for drilling cored boreholes) and MD 610.003 (Method description for percussion drilling). An SKB chemical-type borehole requires cleaning procedures to be carried out on all equipment used in the borehole, both during and after drilling, according to level 2 in the cleaning instructions outlined in MD 600.004 (Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning).

Activity plan	Number	Version
Fullständig kemikaraktärisering med mobilt fältlaboratorium i KFM10A.	AP PF 400-06-095	1.0
Method descriptions and documentations	Number	Version
Metodbeskrivning för fullständig kemikaraktärisering med mobilt fältlaboratorium.	SKB MD 430.017	2.0
Enkel provtagning i hammarborrhål och kärnborrhål.	SKB MD 423.002	2.0
Instruktion för rengöring av borrutrustning och viss markbaserad utrustning.	SKB MD 600.004	1.0
Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhål- sutrustning, mobil ytChemmac och dataapplikation.	SKB MD 434.004 SKB MD 434.005 SKB MD 434.006 SKB MD 434.007 SKB MD 433.018	1.0 1.0 1.0 1.0 1.0
Mätsystembeskrivning för fraktionering av humus- och fulvosyror	SKB MD 431.043	1.0
Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror.	SKB MD 431.044	1.0
Provtagning och analys-kemilaboratorium.	SKB MD 452.001-019	-

#### Table 1-1. Controlling documents for performance of the activity.



*Figure 1-1.* The investigation area at Forsmark (approximately the area shown) with the candidate area selected for more detailed investigation. The current telescopic and conventional core drilled boreholes are marked with pink filled circles.



*Figure 1-2.* Location and projection on the horizontal plane of the telescopic borehole KFM10A and the percussion borehole HFM24 which served as flushing water well at drill site DS10.

# 2 Objectives and scope

Complete chemical characterisation using an SKB mobile field laboratory (MFL) is the most extensive chemical investigation method performed in core-drilled boreholes. The method is carried out in order to obtain as much information as possible about the chemical conditions in the groundwater from individual water-bearing fractures or fracture zones. Considerable effort is put into obtaining representative samples from a limited rock volume. Careful pumping and continuous control of the pressure in the sampled borehole section, as well as above the section, is maintained in order to minimise the risk of mixing with groundwaters from other fracture systems.

It has been decided to prioritise the north-western part of the Forsmark candidate area for the continuing investigations /4/. Borehole KFM10A is located at the southern limit of this prioritised part, and hydrochemical investigations in this borehole are interesting mainly for two reasons: 1) in order to verify the hypothesis that the groundwater conditions are different within and above the deformation zone ZFMA2 compared to below the zone /5/ and 2) in order to obtain hydrochemical data from an additional location/borehole section representing the deformation zone ZFMA2.

The analytical programme was carried out according to SKB chemistry class 3 (SLT), class 4 and class 5 (MFL) including all options /1/. Furthermore, pH, redox potential (Eh) and water temperature were measured in flow-through cells downhole as well as at the ground surface. The flow-through cell at the surface also measured electrical conductivity and dissolved oxygen. Samples were collected in situ in the borehole sections for determination of gas content and composition, microbe content and their physiological characteristics, and determinations of colloid contents by LIBD technique as well as by colloid filtration. Fractionation of organic acids and inorganic species were performed in order to investigate size distribution (DOC and ICP analyses), and enrichment of organic acids was conducted in order to determine  $\delta^{13}$ C and pmC in organic constituents.

# 3 Background

## 3.1 Flushing water history

The percussion drilled borehole HFM24 /6/ served as a supply well for the flushing water used to drill borehole KFM10A. The chemical composition of the flushing water was analysed once to check the suitability before drilling and once during drilling of KFM10A /3/. The composition of the flushing water was of dilute groundwater type, with a chloride concentration of 500 mg/L. The core drilling of the 500.16 m long borehole consumed 479 m<sup>3</sup> of flushing water and the volume of returned water pumped from the borehole by air-lift pumping during drilling was 926 m<sup>3</sup>. After drilling, nitrogen flushing was carried out four times from the bottom of the borehole, resulting in the discharge of an additional volume of 20 m<sup>3</sup> borehole water.

Automatic dosing equipment for injection of Uranine was installed in the water line that supplies flushing water to the drilling head. The Uranine concentration in the flushing water and returned water was checked regularly and a total of 80 samples of each sample type were analysed. The Uranine concentrations in the flushing water and in the returned water are presented in Figure 3-1. A water budget, presenting the amount of Uranine added to the borehole via the flushing water and the estimated amount recovered in the return water, is given in Table 3-1.

Table 3-1. Amount of Uranine added to KFM10A via the flushing water during core drilling and the amount recovered from the air-lift pumping.

Uranine	(g)
Added, according to the log book.	95
Added, calculated from the average Uranine concentration and the total volume of flushing water.	84
Recovered, estimated from the average Uranine concentration and the total volume of returned water.	116



*Figure 3-1.* Uranine concentrations in the flushing water and in the recovered water versus borehole length.

The Uranine budget in Table 3-1 suggests that only a few cubic metres (corresponding to the error in the budget calculation) of the flushing water might have been lost to the borehole and the adjacent host bedrock during drilling. Additional cleaning was also carried out by nitrogen flushing after drilling. However, no Uranine analyses were performed on the discarded water during cleaning.

Borehole HFM24 was selected to supply flushing water although the concentration of total organic carbon (TOC) was too high. The TOC concentration should preferably be below 5 mg/L but the concentration in all three samples collected in HFM24 was 10 mg/L. A high TOC concentration in the flushing water could have an influence on the determinations of carbon isotopes, humic- and fulvic acids, and also on the microbe population in the investigated groundwater. As borehole KFM10A is of SKB chemical-type, the following special precautions were taken in order to minimise contamination via the flushing water:

- The supply well was also of SKB chemical-type.
- Dosing equipment for Uranine was installed, thereby removing the need for an in-line flushing water storage tank placed after the UV-system.
- In order to minimise oxygen contamination, pressurised nitrogen gas was passed through the water storage tank placed before the UV-system in the flushing water line.

The microbe content in the flushing water was not determined during drilling of this borehole. Results from borehole KFM06A /7/ convincingly showed that the cleaning procedure works well and it was concluded that checking for microbes at all drilling occasions was no longer necessary.

## 3.2 Previous events and activities in the borehole

KFM10A is an SKB chemical-type core borehole and thus specially intended for complete hydrochemical characterisation. Only those borehole activities that are necessary in order to select borehole sections for hydrochemical sampling are carried out in the borehole prior to the chemistry campaign. The more downhole equipment used in the borehole, the greater is the risk of contamination and effects on, for example, the in situ microbiological conditions. The activities/investigations performed in KFM10A prior to the chemistry campaign are listed in Table 3-2 below.

Activities performed	Date of completion	Length or section (m)	Comment
Percussion drilling Core drilling	2006-02-19 2006-06-01	0–60.7 0–500.2	HFM24 was the source of flushing water for drilling the cored part of KFM10A. HFM24 is a SKB chemical- type borehole /3, 6, 7/. Flushing water volume = 479 m <sup>3</sup> .
Flushing water treatment	-	-	Automatic dosing of Uranine was used during drilling of KFM10A. In this way there was no need for an in-line storage tank placed after the UV-system /3/.
Pressure measurements, wire-line	2006-06-20 2006-06-30	14.9–494.8 33.0–494.4	/3/
Geophysical logging	2006-06-08	0–498	/8/
BIPS-logging	2006-03-14	62–496	/9/
Differential flow logging	2006-06-29	51–494	/10/
Microbe investigation	2006-10-31	478.0-487.5	/2/
Microbe investigation	2006-11-27	298.0-305.1	/2/

Table 3-2. Activities performed in KFM10A prior to and in connection with the chemical
characterisation.

## 3.3 Choice of borehole sections

The differential flow logging /10/ of the borehole prior to the chemical investigation revealed relatively few water-bearing fractures and fracture zones. Figure 3-2 presents the hydraulic transmissivities along the borehole. The deepest fracture with high enough transmissivity to allow pumping was an obvious choice as it is located at repository depth and represents the deformation zone ZFMA2. Furthermore, it is more likely that the flushing water content is low due to the location at the bottom of the 500 m long borehole. Shorter exposure times to high pressure flushing water during drilling, as at the bottom of a borehole, is favourable from a flushing water contamination aspect.

#### Forsmark, borehole KFM10A Transmissivity and head of detected fractures

+ Fracture head

- + Transmissivity of fracture
- Head in the borehole without pumping (L = 5 m, dL = 0.5 m) 2006-06-20 – 2006-06-21
- Head in the borehole with pumping (L = 1 m, dL = 0.1 m) 2006-06-28 – 2006-06-30



*Figure 3-2. Hydraulic transmissivity along borehole KFM10A /10/. Selected fractures for chemical sampling are indicated with arrows or circles; red = hydrochemical characterisation, green = sampling of low-transmissive fractures.* 

A second water-yielding fracture at 300 m borehole length above the deformation zone ZFMA2 was selected to obtain complementary data from one more section of the borehole. Moreover, data from a section above ZFMA2 in the target area may verify the theory that the different connective properties above and within this zone affect the water composition /5/. The hydraulic transmissivity of this fracture is rather low, just exceeding 10<sup>-8</sup> m<sup>2</sup>/s, which increases the possibility of reaching sufficiently low flushing water contents within the planned pumping/measurement period.

Two or three sections were selected for sampling using the equipment for fractures with low transmissvity (SLT). This equipment has been used successfully in one previously investigated borehole (KFM01D) /11/, PIR-06-32 (Test av provtagningsutrustning för sprickor med låg hydraulisk transmissivitet i KFM01D). It is likely that groundwater in such fractures represent the type of water that will prevail at the location of a future repository for spent nuclear fuel. Therefore, it is interesting to investigate this type of water in more than one borehole.

The selected low-transmissive fractures that fulfil the equipment requirements, i.e. welldefined single, water-bearing fractures ( $1E-9 \le T < 1E-8 \text{ m}^2/\text{s}$ ) with adjacent bedrock of good quality are indicated in green colour in Figure 3-2. The other two sections for complete chemical characterisation are indicated in red. Section limits, vertical depths and hydraulic transmissivity values are given in Table 3-3.

The differential flow logs for relevant parts of the borehole are presented in Appendix 2 and the corresponding images from BIPS-logging (Borehole Image Processing System) are presented in Appendix 3. No image from the BIPS-logging of the investigated low- transmissive fracture is presented, as the fracture/fractures are too diffuse features to be displayed.

Section (m)	Elevation mid sect. (m.b.s.l.)	T <sub>D</sub> (m²/s) /11/	Comments
254.9 (fracture position)	183	2.6E-9	Planned for SLT but not investigated
297.99–302.99	214	3.4E-8	T (5 m), hydrochemical characterisation (MFL)
368.4 (fracture position)	258	3.3E–9	Planned for SLT but not investigated
436.9–437.9	301	4.7E–9	T (fracture), SLT equipment
478.23-483.23	327	5.0E-8	T (5 m), hydrochemical characterisation (MFL)

Table 3-3. Selected borehole sections for hydrochemical sampling and corresponding hydraulic transmissivities calculated from differential flow logging ( $T_D$ ).

# 4 Equipment

## 4.1 The mobile field laboratory

The mobile field laboratories used by SKB for water sampling and downhole measurements consist of a laboratory unit, a separate computer unit (MYC), a hose unit with downhole equipment and a Chemmac measurement system. The equipment setup is presented in Figure 4-1. The different parts of the system are described in the SKB internal controlling documents SKB MD 434.004, 434.005, 434.006, 434.007 and SKB MD 433.018 (Mätsystembeskrivningar för mobila kemienheter – Allmän del, Slangvagn, Borrhålsutrustning, Mobil Yt-chemmac and Dataapplikation).



*Figure 4-1.* The mobile laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.

The Chemmac measurement facilities include communication systems, measurement application and flow-through cells with electrodes and sensors at the ground surface (surface Chemmac) and downhole (borehole Chemmac).

The downhole equipment comprises inflatable packers, pump, borehole Chemmac and the in situ sampling unit (PVP), allowing measurement (borehole Chemmac) and sampling in situ in the borehole section (PVP sampling unit). The four sampled portions of groundwater collected with the PVP sampling unit maintain the pressure from the borehole section when raised to the surface. The portions are used for colloid and gas analysis and microbe investigations.

The mobile units used for the investigation of borehole KFM10A consisted of the hose unit S3 together with the computer unit MYC 3 including surface Chemmac. The laboratory unit L3 was employed for analytical work but was located close to the core mapping facility and not at drill site DS10.

## 4.2 Sampling equipment for low-transmissive fractures

The new unit, SLT, for sampling of groundwater in low-transmissive fractures, consists of upper and lower inflatable packers delimiting a borehole section of one metre borehole length. Furthermore, a dummy is mounted between the packers in order to reduce the water volume in the section to 0.3 L. The surface of the dummy is coated with Teflon<sup>®</sup>. The sample container (1.2 L), which is in hydraulic connection with the section, is placed above the upper packer. The different parts of the system are presented in Figure 4-2 and described in PIR-06-32 (Test av provtagningsutrustning för sprickor med låg hydraulisk transmissivitet i KFM01D).



Figure 4-2. Outline of the sampling equipment for low-transmissive fractures (SLT).

The sample container is filled with nitrogen gas at a pressure exceeding that of the hydrostatic pressure in the section during lowering of the equipment to the sampling depth. Prior to sampling, the entire system (including the sampled section, the sample container and tubings) is flushed with nitrogen gas. The flushing may be repeated in order to exchange several system volumes of water. Nitrogen gas is then slowly evacuated to decrease the pressure in the system to 200 kPa below the natural pressure, resulting in an inflow of water into the section, the sample container and into the tubing connecting to the ground surface. The filling of water is recorded by a pressure sensor. After completed sampling, the equipment is raised to the ground surface and the water is portioned into bottles and sent to laboratories for analyses.

# 4.3 Colloid filtering equipment

The colloid filtering equipment is adapted to the sample containers (PVB) from the PVP water sampling unit and consists of holders for two PVB-containers, a separate tube and valve system for water and gas, a filter holder package for five filters, and a collecting container. The pore sizes of the five connected filters were 2.0, 2.0, 0.4, 0.2 and 0.05  $\mu$ m in section 298.0–305.1 m and 0.4, 0.4, 0.2, 0.05 and 0.05  $\mu$ m in section 478.0–487.5 m. The equipment is described in SKB MD 431.045 (Mätsystembeskrivning för kolloidfiltreringssystem, handhavandedel, SKB internal controlling document to be published). Figure 4-3 shows the equipment set-up.



*Figure 4-3.* The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1 to 4, show the flow direction of the sample water through the system.

The major features are:

- Filtering is performed in a closed system under an argon atmosphere, thus avoiding the risk of iron precipitation due to contact between the groundwater sample and air.
- Filtering is performed at a pressure similar to that of the groundwater in the borehole section. The system is adjusted to create a pressure difference between the inlet of the filter package and the outlet side. The pressure difference drives the sample water through the filters.
- The design of the sample containers, and the mounting with the outlet at the top, prevents migration of larger particles that may clog the filters. Furthermore, clogging is prevented by the first two filters with pore sizes 2.0 or  $0.4 \,\mu\text{m}$  which are mounted parallel to each other.

Disadvantages/drawbacks, which may cause modifications of the equipment later on, are:

- The sample volume is limited to a maximum of  $2 \times 190$  mL.
- The PVB sample containers are made of stainless steel which may contaminate the samples. An improvement could be to use Teflon coating on the insides of the cylindrical containers.

# 4.4 Equipment for enrichment of humic and fulvic acids

Enrichment of humic and fulvic acids is conducted in order to collect enough material to determine  $\delta^{13}$ C and pmC (percent modern carbon) on organic constituents in the groundwater. The equipment for enrichment includes a porous column filled with an anion exchanger (DEAE-cellulose) and a textile filter with a well-defined pore size. The textile filter is placed inside the column in order to prevent the ion exchange resin from diffusing through the column. The equipment and performance is described in SKB MD 431.044 (Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror). Figure 4-4 shows the equipment setup. Since the ion exchange resin in the column creates a counter-pressure that disturbs the water flow through the surface Chemmac, a pump was used for pumping a portion of the outlet water through the column (approximately 1.8 L/hour).



Figure 4-4. The ion exchange column. The arrows show the water flow direction.

# 4.5 Equipment for fractionation of humic and fulvic acids

The equipment consists of membrane filters with a defined cut-off (pore size), a membrane pump, flexible tubing and vessels. Generally, two sample portions from each section are passed through filters with cut-offs of 1,000 D and 5,000 D, respectively (D = Dalton, 1D = 1 g/mol). The equipment and performance are described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror). Figure 4-5 schematically describes the function of a membrane filter and Figure 4-6 shows the equipment setup.



Figure 4-5. Outline of membrane filter with water flow directions.



Figure 4-6. Equipment for fractionation of humic and fulvic acids.

# 5 Performance

## 5.1 General

Chemical characterisation in borehole KFM10A was conducted according to activity plan AP PF 400-06-095 following the method described in SKB MD 430.017 (Metodbeskrivning för fullständig kemikarakterisering med mobilt fältlaboratorium). Table 5-1 gives an overview of the investigation sequence in KFM10A.

# 5.2 Chemical characterisation

### 5.2.1 Overview of field work procedure

A short chronological summary of the different steps that constitute chemical characterisation of groundwater in a borehole section is given below.

Preparations before the downhole equipment is lowered in the borehole include:

- Cleaning the inside of the umbilical hose (the sample water channel) with de-ionised and de-oxygenated water. Finally, the sample water channel is filled with de-ionised and de-oxygenated water prior to lowering.
- Cleaning and preparation of the four sample containers (PVB) belonging to the in situ water sampling unit (PVP). The containers are cleaned on the outside using 70% denatured ethanol and on the inside using chlorine dioxide. One of the containers is used for microbe sampling and sterile conditions are desirable. The containers are purged with nitrogen or argon gas and a small gas pressure is maintained in the containers. The magnitude of the pressure depends on the depth of the section to be sampled and in this case an overpressure of 5 bars was used.
- Calibration of the pH and redox electrodes in the downhole Chemmac equipment.

The different downhole units are assembled during lowering of the equipment down the borehole and the following steps are taken:

- The outside of the umbilical hose is cleaned with 70% denatured ethanol (SKB MD 600.004).
- Calibration of the umbilical hose length is conducted at least once for each borehole. For this purpose, a length mark detector unit (caliper) is mounted together with the regular downhole equipment. The length mark detector indicates length calibration marks milled into the borehole wall at almost every 50 m along the borehole /3/. At each indication, a reading is made of the corresponding length mark on the umbilical hose. The correct distance to each length mark is obtained from the Sicada database.

Start date/ Stop date	Investigation	Section	Comment
2006-10-09/	Complete chemical characterisation	478.0-487.5	Pumped volume = 4.9 m <sup>3</sup> .
2006-11-03			Flow rate approx. 160 mL/min.
2006-11-02/	Complete chemical characterisation	298.0-305.1	Pumped volume = 1.7 m <sup>3</sup> .
2006-11-28			Flow rate approx. 50 mL/min.
2006-11-29/ 2006-11-30	Sampling of a low- transmissivie fracture	436.9–437.9	-

#### Table 5-1. Investigation sequence in KFM10A.

When the pump is started and the packers are inflated at the desired positions in the borehole, a pumping and measurement period begins. Typical measures taken and activities carried out during this period are:

- Calibration of the pH and redox electrodes as well as the electrical conductivity and oxygen sensors in the surface Chemmac is conducted when the pumped water from the borehole section has reached the surface.
- Careful attention is paid in order to ensure that the packed-off section is well isolated from the rest of the borehole. A significant drawdown in the section during pumping is one indication that the section is properly sealed off. Leakage would cause pumping of water from the borehole column above and/or below the packers and not only from the fracture zone of interest. However, the drawdown in the borehole section must not be too large, because the greater the drawdown, the larger the bedrock volume affected by the pumping, and the risk of mixing with groundwater from other shallower and/or deeper fracture systems increases. The pumping flow rate is adjusted depending on the flow yield from the fracture or fracture zone (to between 50 and 200 mL/min) and maintained more or less constant during the pumping and measurement period.
- Water samples are collected regularly once or twice a week during the pumping period. Changes in water composition are monitored by conductivity measurements and by immediate analyses (pH, Uranine, chloride, alkalinity, ferrous and total iron, and ammonium) at the site.
- Enrichment of humic and fulvic acids is conducted for as long a time as possible in each section. The time needed depends on the organic carbon concentration in the water and the flow rate through the ion-exchanger. Generally, a period of at least two weeks is needed to collect the amount of carbon required to determine δ<sup>13</sup>C and pmC.
- Fractionation of humic and fulvic acids, as well as inorganic species to determine the size distribution, is performed at the end of the pumping period.
- A decision when to terminate the sampling work in the section is made during a suitable stage of the pumping and measurement period. The investigation might be prolonged if the concentration of flushing water exceeds 1% or if the redox potential measurements have not reached stable values. A final SKB Class 5 sample including options is collected the day before termination.

Completion of the investigation in the section and lifting of the downhole equipment entails:

- Collection of in situ samples prior to lifting the equipment. The valves to the PVB sampling containers in the borehole section are opened in order to rinse the system and fill the containers. After a few hours the valves are closed and the water sample portions for analyses of colloids, dissolved gases and microbes are secured.
- Following stopping of the borehole pump and deflation of the packers, the equipment is lifted and the different downhole units are dismantled.
- Calibration of the electrodes in the downhole Chemmac and surface Chemmac.

## 5.2.2 Performance in section 298.0–305.1 m

The chemical characterisation in section 298.0–305.1 m was performed using the following configuration of the downhole equipment in the borehole, from the top: umbilical hose, length mark detector, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP), and lower packer, see Appendix 4. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping flow rate was about 50 mL/min and the drawdown approximately 45 m at the end of the measurement period. Diagrams showing the pressures above and within the borehole section and the flow rate during the pumping/measurement period are presented in Appendix 5. The events during the investigation are listed in Table 5-2.

Date	Event	Sample no.
061102	Calibration of borehole Chemmac	
	Lowering of downhole equipment S3 (298.00–305.14 m)	
	Start of Chemmac measurements	
061103	Calibration of surface Chemmac, MYC3	
061103	Water sampling: SKB class 2	12520
061106	Loss of contact with the borehole equipment. Restart of the measurement application	
061109	Lifting due to loss of contact with the borehole equipment	
	Lowering of equipment	
061110	Lifting of the equipment due to defective umbilical hose	
	Lowering of equipment	
061113	Water sampling: SKB class 4	12541
061115	Lifting due to repair of the umbilical hose	
	Calibration of borehole Chemmac	
	Lowering of equipment	
061117	Humic and fulvic acids; enrichment start	
061117	Water sampling: SKB class 5	12543
061120	Water sampling: SKB class 5	12544
061122	Humic and fulvic acids; fractionation 1 kD	12552
061123	Humic and fulvic acids; fractionation 5 kD	12552
061123	Water sampling: SKB class 4	12551
061126	Humic and fulvic acids; enrichment stop	
061127	Water sampling: SKB class 5, all options	12552
	PVP-sampler: raised pressure and opening of valve at 12:17	
061128	PVP-sampler: closure of valve at 06:00	
	Sampling for colloids, microbes and dissolved gases	12552
	Humic and fulvic acids; enrichment eluation	12552
	End of Chemmac measurements	
	Raising equipment	
	Calibration of borehole Chemmac	
	Calibration of surface Chemmac	

 Table 5-2. Events during the complete chemical characterisation pumping/measurement.

#### 5.2.3 Performance in section 478.0–487.5 m

The chemical characterisation in section 478.0–487.5 m was performed using the following configuration of the downhole equipment in the borehole, from the top: umbilical hose, length mark detector, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP), 2 m long extension and lower packer, see Appendix 4. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively. The estimated average pumping flow rate was 160 mL/min and the drawdown approximately 0.4 m at the end of the measurement period. Diagrams showing the pressures above and within the borehole section and the flow rate during the pumping/measurement period are presented in Appendix 5. The events during the investigation are listed in Table 5-3.

Date	Event	Sample no.
061009	Calibration of borehole Chemmac	
061011	Lowering of downhole equipment S3 (478.00–487.49 m)	
	Start of Chemmac measurements	
061012	Calibration of surface Chemmac	
061012	Water sampling: SKB class 2	12504
061016	Humic and fulvic acids; enrichment start	
061016	Water sampling: SKB class 4	12505
061018	Water sampling: SKB class 5	12508
061023	Water sampling: SKB class 5	12509
061023	Loss of contact with the equipment, restart of the measurement application	
061025	Humic and fulvic acids; fractionation 1 kD	12517
061026	Humic and fulvic acids; fractionation 5 kD	12517
061027	Water sampling: SKB class 4	12516
061030	Water sampling: SKB class 5, all options	12517
	PVP-sampler: raised pressure and opening of valve at 17:39	
	Humic and fulvic acids; enrichment stop	
061031	PVP-sampler: closure of valve at 06:10	
	Sampling for dissolved gases and microbes	12517
	Raising equipment	
	Lowering of equipment	
061102	PVP-sampler: raised pressure and opening of valve at 08:35	
	PVP-sampler: closure of valve at 09:37	
	Sampling for colloids (LIBD and colloid filtration)	12517
	End of Chemmac measurements	
	Raising equipment	
	Calibration of borehole Chemmac	
	Humic and fulvic acids; enrichment eluation	12517
061103	Calibration of surface Chemmac	

Table 5-3. Events during the complete chemical characterisation pumping/measureme	ent
period in section 478.0–487.5 m.	

## 5.2.4 Water sampling, sample treatment and analyses

The pumped water from the borehole section is led from the hose unit into a container furnished with a sink and a tank for collecting the outlet water. Filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. A water sample is defined as groundwater collected during one day and consists of several sample portions, labelled with the same sample number.

An overview of sample treatment and analysis methods is given in Appendix 6. The routines are applicable independently of sampling method or type of sampling object.

## 5.2.5 Collection of in situ water samples

The in situ water sampling in the borehole section was conducted successfully in both of the borehole sections. In section 478.0–487.5 m the in situ sampling was repeated in order to obtain samples also for colloid determination using laser-induced breakdown detection, LIBD, see Appendix 7. The purpose of each sample portion is given in Table 5-4.

All of the PVB-containers were quality controlled before use; this procedure includes disassembling of the container, thorough cleaning, reassembling and measurement of piston friction. The filled PVB-containers were packed together with ice packs in insulated bags and sent to the laboratories by express delivery service immediately after sampling.

Sample portion no.	Section 298.0–305.1 m 2006-11-28	Section 478.0–487.5 m 2006-10-31	Section 478.0–487.5 m 2006-11-02
1	Dissolved gas	Dissolved gas	Colloids (LIBD)
2	Microbes	Dissolved gas	Colloids (LIBD)
3	Colloids	Microbes	Colloids
4	Colloids	-	Colloids

 Table 5-4. Collection and purpose of in situ water sample portions.

## 5.2.6 Colloid filtration

The method for sampling of colloids in groundwater entails filtering the groundwater through a series of connected filters in a closed system under an argon atmosphere. The pressure in the system is maintained at the same level as the pressure in the sampled borehole section. The intention is that colloids should be collected on the different filters (descending pore sizes) according to their sizes. Two of the sample portions from each section were used for colloid filtration. Data on performance of the filtration runs are given in Table 5-5.

A leakage test of the system at 10 bars was also carried out prior to the sample filtrations in order to eliminate the risk of leakage.

Each filtration results in five filter samples and two water samples (water in and water out). The filter pore size sequences were 2.0  $\mu$ m, 2.0  $\mu$ m, 0.4  $\mu$ m, 0.2  $\mu$ m and 0.05  $\mu$ m for section 298.0–305.1 m and 0.4  $\mu$ m, 0.4  $\mu$ m, 0.2  $\mu$ m, 0.05  $\mu$ m and 0.05  $\mu$ m sizes for section 478.0–487.5 m. All samples were sent for ICP analyses (major constituents and common trace metals).

## 5.2.7 Enrichment of humic and fulvic acids

Enrichment of humic and fulvic acids was conducted in order to collect enough material to determine  $\delta^{13}$ C and pmC in organic constituents in the groundwater. The method is described in SKB MD 431.044 (Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror). The enrichment method entails collection of organic acids on an ion exchanger, eluation of the resin and evaporation of the resulting solution. The dry residue is used for isotope determination and a minimum amount of 10 mg organic carbon is needed. In addition to organic material, the residue also contains sodium hydroxide from the eluation. The sample is acidified in order to prevent the formation of carbon dioxide.

Estimates of total time duration and water volume through the ion exchanger are given in Table 5-6.

Section/ date	Entering pressure [bar]	Max. differential pressure over filter package [bar]	Temp. [°C]	Filtering time [min]	Filtered volume [ml]	Comments	
298.0–305.1 m /20061128	~22	3.4	~13	28	269	Leakage test prior to filtration. No leakage was noticed. No broken filters.	
478.0–487.5 m /20061102	~32	3.1	~10	120	276.5	Leakage test prior to filtration. No leakage was noticed. No broken filters.	

Table 5-5.	Colloid	filtration.	data on	performance.

Table 5-6. Enrichment time and water volume through the ion exchanger.

Borehole section (m)	Duration of enrichment (days)	Volume through ion exchanger (L)
298.0-305.1	9	383
478.0–487.5	14	1,206

#### 5.2.8 Fractionation of organic and inorganic species

Humic and fulvic acids were fractionated with respect to molecular weight using an ultrafiltration technique. The method is described in SKB MD 431.043 (Mätsystem-beskrivning för fraktionering av humus- och fulvosyror).

Sampled water from the investigated section was first filtered through a 0.40  $\mu$ m filter and then through special membrane filters with cut-off sizes of 1,000 D and 5,000 D, respectively. The initial water volume, prior to filtration, was approximately 5 litres. The final retentate and permeate volumes following the filtration runs were approximately 1 and 4 litres, respectively, which gave an enrichment factor of five in the retentate.

Water samples were collected from the retentate and permeate as well as from the untreated groundwater. Each sample was analysed for dissolved organic carbon (DOC), major constituents, common trace metals and uranium. The analyses of metal ions indicate if metals such as Al, Si, Mn, Fe and U exist as colloidal species.

# 5.3 Sampling of a low-transmissive fracture (SLT), section 436.9–437.9 m

The equipment for sampling of groundwater in low-transmissive fractures (SLT) was used in section 436.9–437.9 m on November 29–30, 2006. The sampling method is discussed thoroughly in PIR-06-32 (Test av provtagningsutrustning för sprickor med låg hydraulisk konduktivitet i KFM01D). Registrations of the hydrostatic pressure as well as the pressure in the sample container make it possible to follow the course of sampling. The resulting pressure curves during flushing and sampling as well as lifting the equipment are presented in Figures 5-1 to 5-3 below.

Table 5-7 compares the theoretical filling time calculated from the hydraulic transmissivity with the real filling time. The discrepancy may be due to either water intrusion at a point between the sample container and the valve system or misplaced packers giving a section that includes also one of the adjacent more transmissive fractures. However, the cause may also be error in the determined T-value or a change in the transmissivity caused by the pumping. Compared to the pressure graphs from KFM01D, the KFM10A graphs show less distinct features /11/. The reason for this is not known.

Section (m)	Mid.section elevation (m.b.s.l.)	Transmissivity (m²/s)	Number of nitrogen flushings	Theoretical filling time (min)	Real filling time (min)	Sample no
436.9–437.9	301	4.7E–9	1	298	11	12553 SKB class 3

$\cdots$
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*Figure 5-1.* Registration of pressures during flushing, section 436.9–437.9 m. P1V (hydrostatic pressure), P2V (pressure in sample container), A (nitrogen flushing), B (all the water in the borehole section is pressed out after the second flushing), C (lowering of the pressure (P2V compared to the hydrostatic pressure (P1V)).



**Figure 5-2.** Registration of pressures during filling, section 436.9–437.9 m. P1V (hydrostatic pressure), P2V (pressure in sample container). When the desired depression of two bars is reached, filling of the section and the sample unit begins at (D). Filling of the section and the sample unit has been completed at (E). At (F) the pressures are equal and no more water enters the system.



**Figure 5-3.** Registration of pressures while raising the equipment, section 436.9–437.9 m. P1V (hydrostatic pressure), P2V (pressure in sample container). Increase of pressure in sample container (P2V) to 4–5 bars above the hydrostatic pressure P1V at (G). The pressure difference is maintained (H).

# 6 Nonconformities

The hydrochemical characterisation in KFM10A has been conducted according to the SKB internal controlling documents AP PF 400-06-095 and SKB MD 430.017 with the following deviations and remarks:

- During the period November 7–15<sup>th</sup>, the borehole Chemmac measurements were not recorded in section 298.0–305.1 m due to a malfunction of the measurement device. The borehole electrodes were calibrated before resuming the measurements.
- The allowed upper limit for flushing water content, 1%, was exceeded in sections 298.0–305.1 m (4–5%), and 436.9–437.9 m (4%). In section 478.0–487.5 m, the limit was partly exceeded (0.5–3.6%).
- Only one of the planned low-transmissive sections was sampled with the SLT equipment, partly due to time constraints. When raising the equipment from this first section, it got stuck in the borehole cone at about 60 m borehole length, and the borehole cone was elevated together with the equipment. A necessary restoration of the borehole was conducted which prevented further sampling.
- In section 298.0–305.1 m the determination of pmC for organic constituents resulted in an incredibly high value (530.5%). The conclusion was that this was caused by the use of contaminated de-ionised water from the nuclear power plant for laboratory purposes. The corresponding activity was estimated to only 4.5 mBq/L, which is very far from any emission limit value. However, the incident is a reminder of that closeness to nuclear reactors or supply of water from a power plant may cause artefacts.
- The ICP analyses of the element Si on filters may be erroneous due to an unsuitable method for dissolution of the filters prior to the analyses.  $HNO_3$  has been used for the dissolution instead of HF and all Si contents less the 20  $\mu$ g may be too low. This is the case also for filter samples from previous boreholes and comments on the Si results are inserted in Sicada.

# 7 Data handling and interpretation

# 7.1 Chemmac measurement data

The processing of Chemmac data is described in SKB MD 434.007 version 2 (Mätsystembeskrivning för Chemmac mätsystem, SKB internal controlling document, in progress).

## 7.1.1 Data file types and calculation software

The on-line measurements in a borehole section produce the following types of raw data files:

- Calibration files from calibration measurements (\*.CRB) and corresponding comment files (\*.CI). The files are used for calculation of calibration constants (pH and Eh) and the calibration factor (electrical conductivity). For the surface Chemmac ten \*.CRB and ten \*.CI files are produced, and for borehole Chemmac six \*.CRB and six \*.CI files.
- Raw data file containing the logged measurements from the borehole section and the surface (\*K.MRB) as well as a corresponding comment file (\*.MI). The logged voltage values need to be converted to pH and Eh values (also in mV) using the calibration constants obtained from instrumental calibration.
- Measurement file including equipment and environment parameters (\*O.MRB), such as power consumption in the downhole Chemmac unit and temperature inside the hose unit.

The original raw data files listed above are stored in the Sicada file archive. Furthermore, the files are re-calculated and evaluated to obtain pH and redox potential values and to correct the electrical conductivity values using the specially designed calculation software (Hilda). The resulting files containing calculated and evaluated values as well as comments on the performance are:

- A file *\*constants.mio* containing all the calculated calibration constants (one constant for each electrode in each buffer solution). The file is stored in the Sicada file archive and is useful for following the performance of single electrodes.
- A file *\*measurements.mio* containing the calculated and evaluated measurement values (pH, redox potential, electrical conductivity and water temperature). The data from the file are exported to the data tables "redox" and "ph\_cond" in Sicada. As the file also contains some measured parameters that are not included in the tables mentioned above (e.g. pressure registrations), the complete file is also stored in the Sicada file archive.
- A file *\*comments.mio* containing comments on the field work and the calculation/evaluation. The comments in the file are imported as activity comments in Sicada.

## 7.1.2 Calculation and evaluation of redox potential and pH

The redox potential is measured by three electrodes at the surface and three in the borehole section. In addition, pH is measured by two electrodes at the surface and two downhole in the borehole section. The registrations by the redox and the pH electrodes are logged each hour during a measurement period of approximately three weeks and a calibration is performed before and after the measurement period. The treatment of the raw data includes the following steps:

- Calculation and choice of calibration constants.
- Calculation of one pH and one redox potential sequence for each electrode (i.e. three or six redox electrodes and two or four pH electrodes).
- Determination of representative pH and redox potential values as well as estimated measurement uncertainties for the investigated borehole section.

One calibration constant is selected for each electrode using one of the following alternatives:

- Case 1: Calculation of the average calibration constant value and the standard deviation. The initial and the final calibration measurements result in four constants for each redox electrode (in pH 4 and pH 7 buffer solutions) and six constants for each pH electrode (in pH 4, 7 and 10 buffer solutions).
- Case 2: The calibration constant obtained from the initial calibration measurement at pH 7 is selected since it is closest to the pH of the borehole water. This alternative is chosen if the calibration constants obtained in the different buffers show a large variation in values (generally a difference larger than 20 mV between the highest and the lowest value). The standard deviation is calculated in the same way as in Case 1.
- Case 3: If the final calibration constants turn out to be very different (more than 20 mV) from the initial constants, a linear drift correction is needed. The reason for this is most often a drift in the reference electrode. The values and standard deviations are calculated for the initial and the final calibration constants separately and a linear correction is made between the selected initial and the selected final constant. The higher of the two standard deviation values is used in the estimation of the total measurement uncertainty.

The values in the measurement raw data file are converted to pH and Eh measurement sequences for each pH and redox electrode using the calibration constant selected as stated above.

The next step is to choose a logging occasion in a stable part of the measurement period and select a representative result for each electrode. The average values are calculated for each electrode group in order to obtain one representative value of redox potential, pH (borehole Chemmac) and pH (surface Chemmac), respectively. Obviously erroneous electrodes are omitted. The corresponding total measurement uncertainties are estimated using the standard deviations of the calibration constants and the standard deviations of the Eh and the pH values obtained by the different sets of electrodes. It is useful to evaluate pH at the surface and pH in the borehole section separately, since pH in the pumped water might differ from the pH measured in the borehole section. This is due to changes in gas pressure conditions which affects the carbonate system.

Factors considered when evaluating the measurement uncertainties in pH and redox potential (Eh) values are:

- Difference in calibration constants for each electrode and calibration/buffer solution.
- Drift in calibration constants between the initial and the final calibration.
- Stability in voltage value during the final part of the on-line measurement. A successful measurement shows no tendency of a slope.
- Agreement between the different pH and redox electrodes on the surface and in the downhole Chemmac.
- Number of electrodes showing reasonable agreement. Obviously erroneous electrodes are excluded from the calculation.

# 7.2 Water analysis data

The following routines for quality control and data management are generally applied for hydrogeochemical analytical data, independently of sampling method or sampling object.

Several components are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure on every fifth or tenth sample. All analytical results are stored in the Sicada database. The applied hierarchy path "Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database" contains two types of tables, raw data tables and primary data tables (final data tables).

Data on basic water analyses are inserted into the raw data tables for further evaluation. The evaluation results in a final reduced data set for each sample which is compiled in a primary data table named "water composition". The evaluation is based on:

- Comparison of the results from different laboratories and/or methods. The analyses are repeated if a large disparity is noted (generally more than 10%).
- Calculation of charge balance errors according to the equation below. Relative errors within  $\pm 5\%$  are considered acceptable (in surface waters  $\pm 10\%$ ).

Relative error (%)=100×
$$\frac{\sum cations(equivalents) - \sum anions(equivalents)}{\sum cations(equivalents) + \sum anions(equivalents)}$$

• General expert judgement of plausibility based on earlier results and experience.

All results from special analyses of trace metals and isotopes are inserted directly into primary data tables. In those cases where the analyses are repeated or performed by more than one laboratory, a "best choice" notation will indicate the results that are considered most reliable.

An overview of the data management is given in Figure 7-1.



Figure 7-1. Overview of data management for hydrogeochemical data.

# 7.3 Data obtained using special sampling methods

Special sampling methods include collection of in situ samples (dissolved gases and colloids) and enrichment and fractionation of humic and fulvic acids.

Separate activities, methods and sample numbers are defined in Sicada for data on dissolved gases, colloids, fractions of humic and fulvic acids as well as  $\partial^{13}$ C and pmC determined on organic constituents. All data are subjected to quality control.

## 7.3.1 Colloid filtration

The concentration of the colloid portion caught on each filter is calculated with the assumption that the water volume entering the collecting container is equal to the volume going into the system. This is not quite true as up to ten millilitres will be left in cavities in the filter holder package, and in the tubing and valves. A small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its content of the different elements is included in the analysis. The measurement uncertainty of each colloid concentration is calculated according to the equation below.

$$U = \sqrt{\left(\frac{1}{V^2} \cdot (\Delta m)^2 + \frac{m^2}{V^4} (\Delta V)^2\right)}$$

where

- U = measurement uncertainty  $[\mu g/L]$
- V = water volume through the system [L]

 $\Delta V$  = estimated volume error, 0.010 L

- m = amount on filter  $[\mu g]$
- $\Delta m$  = measurement uncertainty of the filter analysis, 20% [µg]

The calculated results of the colloid filtration are stored in Sicada.

## 7.3.2 Dissolved gases

Results from gas analyses are stored in a primary data table in Sicada without post processing or interpretation.

## 7.3.3 Enrichment of humic and fulvic acids

The pmC and  $\delta^{13}$ C values for enriched organic acids are stored in a primary data table in Sicada without post processing or interpretation.

## 7.3.4 Fractionation of organic and inorganic species

The concentrations of organic and inorganic constituents in the retentate and permeate are re-calculated to concentrations of each fraction of carbon and metal ions with molecular weight lower or higher than the cut-off size of the filter. This is done using mass balance equations as described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror). Comparison of the four concentration values from the two filters results in values for three fractions, i.e. < 1,000 D; 1,000–5,000 D and > 5,000 D, which are stored in a primary data table in Sicada.

# 8 Results

## 8.1 Chemmac measurements

The data sequences of pH, Eh, electrical conductivity, oxygen and temperature values from the Chemmac measurements in borehole sections 298.0–305.1 m and 478.0–487.5 m are plotted versus time in Appendices 8 and 9, respectively. The measured time series of data were evaluated in order to obtain one representative value of Eh, pH, electrical conductivity and dissolved oxygen for the borehole sections as described in section 7.1. Data were selected from a part of the measured time series (where the electrodes show stable values), and marked with an arrow in the diagrams in Appendices 8 and 9. The evaluated results from the measurements in the investigated sections are given in Table 8-1 together with the corresponding results from the LIBD experiments.

In section 298.0–305.1 m, the surface Chemmac electrodes stabilised at a lower level than the borehole Chemmac electrodes, which obviously had slow responses and did not stabilise properly. Therefore, only the surface electrodes were used for calculating a representative Eh value. Possible reasons for the slow response of the borehole electrodes are oxidation on electrode surfaces (which can be remediated by polishing) or clogging of the drain plug in the reference electrode.

In section 478.0–487.5 m, all six redox electrodes showed stable and consistent values at the end of the measurement period and all of them were therefore included in the calculation of the representative Eh value. As indicated by some variation in Eh and water composition, as well as drilling water content, the chemical conditions were not as stable as is usually the case. The flushing water content increased from 1% to 3% during the last three days of the measurement period. Therefore, the representative value was chosen at a point when the flushing water content was still 1%, see Appendix 9.

The pH-electrodes in the borehole and at the surface show excellent agreement in both borehole sections.

Borehole section [m]	EC* [mS/m]	pH (surface Chemmac)**	pH (borehole Chemmac)**	Eh Chemmac)** [mV]	Dissolved oxygen*** [mg/L]
298.0–305.1	1,190 ± 40	8.2 ± 0.1	8.1 ± 0.2	–281 ± 10 <sup>s</sup>	0.00 ± 0.01
478.0–487.5	1,280 ± 40	7.7 ± 0.2	7.7 ± 0.2	–258 ± 10	0.00 ± 0.01
478.0–487.5 (1)****	1,094	7.86	_	-50	< 0.023
478.0–487.5 (2)****	1,064	7.76	_	-22	< 0.018

Table 8-1. Evaluated results from the	Chemmac measurement in KFM10A.
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\* The electrical conductivity is measured between 0–10,000 mS/m with a measurement uncertainty of 3%.

\*\* Evaluated result and measurement uncertainty calculated as described in section 7.1. \*\*\* Measuring interval 0–15 mg/L, resolution 0.01 mg/L.

\*\*\*\* See Appendix 7.

<sup>s</sup> = Only values from surface Chemmac have been used in the calculation. Water analyses.

### 8.1.1 Basic water analyses

The basic water analyses include the major constituents Na, K, Ca, Mg, S, Sr,  $SO_4^{2-}$ , Cl<sup>-</sup>, Si and  $HCO_3^-$  as well as the minor constituents Fe, Li, Mn, DOC, Br<sup>-</sup>, F<sup>-</sup>, I, HS<sup>-</sup> and NH<sub>4</sub><sup>+</sup>. Furthermore, batch measurements of pH (lab-pH) and electrical conductivity (lab-EC) are included. Another important parameter is the flushing water content in each sample. The basic water analysis data and relative charge balance errors are compiled in Appendix 10, Table A10-1. Existing lab-pH and lab-Eh values are compared to the corresponding on-line Chemmac measurement values in Appendices 8 and 9.

The charge balance errors give an indication of the quality and uncertainty of the analyses of major constituents. The errors do not exceed  $\pm$  5%, in any of the analysed samples. Furthermore, the last sample in each section was also analysed by a second laboratory. A comparison between results from different laboratories and methods shows that the agreement is acceptable in most cases. Generally, depending on constituent and concentration range, the difference in concentrations between laboratories/methods for each analysed constituent in a sample is less than 10%.

The flushing water contents in the sample series collected from the two borehole sections are presented in Figure 8-1. The content should not exceed 1% in order for a sample to be considered representative for the groundwater of the sampled fracture. This condition was not met for any of the samples from section 298.0–305.1 m. The flushing water content reached its lowest value of 4.5% at the end of the measurement period. In section 478.0–487.5 m the condition was met for two out of six collected samples and three of them had values of 1% or just above. The last collected sample reached a higher value of 3.6%. The flushing water content in the sample collected with the SLT equipment was 3.8%. The percentage of flushing water in the samples was calculated using the nominal Uranine concentration (0.20 mg/L).

The chloride, calcium and sodium concentrations versus date are presented in Figures 8-2 and 8-3. The concentrations of these major constituents showed a slightly increasing trend in section 298.0–305.1 m. In section 478.0–487.5 m the flushing water content and the concentrations of major ions show opposite trends with the lowest chloride concentration at the end of the sampling period.



*Figure 8-1.* Flushing water content in the groundwater samples from sections 298.0–305.1 m and 478.0–487.5 m.



Figure 8-2. Chloride, calcium and sodium concentrations from sample series at 298.0–305.1 m.



Figure 8-3. Chloride, calcium and sodium concentrations from sample series at 478.0–487.5 m.

The iron concentrations determined by ICP-AES (total Fe) and by spectrophotometry (Fe(II) and Fe-tot) are compared in Figures 8-4 and 8-5. The total iron concentrations determined by ICP agree well with the results obtained by spectrophotometry. The iron concentrations are high in both sections but especially in section 478.0–487.5 m, where even an increasing trend is observed at the end of the sampling period. This may be an artefact from the drilling (material from wear of drilling equipment) or contamination from iron hydroxide deposits in the water channel of the umbilical hose.

Sulphate analysed by ion chromatography (IC) is compared to sulphate determined as total sulphur by ICP-AES in Figures 8-6 and 8-7. The agreement between the two analysis methods (IC and ICP-AES) is very good for the samples from section 298.0–305.1 m. In section 478.0–487.5 m, the results differ more. The discrepancies apparent in the figures are most probably due to the analytical error but presence of sulphur as other species is also possible. The results from the ICP measurements are considered more reliable, by experience, since the variations in time series often are smaller. The sulphate concentration is somewhat increasing during the sampling period in section 298.0–305.1 m, whereas in section 478.0–487.5 m, the concentration is higher and tends to decrease at the end of the measurement period.

A plot of the variation in DOC concentrations with experimental day number for the two sections 298.0–305.1 m and 478.0–487.5 m is shown in Figure 8-8. It is apparent that the DOC concentration changes very much for the last sample in the series from section 478.0–487.5 m.

The chloride concentrations are plotted versus the corresponding electrical conductivity values in Figure 8-9. The plot gives a rough check of both the measured EC values and the chloride concentrations. As shown, the data from the KFM10A agree well with the regression line obtained by previous data from the site investigation at Forsmark.



*Figure 8-4. Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole section 298.0–305.1 m.* 



*Figure 8-5. Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole section* 478.0–487.5 *m.* 



*Figure 8-6.* Sulphate (SO<sub>4</sub> by IC) to total sulphate calculated from total sulphur ( $3 \times SO_4$ -S by ICP) versus date, borehole section 298.0–305.1 m.


*Figure 8-7.* Sulphate (SO<sub>4</sub> by IC) to total sulphate calculated from total sulphur ( $3 \times SO_4$ -S by ICP) versus date, borehole section 478.0–487.5 m.



Figure 8-8. DOC concentrations in the sample series versus experimental day number.



*Figure 8-9.* Chloride concentrations versus electrical conductivity. Data from previous investigations at Forsmark are used to show the linear trend. Data from KFM10A are shown in pink.

#### 8.1.2 Trace elements (rare earth metals and others)

The analyses of trace and rare earth metals include Al, B, Ba, U, Th, Sc, Rb, Y, Zr, In, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Commonly occurring metals, such as Cu, Zn, Pb and Mo, are not included in the analysis programme due to contamination considerations. The risk of contamination is large also for aluminium but its concentration is still reported due to its importance for the modelling work. The trace element data are compiled in Appendix 10, Table A10-2.

#### 8.1.3 Stable and radioactive isotopes

The isotope determinations include the stable isotopes δD, δ<sup>18</sup>O, <sup>10</sup>B/<sup>11</sup>B\*, δ<sup>34</sup>S, δ<sup>13</sup>C, δ<sup>37</sup>Cl and <sup>87</sup>Sr/<sup>86</sup>Sr as well as the radioactive isotopes Tr (TU), <sup>14</sup>C (pmC), <sup>238</sup>U, <sup>235</sup>U, <sup>234</sup>U, <sup>232</sup>Th, <sup>230</sup>Th, <sup>226</sup>Ra and <sup>222</sup>Rn. Available isotope data at the time of reporting are compiled in Appendix 10, Table A10-3 and Table A10-4

The <sup>3</sup>H and  $\delta^{18}$ O results for section 298.0–305.1 m and 478.0–487.5 m are presented in Figures 8-10 and 8-11.

The carbon isotopes ( $\delta^{13}$ C and pmC) were determined both in inorganic carbon (hydrogen carbonate) and in organic constituents (enriched samples). In section 298.0–305.1 m, the alkalinity was too low for determination of carbon isotopes and the organic pmC was enhanced due to contamination and therefore rejected, see Chapter 6. The organic pmC was high (93.1%) also in section 478.0–487.5 m and it cannot be excluded that the value is affected by contamination. The inorganic pmC from the latter section is not reported yet at the printing date of this report.



*Figure 8-10.*  $\delta^{18}O$  and <sup>3</sup>H data versus sampling date, section 298.0–305.1 m.



*Figure 8-11.*  $\delta^{18}O$  and <sup>3</sup>*H* data versus sampling date, section 478.0–487.5 m.

## 8.2 Dissolved gas

The analyses of dissolved gases include argon (Ar), helium (He), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), oxygen (O<sub>2</sub>), hydrogen (H<sub>2</sub>), carbon monoxide (CO), ethane (C<sub>2</sub>H<sub>6</sub>), ethene (C<sub>2</sub>H<sub>4</sub>), ethyne (C<sub>2</sub>H<sub>2</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and propene (C<sub>3</sub>H<sub>6</sub>). The gas data are compiled in Appendix 10, Table A10-5.

Total gas content in the groundwater as well as the detected oxygen content is given in Table 8-2.

In total, three containers were analysed, one from section 298.0–305.1 m and two from section 478.0–487.5 m. The containers were analysed at the same laboratory using nitrogen gas for purging the samples from section 298.0–305.1 m, and argon gas (1) and nitrogen gas (2), respectively, for purging the two samples from section 478.0–487.5 m.

Table 8-2	. Total	content	of	dissolved	gas.
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	Section 298.0–305.1 m	Section 478.0–487.5 m (1)	Section 478.0–487.5 m (2)
Total gas content [mL <sup>-1</sup> ]	127	69	68
Oxygen content [mL <sup>-1</sup> ]	0.08	0.032	0.052

The total gas content is higher in section 298.0–305.1 m than in section 478.0–487.5 m and it is mainly the nitrogen content that contributes to the difference. It cannot be completely excluded that this condition, at least partly, is due too leakage of nitrogen from behind the piston of the PVB-container when purging the sample at the consulted laboratory.

When comparing the two samples from section 478.0–487.5 m, a higher argon content could be seen in container (1). When comparing the gas components, they are within the 20% margin error except for argon and oxygen. Therefore, the likely explanation for the diverging argon content is leakage of argon into the PVB-container when purging the sample at the consulted laboratory. The gas compositions of the groundwater are presented in Figures 8-12 and 8-13.

## 8.3 Colloids

The presence of colloids in section 478.0–487.5 m was investigated by two or three methods, 1) filtration through a series of connected filters in an argon atmosphere, 2) fractionation/ultra filtration using two cylindrical filters with cut-offs of 1,000 D and 5,000 D, and 3) Laser-Induced Breakdown Detection, LIBD, Appendix 7. The LIBD test was performed only in section 478.0–487.5 m.



*Figure 8-12.* Gas components of high concentrations ( $N_2$ , He, Ar, CO<sub>2</sub>, and O<sub>2</sub>) in the samples collected in sections 298.0–305.1 m and 478.0–487.5 m using the in situ sampling equipment. Bars with diagonally striped and solid colour fill patterns refer to the left and right hand axis, respectively.



**Figure 8-13.** Gas components of low concentrations (CO,  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_3H_8$  and  $C_3H_6$ ), in the samples collected in sections 298.0–305.1 m and 478.0–487.5 m using the in situ sampling equipment. Bars with diagonally striped and solid colour fill patterns refer to the left and right hand axis, respectively.

Results from the filtration experiment and the conducted LIBD test are compared in Table 8-3. The results from the filtration run are corrected by considering the remaining water volume in each filter (indicated by the sodium content) and excluding the amounts of the different dissolved elements. Furthermore, the analysed elements are re-calculated to the amounts of their most probable mineral phases (illite and iron hydroxide).

An overview of colloid concentrations in groundwater samples from boreholes KFM06A, KFM07A, KFM08A, KFM10A and KFM01D determined by LIBD has been presented in /12/.

Filtration throug Idcode/ secup/	gh series c Filtrate volume	of connec Elemer filter pe	onnected filters Element content on each Elter per litre of water (µg/L)				l phases (j	LIBD Idcode/ secup/	Content (uɑ/L)***	
filter pore size (µm)	(mL)	AI	Са	Fe	M'n	Total/ filter*	Calcite/ filter	Sum**/ three filters	run no.	
KFM10A/ 478/0.2	276.5	0.12	0	8.47	0	17.9	0		KFM10A/ 478.0/1	40
KFM10A/ 478/0.05	276.5	0.065	0	9.02	0	18.2	0			
KFM10A/ 478/0.05	276.5	0.11	0	11.3	0	23.2	0	59.3	KFM10A/ 478.0/2	31

 Table 8-3. Colloid concentrations measured in the groundwater sample from section

 478.0–487.5 m. Comparison of results obtained by filtration and by the LIBD technique.

\* Total content on each filter. Aluminium is calculated as 2.3 Al in K- Mg-illite (383.9 g/mol), and iron is calculated as  $Fe(OH)_3$  (106.8 g/mol). The silicon contents on the filters were below detection limit (see Chapter 6 for comment on reliability), the sulphur contents were also below or close to the detection limit, and the uranium contents were close to the detection limit.

\*\* Sum of content (mineral phases) on the three filters.

\*\*\* Average of all reported results, except for FOR7e (Appendix 7).

## 8.3.1 Inorganic colloids – colloid filtration

The results from the colloid filtration method for section 298.0–305.1 m and 478.0–487.5 m are presented in Figures 8-14 to 8-27.

The bars in the diagrams represent amounts ( $\mu$ g) of aluminium, iron, silicon, manganese, calcium, sulphur and uranium entering the filter package, accumulated on each filter and present in the collecting container. The amounts are calculated assuming that the water volume passing through the filters and into the collecting container is equal to the volume going into the system. This is not quite the case, as up to ten millilitres will be left in cavities in the filter holder package, and in the tubing and valves. Further, a small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its salt content is included in the analysis. The presented input amounts, in the diagrams below, represent samples taken on-line at the surface just before opening the PVB-containers for sampling.

The concentrations in blank samples (rinsing water), PVB-containers, collecting container and pumped groundwater are given in Table 8-4. The remaining water in the PVB containers after filtration was in both cases contaminated by aluminium and possibly by iron.

Analysis of blank filters showed that the contributions of iron, silica and uranium from filters were insignificant. The amounts of aluminium and manganese were of the same magnitude or lower as in the filtration test.

The following conclusions may be drawn from the colloid filtration results:

- The amounts present as colloids on the filters are generally very low.
- The amount of aluminium in the filters and found in the collecting container does not balance the input amount for section 478.0–487.5 m. As the amount of aluminium in the remaining water in the PVB was very high, a probable explanation is that settling of particles occurs, which reduces the actual input concentration.
- The amount of uranium in the filters from section 478.0–487.5 m exceeded the detection limit, which may indicate that colloidal uranium is present in this groundwater. As seen in Figure 8-25, the uranium input values were rather high which means that the percentage of uranium present as colloids is very small.

Section m	Sample origin	Al µg/L	Ca mg/L	Fe mg/L	Mn μg/L	Si mg/L	S mg/L	U µg/L
298.0–305.1	Blank, deionised water	7.9	< 0.1	< 0.002	0.114	< 0.03	< 0.2	< 0.0005
	Blank	24.8	0.455	0.0262	4.11	0.03	0.224	0.0055
	Rest volume PVB (input conc)	197	1,090	9.155	304	6.51	77.5	1.3995
	Collecting container	18.4	1,090	1.31	190	5.6	77	0.1730
	Pumped water (alt. input conc)	24.8	1,100	1.84	189	5.84	78.8	0.1650
478.0–487.5	Blank, deionised water	6.32	< 0.1	0.0014	< 0.03	< 0.03	< 0.2	< 0.0005
	Blank	10.7	0.266	0.0422	5.47	< 0.03	< 0.2	0.0079
	Rest volume PVB (input conc)	1,250 989	693 716	25.0 32.3	1,330 1,440	9.55 8.74	134 134	12.1 11.3
	Collecting container	9.57	700	11.3	1,130	6.51	138	27.9
	Pumped water (alt. input conc)	151	665	12.7	1,140	6.79	132	8.16

## Table 8-4. Element concentrations in blank water, remaining water in PVB container, collected output water from the filter system and in pumped water that has not passed the filter system.

Blank, deionised water = Deionised water from the tap, input concentration in leakage test.

Blank = rinsing water after filtration, leakage test.

Rest volume PVB = remaining water in the PVB container after filtering experiment.

Collecting container = water that has passed the filter system.

Pumped water = regular sample collected at the surface and not in situ in the borehole section.

#### Results of colloid filtering experiment, section 298.0–305.1 m.



*Figure 8-14.* Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-15.* Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-16.* Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-17.* Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-18.* Amount of uranium entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-19.* Amount of calcium entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-20.* Amount of sulphur entering the filter system (m in), in the filters and in the collecting container (m out).



Results of colloid filtering experiment, section 478.0-487.5 m

*Figure 8-21.* Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-22.* Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-23.* Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-24.* Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-25.* Amount of uranium entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-26.* Amount of calcium entering the filter system (m in), in the filters and in the collecting container (m out).



*Figure 8-27.* Amount of sulphur entering the filter system (m in), in the filters and in the collecting container (m out).

#### 8.3.2 Inorganic colloids – fractionation

Fractionations were performed from 2006-11-22 to 2006-11-23 (298.0–305.1 m) and from 2006-10-25 to 2006-10-26 (478.0–487.2 m). The samples from the fractionation experiments were analysed using ICP and the determined elements were; Ca, Fe, K, Mg, Na, S, Si, Al, Ba, Cd, Co, Cr, Cu, Hg, Li, Mn, Mo, Ni, P, Pb, Sr, V, Zn and U. Only iron, silicon, aluminium, calcium, sulphur, manganese and uranium were considered important as colloid species.

The fractionation results (see Tables 8-5 and 8-6) indicate that Si, Ca, S, and Mn exist solely as species with a molecular weight less than 1,000 g/mol. Such species are too small to be referred to as colloids. No calcite precipitation was detected. Small fractions of uranium with molecular weights more than 1,000 D and 5,000 D were observed. Furthermore, it seems that small fractions of silicon (478.0–487.2 m) and uranium (298.0–305.1 m) were precipitated during the filtering process or the directions of analytical errors have affected the calculated results unfavourably.

The results for iron and aluminium were omitted due to inconsistent analytical results. This may be due to precipitation reactions or adsorption before and during the filtering process. In addition, the error in the aluminium analyses is high due to low concentration.

The blanks (de-ionised water after passing through the washed filters) showed insignificant concentrations of silicon, calcium, sulphur, manganese and uranium.

Fraction	Si (mg/L)	Ca (mg/L)	S (mg/L)	Mn (μg/L)	U (µg/L)
< 1,000 D	4.65 ± 0.68	976 ± 117	59.6 ± 7.4	170 ± 20	0.104 ± 0.019
< 5,000 D	4.81 ± 0.70	997 ± 120	62.1 ± 7.7	168 ± 20	0.100 ± 0.020
> 1,000 D but < 5,000 D	< 0.1	< 15	< 1	< 1	< 0.004
> 5,000 D	< 0.1	< 7	< 1	< 2	0.013 ± 0.010
Adsorption 1,000 D	< 0.4	< 102	< 6	< 11	0.044 ± 0.034
Adsorption 5,000 D	< 0.5	< 106	< 7	< 15	$0.049 \pm 0.030$

Table 8-5. Inorganic fractions (< 1,000 D, 1,000 D to 5,000 D and > 5,000 D) in section 298.0–305.1 m.

Table 8-6. Inorganic fractions (< 1,000 D, 1,000 D to 5,000 D and > 5,000 D) in section 478.0–487.1 m.

Fraction	Si (mg/L)	Ca (mg/L)	S (mg/L)	Mn (μg/L)	U (µg/L)
< 1,000 D	5.93 ± 0.86	849 ± 103	161 ± 20	1,260 ± 152	5.20 ± 0.79
< 5,000 D	6.24 ± 0.91	829 ± 99	162 ± 20	1,240 ± 150	5.41 ± 0.81
> 1,000 D but < 5,000 D	< 0.03	< 5	< 2	< 12	0.28 ± 0.16
> 5,000 D	< 0.01	< 1	< 5	< 1	< 0.2
Adsorption 1,000 D	1.19 ± 0.89	< 125	< 24	< 178	< 0.6
Adsorption 5,000 D	< 0.8	< 117	< 16	< 160	< 0.3

## 8.3.3 Humic and fulvic acids – fractionation

The results from fractionation of organic acids in sections 298.0–305.1 m and 478.0–487.5 m are summarised in Table 8-7. The groundwater from section 298.0–305.1 m contains mainly organic acids with molecular weights less than 1,000 D.

This is true also for water from section 478.0–487.5 m. However, two heavier fractions (1,000 D to 5,000 D and > 5,000 D) were observed also. The results from the 1,000 D and 5,000 D filters were consistent.

Fraction	DOC 298.0–305.1 m (mg/L)	DOC 478.0-487.5 m (mg/L)
< 1,000 D	2.1 ± 0.3	2.2 ± 0.3
> 1,000 D but < 5,000 D	$0.05 \pm 0.04$	1.0 ± 0.1
> 5,000 D	< 0.02	0.4 ± 0.1
Adsorption 1,000 D	$0.6 \pm 0.4$	< 0.01
Adsorption 5,000 D	< 0.02	< 0.2

 Table 8-7. Summary of fractionation results.

## 9 Summary and discussion

The results from sampling and measurements in KFM10A add important information about the groundwater composition above and within the deformation zone ZFMA2 in the target area /5/. The shallow section at 298.0–305.1 m borehole length is of special interest since the groundwater represents bedrock between zones (in this case fracture domain FFM03). Most of the collected groundwater samples from Forsmark originate from geological entities interpreted as deformation zones in the geological model.

Figure 9-1 displays chloride concentrations versus depth for KFM10A together with corresponding data from other boreholes at Forsmark. High magnesium to chloride ratio indicates a marine origin of the groundwater. Figure 9-2 shows magnesium concent-rations versus chloride concentrations.

The main conclusions from the experimental results in KFM10A are:

- In section 478.0–487.5 m (vertical depth 327 m), located in the ZFMA2 deformation zone, the high magnesium content and the chloride concentration of the groundwater clearly indicates mainly Littorina origin of the water. The Littorina signature is present also in the intermediate section at 436.9–437.9 m (vertical depth 301 m), however, it is less pronounced and the water is more dilute. The water in section 298.0–305.1 m (vertical depth 215 m), on the other hand, shows a clearly non-marine origin with low magnesium concentration and the lowest  $\delta^{18}$ O signature observed so far in Forsmark ( $\delta^{18}$ O ‰ SMOW = -14). The low  $\delta^{18}$ O signature indicates a significant contribution of glacial meltwater. As expected, the groundwater conditions in the two MFL-investigated sections, representing different geological entities, proved to be very different.
- The redox measurements in sections 298.0–305.1 m and 478.0–487.5 m performed well. The measured Eh-value differs between the groundwaters of section 298.0–305.1 m (–281 mV) and section 478.0–487.5 m (–258 mV) and the deepest section shows the highest value. This may be related to different properties of zones compared to bedrock between zones and especially the connective properties of the deformation zone ZFMA2.



Figure 9-1. Chloride concentrations versus depth (m) at the Forsmark site.



Figure 9-2. Magnesium concentrations versus chloride concentrations at the Forsmark site.

- Generally, the flushing water content in the samples was somewhat high also from this borehole. However, in section 478.0–487.5 m the content was just around or below 1%, which is the allowed upper limit for a fully representative water sample. Due to the higher flushing water content in the last sample, it was decided to choose representative Chemmac values from the intermediate part of the measurement sequence where the flushing water content was lower.
- The quality of the water analyses is generally high, based on comparison between results from different laboratories and methods and acceptable charge balance errors. The relative charge balance errors are within  $\pm$  5%.
- The sample series showed somewhat unstable groundwater compositions from both borehole sections (slight increase in salinity at 298.0–305.1 m and increase followed by decrease at 478.0–487.5 m). However, the variations were more pronounced in section 478.0–487.5 m. This might reflect the fact that this section is contained in a highly connective major deformation zone and pumping caused mixing of groundwater from different water regimes.
- The uranium concentrations in the groundwater from KFM10A are reasonably low (5-7  $\mu$ g/L) in section 478.0–487.5 m, and even lower (< 0.1  $\mu$ g/L) in section 298.0–305.1 m. This is far from the concentrations reached in some of the previous borehole sections at intermediate depths in boreholes KFM02A and KFM03A (90–120  $\mu$ g/L). The presence of uranium as a minor colloidal phase is indicated from both fractionation and colloid filtration experiments.
- The colloid content measured by LIBD amounted to  $30-50 \ \mu g/L$  in section 478.0–487.5 m which is in agreement with a rough estimation from the colloid filtration study.
- Organic constituents exist in the groundwater mainly as low molecular weight fulvic acids and other low molecular weight organic acids such as citric acid and oxalic acid. However, in section 478.0–487.5 m fractions with higher molecular weights were observed as well. Worth observing is the exceptional increase in DOC concentration (from 4 to 15 mg/L) for the last sample in this sample series. This increase coincides with an increase in the drilling water content.
- Contamination occurred causing an incredibly high organic pmC value for section 298.0–305.1 m and the value is rejected. This was most probably due to the use of de-ionised water from the nuclear power plant for laboratory purposes, see Chapter 6. It is possible that also the pmC value for section 478.0–487.5 m (93.1%) is affected. The latter value is, however, reported to Sicada.

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## Design of cored borehole KFM10A



## Selected results from differential flow logging, KFM10A

Forsmark, borehole KFM10A

Flow rate, caliper and single point resistance



*Figure A2-1.* Borehole KFM10A: differential flow measurements from 280–300 m including the water bearing fracture zone at 300 m /10/.

#### Forsmark, borehole KFM10A Flow rate, caliper and single point resistance

- △ Without pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- Vithout pumping (L=5 m, dL=5 m), (Flow direction = into the bedrock)
- △ With pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- With pumping (Drawdown 4 m, L=5 m, dL=0.5 m), 2006-06-27 2006-06-28 With pumping during flow logging and fracture-EC
- (Drawdown 4 m, L=1 m, dL=0.1 m), 2006-06-28 2006-06-30
- Lower limit of flow rate.



*Figure A2-1.* Borehole KFM10A: differential flow measurements from 480–500 m including the water bearing fracture zone at 484 m /10/.

#### Forsmark, borehole KFM10A Flow rate, caliper and single point resistance



*Figure A2-3.* Borehole KFM10A: differential flow measurements from 420–440 m including the water bearing fracture zone at 436 m /10/.



## Selected BIPS logging images, KFM10A

*Figure A3-1.* Borehole KFM10A: selected BIPS logging image from 299.1 to 299.7 m borehole length, including the water bearing fracture at 300 m. The non-adjusted length is marked with black and the adjusted true length is marked with red /9/.



*Figure A3-2.* Borehole KFM10A: selected BIPS logging image from 483.8 m to 484.3 m borehole length, including the water bearing fracture at 484 m. The non-adjusted length is marked with black and the adjusted true length is marked with red /9/.

## **Appendix 4**



## **Measurement information, KFM10A**

Figure A4-1. Electrode configuration, section 298.0–305.1 m.



Figure A4-2. Configuration of downhole equipment, section 298.0–305.1 m.



Figure A4-3. Length calibration, section 298.0–305.1 m.

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RÅ	pH7	KFM10A1115IpH7	B.CRB KI	FM10A1115IpH7B.CI	KFM10A11280	PH7B.CR	3	KFM10A1128UpH7B.	C1	
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Figure A4-4. Administration, section 298.0–305.1 m.

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Figure A4-5. Electrode configuration, section 478.0–487.5 m.

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		Sektion	islängd: 9490, m	m					

*Figure A4-6. Configuration of downhole equipment, section 478.0–487.5 m.* 



Figure A4-7. Length calibration, section 478.0–487.5 m.

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	pH7	KFM10A1012IpH7	Y.CRB	KFM1	0A1012IpH7Y.CI							
Υ T	vH10	KFM10A10121pH1	OY.CRB	KFML	0A10121pH10Y.CI							
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	0.1M	KFM10A1012[kd1]	Y.CRB	KFM1	0A10121kd114.CI							
В -	nH4	FM10A1010IpH4B.	.CRB	FM10	A 1010[pH4B.CI							
0 H	pH7	FM10A1010[pH7B	.CRB	FM10	A 1010[pH7B.CI							
BL	nH10	FM10A10101pH101	B.CRB	EM10	A 10 10ToH 10B.CT							
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Figure A4-8. Administration, section 478.0–487.5 m.



## Flow and pressure measurements, KFM10A

*Figure A5-1. Pressure measurements (P1V, P2V and PB), section 298.0–305.1 m. The sensors P1V and P2V measure the pressure within the section and are both placed in the in situ sampling unit. The sensor PB, placed in the borehole Chemmac, measures the pressure above the section.* 



Figure A5-2. Pumping flow rate (Q), section 298.0–305.1 m.



*Figure A5-3. Pressure measurements (P1V, P2V and PB), section 478.0–487.5 m. The sensors P1V and P2V measure the pressure within the section and are both placed in the in situ sampling unit. The sensor PB, placed in the borehole Chemmac, measures the pressure above the section.* 



*Figure A5-4. Pumping flow rate (Q), section 478.0–487.5 m.* 

## Appendix 6

## Sampling and analytical methods

 Table A6-1. Sample handling routines and analytical methods.

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Analysis within – or delivery time to lab.
Anions 1	HCO₃ pH(lab) cond (lab)	Plastic	250	No	No	Titration Pot. meas, Cond. meas	The same day – maximum 24 hours
Anions 2	CI, SO₄, Br-, F-, I-	Plastic	100	Yes (not in the field)	No	Titration (Cl⁻) IC (Cl⁻, SO₄, Br⁻, F⁻) ISE (F⁻)	Not critical (month)
	Br, I	Plastic	100	Yes (not in the field)	No	ICP MS	Not critical (month)
Cations, Si and S according to SKB class 3	Na, K, Ca, Mg, S(tot), Si(tot), Li, Sr	Plastic (at low conc. acid washed bottles)	100	Yes (not in the field)	Yes (not in the field, 1 mL HNO $_3$ )	ICP-AES ICP-MS	Not critical (month)
Cations, Si and S according to SKB class 4 and 5	Na, K, Ca, Mg, S(tot), Si(tot), Fe, Mn, Li, Sr	Plastic (Acid washed)	100	Yes (imme- diately in the field)	Yes (1mL HNO₃)	ICP-AES ICP-MS	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic (Acid washed)	500	Yes	Yes (5 mL HCI))	Spectrophotometry Ferrozine method	As soon as possible the same day
Hydrogen sulphide	HS⁻	Glass (Winkler)	About 120×2	Yes	Ev 1 mL 1 M NaOH+ 1 mL 1M ZnAc	Spectrophotometry	Immediately or if conserved, a few days
Environmental metals	s Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn	Plastic (Acid washed)	100	Yes	Yes (1 mL HNO₃)	ICP-AES ICP-MS	Not critical (month)
Lantanoids, U, Th and so on.	Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th	, Plastic (Acid washed)	100	Yes	Yes (1 mL HNO <sub>3</sub> )	ICP-AES ICP-MS	Not critical (month)
Dissolved organic Carbon, dissolved inorganic Carbon	DOC, DIC	Plastic	250 25	Yes	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Short transportation time

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Analysis within – or delivery time to lab.
Total organic Carbon	ТОС	Plastic	250 25	No	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Short transportation time
Environmental isotopes	δ²Η, δ¹ <sup>8</sup> Ο	Plastic	100	No	-	MS	Not critical (month)
Tritium	<sup>3</sup> H (enhanced.)	Plastic (dry bottle)	500	No	-	LSC	
Chlorine-37	<sup>37</sup> Cl	Plastic	100	No	-	ICP MS	Not critical (month)
Carbon isotopes	<sup>13</sup> C, pmC	Plastic (HDPE)	100×2	No	-	(A)MS	A few days
Sulphur isotopes	<sup>34</sup> S	Plastic	500-1,000	No	-	Combustion, MS	No limit
Strontium-isotopes	<sup>87</sup> Sr/ <sup>86</sup> Sr	Plastic	100	No	-	TIMS	Days or Week
Uranium and Thorium isotopes	<sup>234</sup> U, <sup>235</sup> U, <sup>238</sup> U, <sup>232</sup> Th, <sup>230</sup> Th,	Plastic	50 1,000	No	-	Chemical separat. Alfa/gamma spectrom- etry	No limit
Boron isotopes	<sup>10</sup> B/ <sup>11</sup> B	Plastic	100	Yes	Yes (1 mL HNO <sub>3</sub> )	ICP - MS	No limit
Radon and Radium isotopes	<sup>222</sup> Rn, <sup>226</sup> Ra	Plastic	500-1,000	No	No	LSS	Immediate transport
Dissolved gas (content and composition)	$\begin{array}{l} Ar, N_2, CO_2, O_2, CH_4, H_2,\\ CO, C_2H_2, C_2H_4, C_2H_6,\\ C_3H_8 \end{array}$	Cylinder of stainless steel	200	No	No	GC	Immediate transport
Colloids	Filter series	Polycarbonate filter	0.4, 0.2 and 0.05 μm	-	Ar atmosphere	ICP - AES ICP - MS	Immediate transport
Fractionation; Humic and fulvic acids, inorganic constituents	< 1,000 D > 1,000 D but < 5,000 D > 5,000 D	Fractions are collected in plastic bottles	250	-	$N_2$ atmosphere	UV oxidation, IR (DOC)	Immediate transport
Archive samples with acid	-	Plast (washed in acid)	100×2 **	Yes	Yes (1 mL HNO <sub>3</sub> )	-	Storage in freeze container
Archive samples without acid	-	Plastic	250×2 **	Yes	No	-	Storage in freeze containe
Carbon isotopes in humic and fulvic acids	<sup>13</sup> C, <sup>14</sup> C (pmc)	DEAE cellulose (anion exchanger)	-	_	-	(A)MS	A few days
Nutrient salt + silicate	NO <sub>2</sub> , NO <sub>3</sub> , NO <sub>2</sub> +NO <sub>3</sub> , NH <sub>4</sub> , PO <sub>4</sub> , SiO <sub>4</sub>	Sample tubes, plastic	25×2 250	No	No, frozen immediately***	Spectrophotometry	Short transportation time

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Analysis within – or delivery time to lab.
Total concentra- tions of Nitrogen and Phosphorous	N-tot, P-tot	Plastic	100	No	No, frozen immediately***	Spectrophotometry	Short transportation time
Particulate Carbon, Nitrogen and Phosphorous	POC, PON, POP	Plastic	1,000	Yes (within 4 h) prepared filters. Blank filters	Filtering, the filters are frozen immediately 2 filters/sample	Elementar-analysator (N, C) own method 990121 (P)	Short transportation time
Chlorophyll	Chlorophyll a, c and pheopigment	Plastic	1,000–2,000	Yes (within 4 h)	Filtering, the filters are frozen immedi- ately	Spectrophotometry Fluorometry	Short transportation time
Oxygen	Dissolved O <sub>2</sub>	Winkler, glass	2 × ca 120	No	Mn (II) reagent Iodide reagent	Spectrophotometry SIS SS-EN 25813	Within 3 days
Archive samples for supplementary radio nuclides		Plastic	5,000	No	50 mL HNO₃	-	Storage in freeze container

\* Suprapur acid is used for conservation of samples.

\*\* Minimum number. The number of archive samples can vary depending on the number of similar samples collected at the same occasion.

\*\*\* The sample is transported in frozen condition to the laboratory. It is possible that the silicate concentration can change due to polymerisation for this reason.

#### Abbreviations and definitions:

- IC Ion chromatograph
- ISE Ion selective electrode
- ICP-AES Inductively Coupled Plasma Atomic Emission Spectrometry
- ICP-MS Inductively Coupled Plasma Mass Spectrometry
- INAA Instrumental Neutron Activation Analysis
- MS Mass Spectrometry
- TIMS Thermal Ionization Mass Spectrometer
- LSC Liquid Scintillation Counting
- LSS Liquid Scintillation Spectrometry
- (A)MS (Accelerator) Mass Spectrometry
- GC Gas Chromatography

Component	Method	Reporting limits or range		Unit	Measurement uncertainty <sup>2</sup>	"Total" uncertainty <sup>3</sup>
HCO <sub>3</sub>	Alkalinity titration	1		mg/L	4%	< 10%
Cl⁻	Mohr- titration	> 70		mg/L	5%	< 10%
CI⁻	IC	1–100			6%	10%
$SO_4$	IC	1		mg/L	10%	15%
Br Br	IC ICP	0.2 0.001		mg/L	9% 15%	20%
F- F-	IC Potentiometric	0.1 -		mg/L	10% _	20%
I-	ICP	0.001		mg/L	15%	20%
Na	ICP	0.1		mg/L	4%	10%
К	ICP	0.4		mg/L	6%	15%
Са	ICP	0.1		mg/L	4%	10%
Mg	ICP	0.09		mg/L	4%	10%
S(tot)	ICP	0.160		mg/L	21%	15%
Si(tot)	ICP	0.03		mg/L	4%	15%
Sr	ICP	0.002		mg/L	4%	15%
Li	ICP	0.2 <sup>1</sup>	2	mg/L	10%	20%
Fe	ICP	0.4 <sup>1</sup>	4	mg/L	6%	10%
Mn	ICP	0.03 <sup>1</sup>	0.1	µg/L	8%	10%
Fe(II), Fe(tot)	Spectrophotometry	0.02 (DL = 0.005	mg/L)	mg/L	15% (> 30 µg/L)	20%
HS <sup>-</sup>	Spectrophotometry	SKB 0.03 (DL=0.)	02)	mg/L	10%	30%
NO₂ as N	Spectrophotometry	0.1	,	µq/L	2%	20%
NO₃ as N	Spectrophotometry	0.2		ua/L	5%	20%
NO <sub>2</sub> +NO <sub>3</sub> as N	Spectrophotometry	0.2		µg/L	0.2 (0.2–20 μg/L) 2% (> 20 μg/L)	20%
$NH_4$ as N	Spectrophotometry	0.8 50 (SKB)		µg/L	0.8 (0.8–20 μg/L) 5% (> 20 μg/L) 20%	20%
$PO_4$ as P	Spectrophotometry	0.7		µg/L	0.7 (0.7–20 μg/L) 3% (> 20 μg/L)	20%
SiO <sub>4</sub>	Spectrophotometry	1		µg/L	3% (> 200 µg/L)	_
O <sub>2</sub>	lodometric titration	0.2–20		mg/L	5%	_
Chlorophyll a, c pheopig- ment⁴	See table A1-2	0.5		µg/L	5%	-
PON⁴	See table A1-2	0.5		µg/L	5%	_
POP <sup>4</sup>	See table A1-2	0.1		µg/L	5%	-
POC⁴	See table A1-2	1		µg/L	4%	_
Tot-N <sup>₄</sup>	See table A1-2	10		µg/L	4%	_
Tot-P⁴	See table A1-2	0.5		μg/L	6%	_
Al, Zn	ICP	0.2		µg/L	12%	20%⁵
Ba, Cr, Mo, Pb	ICP	0.01		µg/L	7–10%	20%⁵
Cd, Hq	ICP	0.002		µg/L	9 resp 5%	20%⁵
Co. V	ICP	0.005		ua/L	8 resp 5%	20%⁵
Cu	ICP	0.1		µg/L	8%	20%5
Ni	ICP	0.05		µg/L	8%	20%5
Р	ICP	1		µg/L	6%	10%
As	1CP	0.01		µg/L	20%	Correct order of size (low conc.)

Table A6-2.	Reporting	limits an	d measurer	ment unce	rtainties.

Component	Method	Reporting limits or range		Unit	Measurement uncertainty <sup>2</sup>	"Total" uncertainty <sup>3</sup>
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb	ICP	0.0051	0.05	µg/L	10%	Correct order of size (low conc.)
Sc, In, Th	ICP	0.051	0.5	µg/L	10%	Correct order of size (low conc.)
Rb, Zr, Sb, Cs, Tl	ICP	0.025 <sup>1</sup>	0.25	µg/L	10%	Correct order of size (low conc.)
Y, Hf	ICP	0.005 <sup>1</sup>	0.05	µg/L	10%	Correct order of size (low conc.)
U	ICP	0.001 <sup>1</sup>	-	µg/L	12%	Correct order of size (low conc.)
DOC	See Table A1-1	0.5		mg/L	8%	30%
тос	See Table A1-1	0.1		mg/L	10%	30%
δ²H	MS	2		‰ SMOW⁵	1‰	-
δ <sup>18</sup> Ο	MS	0.1		‰ SMOW⁵	0.2‰	-
³Н	LSC	0.8 eller 0.1		TU <sup>6</sup>	0.8 eller 0.1	Correct order of size
<sup>37</sup> Cl	ICP MS	0.2‰° (20 mg/L)		‰ SMOC7	-	-
$\delta^{\scriptscriptstyle 13}C$	A (MS)	-		‰ PDB <sup>8</sup>	-	-
<sup>14</sup> C pmc	A (MS)	-		PMC <sup>9</sup>	-	-
$\delta^{34}S$	MS	0.2‰		‰ CDT <sup>10</sup>	0.3‰	-
<sup>87</sup> Sr/ <sup>86</sup> Sr	TIMS	-		No unit (ratio) <sup>11</sup>	-	_
<sup>10</sup> B/ <sup>11</sup> B	ICP MS	-		No unit (ratio) <sup>11</sup>	-	_
<sup>234</sup> U, <sup>235</sup> U, <sup>238</sup> U, <sup>232</sup> Th, <sup>230</sup> Th <sup>222</sup> Rn, <sup>226</sup> Rn	Alfa spectr.	0.0005		Bq/L13	5%	-
	LSS	0.03		Bq/L	5%	-

<sup>1.</sup> Reporting limits at salinity  $\leq 0.4\%$  (520 mS/m) and  $\leq 3.5\%$  (3,810 mS/m) respectively.

- <sup>2.</sup> Measurement uncertainty reported by consulted laboratory, generally 95% confidence interval.
- <sup>3.</sup> Estimated total uncertainty by experience (includes effects of sampling and sample handling).
- <sup>4.</sup> Determined only in surface waters and near surface groundwater.
- <sup>5.</sup> Per mille deviation<sup>13</sup> from SMOW (Standard Mean Oceanic Water).
- <sup>6.</sup> TU=Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10<sup>-18</sup> (1 Bq/L Tritium = 8.45 TU).
- <sup>7.</sup> Per mille deviation<sup>13</sup> from SMOC (Standard Mean Oceanic Chloride).
- <sup>8.</sup> Per mille deviation<sup>13</sup> from PDB (the standard PeeDee Belemnite).
- <sup>9.</sup> The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: pmC = 100×e(<sup>(1,950-y-1.03t)/8,274)</sup> where y = the year of the C-14 measurement and t = C-14 age.
- <sup>10.</sup> Per mille deviation 13 from CDT (the standard Canyon Diablo Troilite).
- <sup>11.</sup> Isotope ratio without unit.
- <sup>12.</sup> The following expressions are applicable to convert activity to concentration, for uranium-238 and thorium-232: 1 ppm U = 12.4 B1 ppm Th = 3.93 Bq/kg<sup>232</sup>Th.
- <sup>13.</sup> Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:  $\delta y = 1,000 \times (Ksample-Kstandard)/Kstandard, where K= the isotope ratio and yI = <sup>2</sup>H, <sup>18</sup>O, <sup>37</sup>CI, <sup>13</sup>C or <sup>34</sup>S etc.$

# Laser-Induced breakdown colloid detection in natural ground water from Forsmark borehole KFM10A, section 478–487.5 m

W. Hauser, H. Geckeis, R. Götz

Forschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgung (INE) P.O. Box 3640, D-76021 Karlsruhe, Germany

### Introduction

Colloid analysis has been performed in ground water samples collected during the site investigation program at Forsmark, Sweden. Two samples from the same borehole have been collected in a stainless steel cylinder each, avoiding water contact with the atmosphere. They were sent to INE for laboratory analysis. Colloid analysis was subsequently performed by the laser-induced breakdown detection (LIBD) in the laboratory using a closed flow-through detection cell again without atmosphere contact. Furthermore, a thorough chemical analysis of the water samples was performed (not subject of this order).

It is supposed that the geological situation is similar to that found at various places in the Äspö tunnel. The aim of this study is to investigate the natural background colloid concentration in this specific borehole and to compare the data with those obtained from other sites.

## Experimental

#### LIBD instrumentation

The principle of LIBD is based on the generation of a dielectric breakdown in the focus region of a pulsed laser beam. As the threshold energy (irradiance) to induce a breakdown is lower for solids than for liquids or gas, the breakdown can be generated selectively in particles dispersed in solution at a suitable pulse energy.

A schematic diagram of the mobile LIBD set-up used in the present work is shown Figure A7-1. A pulsed laser beam with a frequency of 15 Hz at 532 nm wavelength from a small Nd: YAGlaser (Continuum Minilite I) is focused (15 mm focal length) into the center of a flow-through detection cell, after passing through a variable attenuator and a beam splitter. The plasma generated at a breakdown event is monitored by a microscope equipped with a CCD monochrome camera triggered by the incident laser pulse and recorded by a PC controlled image processing system. A breakdown shock wave propagated in the sample solution is detected simultaneously by an acoustic sensor (piezoelectric transducer) that is connected to the surface of the cell. Both, the energy and the acoustic signal are recorded by an analog-digital converter interface in a PC. Colloid concentrations are derived from the respective breakdown probability, represented by the number of breakdown events per number of laser shots, and the range of breakdown events within the laser beam axis determined by optical inspection of the laser focus area within the flow through cell. Colloid number concentrations (Pt/L) are given relative to a calibration with polystyrene reference colloids. Mass concentrations are calculated by assuming an average colloid density of 2.7 g/cm<sup>3</sup> and spherical particle shape. A more detailed description of data evaluation is given in /1/.

The mobile instrumentation of LIBD is combined with a Millipore ultra-pure water processing unit for on-line cleaning the flow-through detection cell of LIBD and to allow for the frequent control of the instrument background. The whole system, which is set up to a compact mobile unit can be transported by a van for field experiments.



Figure A7-1. Schematic diagram of the mobile laser-induced breakdown detection system.

#### High-pressure flow-through detection cell

The LIBD has been operated in the CRR migration experiments (Grimsel Test-Site, Switzerland) /1/ under low pressure conditions with commercially available quartz detection cells (fluorescence cells) for batch (laboratory experiments) or flow-through sampling. These cells have a sample volume of 3 ml at 10 mm absorption length. A new flow-through detection cell has been developed constraining water pressures of about 35 bar for in situ investigations in the Äspö Hard Rock Laboratory access tunnel (Sweden) /2/, and in the Kraftwerke Oberhasli (KWO) access tunnel close to the Grimsel Test Site /3/. This detection cell has also been applied in connection with a borehole sampling system for the detection of ground water colloids sampled at a natural analogue site (Ruprechtov, Czech Republic).

Figure A7-2 presents the high-pressure detection cell developed by INE. Without changing the optical path of the laser light, the detection cell fits into the same mount used for the silica cell. The new cell, fabricated from PEEK (polyether etherketone) is lined outside with a stainless steel housing (black parts in Figure A7-2). Four optical windows, one at each side are applied for the passing laser light (absorption length 12 mm), the microscope and for inspection. They consist of sapphire with 2 mm thickness. The ground water flow enters the inner cell volume of 0.8 ml from the base via a PEEK tubing. The outlet is on the top of the cell. The high-pressure detection cell is successfully tested for a water pressure up to 60 bar.



*Figure A7-2. LIBD high-pressure flow-through detection cell (left: conventional flow-through silica detection cell).* 

#### Borehole sampling

Two samples were taken at November 2, 2006 from Forsmark borehole KFM10A and a section between 478–487.49 m. The vertical depth was approximately 340 m with a measured pressure in the borehole section of 33.5 bar. The samples are filled in the SKB steel cylinders PVB 9506-8 and PVB 026.

The stainless steel cylinders (Figure A7-3) are ground water sampling cylinders from SKB with a sample volume of about 190 ml each. They are supplied with an internal piston and 3 valves. Further information concerning the sampling procedure is given elsewere (SKB).

One day after sampling both cooled samples arrived at the INE where they have been stored in a fridge (Temp. about 10°C) until colloid detection at November 21 and 22, 2006.

#### Configuration of laboratory experiments

Each sampling cylinder is connected with the LIBD detection cell and the detection cells for pH-, Eh-, electrical conductivity-, oxygen content-detection and for taking samples for chemical ground water analysis. A scheme of the corresponding laboratory setup is plotted in Figure A7-4 with an image of the experimental configuration in Figure A7-5.



Figure A7-3. SKB stainless steel sampling cylinder, (left: piston side, right: mounting adapter side).



*Figure A7-4.* Scheme of the laboratory setup for in-line LIBD colloid analysis and ground water monitoring.



Figure A7-5. Experimental configuration.

At first the tubings around the sampling cylinder are intensively cleaned by evacuation and flushing with Argon. Then a HPLC-pump is used to fill all tubings on the water side of the sampling cylinder with ultra-pure water and to set the water pressure according the hydrostatic pressure of the samples. This was the expected water pressure in the sampling cylinder. The gas side of the sampling cylinder is then filled with the corresponding Argon gas pressure.

Now one of the top valves of the sampling cylinder can be opened without contact of the sampled ground water with atmosphere ogen. With Argon gas the ground water is pressed out from the sampling cylinder through the LIBD detection cell via a degasser to avoid occasionally occurring gas bubbles which interfere the colloid detection. Behind the LIBD system additional detection cells with pressure resistant electrodes for Eh, pH (back pressure regulator 1 set to 40 bar), Oxygen, a sensor for electrical conductivity and a sensor for the pressure detection are arranged downstream.

Before the sampling outlet an additional back pressure regulator, set to 5 bar, is installed. This overpressure in the whole system avoids further contact to oxygen. Data of this geo-monitoring system are stored on a personal computer with a data logger as a function of time. This allows to separate temporary fluctuating data, especially during the starting period when the detection cell and the geo-monitoring system are contaminated and do not contain the sampled ground water, respectively.

Ground water batch samples are collected at the outlet of the pressure regulator for chemical analysis with ICP-AES, ICP-MS and for the detection of inorganic carbon (IC) and dissolved organic carbon (DOC).

Additionally, track-etched Polycarbonate filter samples (pore size 50 nm) have been taken for colloid analysis with REM/EDX.
### Results

Data from geo-monitoring as well as the chemical composition of the two samples from the same ground water, are displayed in Table A7-1.

The detected Eh value (Table A7-1) demonstrates that reducing geochemical conditions are maintained within the sampling container during transport, storage and colloid detection. This indicates that a significant intrusion of atmosphere oxygen did not occur. In both ground water containers an oxygen concentration of  $< 0.020 \ \mu g/l$  was detected. Though this value is higher than the sensors detection limit (0.001 ppm) it might be caused by sensor instabilities (Table A7-1) during the measurement.

The ground water pH of 7.8 is equivalent to the pH detected so far in other Forsmark (7.3–8.4) and Äspö ground water samples (7.3–7.8). The chemical composition of the ground water is characterized mainly by the salinity with about 3,300 and 3,900 mg/l chloride. But the DOC data in both sampling containers are almost by a factor of 10 higher than those detected in Aspö ground water of the same salinity /5/.

Borehole ID Secup Seclow Sampling depth Hydr. pressure Container ID Sample ID	m m m bar	KFM10A 478 487.49 330 33.5 SKB PVB 026 FOR7-2	KFM10A 478 487.49 330 33.5 SKB PVB 9506-8 FOR8-2
pН		7.86	7.76
Redox (Ag/AgCl)	mV	-264	-236
Eh (SHE)	mV	-50	-22
el. cond.	mS/m	1,094	1,064
O <sub>2</sub> content	mg/l	< 0.021	< 0.018
Na⁺	mg/l	1,327	1,375
K+	mg/l	53.9	43.4
Ca <sup>2+</sup>	mg/l	726	731
Mg <sup>2+</sup>	mg/l	16	165
HCO₃⁻(IC)	mg/l	167	168
CI⁻	mg/l	3,934	3,337
SO4 <sup>2-</sup>	mg/l	333	324
Br	mg/l	< 0.01	< 0.01
F⁻	mg/l	6.4	5.9
Si <sup>4+</sup>	mg/l	6.5	6.7
Fe-ICP	mg/l	12.4	11
Mn <sup>2+</sup>	mg/l	1.18	1.17
Li⁺	mg/l	0.048	0.047
Sr <sup>2+</sup>	mg/l	6.01	6.07
DOC	mg/l	30.4	27.1
IC	mg/l	32.8	33.1

### Table A7-1. Monitored data of pH, Eh, el. conductivity, oxygen content and chemical analysis of the ground water samples from Forsmark borehole KFM10A.

Data determined with the laser-induced breakdown detection system are listed in Table A7-2. The volume of the samples was sufficient to perform five or six colloid measurements for each PVB container (see Apendix 7A, 7B).

With image processing average colloid diameters of 200-270 nm with corresponding mass concentrations of  $30-50 \mu g/l$  are calculated. At the end of the elution of container PVB 026 a higher colloid concentration of  $320 \mu g/l$  is detected. This might be caused by mobilized larger colloids (diameter 630 nm) which previously have settled down on the container bottom (piston surface).

Borehole ID Secup Seclow Sampling depth Hydr. pressure Container ID Sample ID	m m m bar	KFM10A 478 487.49 330 33.5 SKB PVB 026 FOR7a	FOR7b	KFM10A 478 487.49 330 33.5 SKB PVB 9506-8 FOR8a	FOR8b
BD-events		944	1,267	1,166	975
Trigger-pulses		2,500	4,000	3,500	3,000
BD-probability		0.378	0.317	0.333	0.325
Colloid diam.	nm	225	204	211	214
Colloid mass conc.	µg/l	43	29	33	33
Sample ID		FOR7c	FOR7d	FOR8c	FOR8d
BD-events		1,079	1,029	851	1,026
Trigger-pulses		3,000	3,000	3,000	4,000
BD-probability		0.36	0.343	0.284	0.257
Colloid diam.	nm	210	274	238	222
Colloid mass conc.	µg/l	36	53	33	26
Sample ID		FOR7e		FOR8e	FOR8f
BD-events		910		855	1,240
Trigger-pulses		2,000		4,000	5,000
BD-probability		0.455		0.214	0.248
Colloid diam.	nm	633		237	285
Colloid mass conc.	µg/l	324		24	39
Sample ID				FOR8g	
BD-events				1,080	
Trigger-pulses				5,000	
BD-probability				0.216	
Colloid diam.	nm			256	
Colloid mass conc.	µg/l			27	

Table A7-2. LIBD data with average colloid diameter and colloid concentration of the analyzed ground water from Forsmark borehole KFM10A.

In the Äspö colloid project  $\frac{5}{a}$  series of boreholes along the access tunnel have been sampled and their ground water was directly analyzed with the mobile LIBD system. A correlation was drawn (Figure-6) between the colloid concentration and the Cl<sup>-</sup> concentration of the ground water. At a Cl<sup>-</sup> concentration of about 4,000 mg/l a remarkable decrease of the colloid concentration over 4 orders of magnitude down to the LIBD detection limit of about 10 ng/l was observed.

The Forsmark KFM10A sample data from 330 m sampling depth fits quite well into this correlation. According to the colloid concentration correlation with ground water salinity we should expect lower colloid concentrations for samples KFM01D and KFM08A from the deeper sampling depths 442 m and 590 m (Figure A7-6). Possible reasons for the somewhat high particle concentrations have been discussed in previous reports.



*Figure A7-6.* Correlation between colloid concentration and chloride concentration in different ground water from Äspö /2, 5/ and in Forsmark samples. (): sampling depths.

### **References Appendix 7**

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# Plot with logged data from elution of sampling container SKB PVB 026 (KFM10A (478–487.49ml))



## Plot with logged data from elution of sampling container SKB PVB 9506-8 (KFM10A (478–487.49ml))





Chemmac measurements in KFM10A, section 298.0–305.1 m

*Figure A8-1.* Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes in the borehole section (EHAUB, EHCB and EHPTB) and at the surface by gold, glassy carbon and platinum (EHAUY, EHCY and EHPTY). The arrow shows the chosen representative Eh values for the borehole section.



**Figure A8-2.** Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.



*Figure A8-3.* Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.



*Figure A8-4.* Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section.



Figure A8-5. Temperature of the groundwater in the borehole section (TB).



Chemmac measurements in KFM10A, section 478.0–487.5 m

**Figure A9-1.** Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes in the borehole section (EHAUB, EHCB and EHPTB) and at the surface by gold, glassy carbon and platinum (EHAUY, EHCY and EHPTY). The arrow shows the chosen representative Eh values for the borehole section.



*Figure A9-2.* Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.



**Figure A9-3.** Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.



*Figure A9-4.* Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section.



Figure A9-5. Temperature of the groundwater in the borehole section (TB).

Appendix 10

### **Compilation February 2007**

Table A10-1. Water Composition.

ldcode	Secup m	Seclow m	Sample no.	Sampling date	RCB (%)	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	HCO₃ <sup>-</sup> mq/L	CI <sup>₋</sup> mg/L	SO₄²− mg/L	SO₄–S mq/L	Br mg/l	F <sup>-</sup> mg/L	Si mg/L	Fe mg/L	Fe-tot mg/L	Fell mg/L
					. ,														
KFM10A	298.00	305.14	12520	2006-11-03	-	-	-	-	-	136	2,960	-	-	-	-	-	-	-	_
KFM10A	298.00	305.14	12541	2006-11-13	-1.62	1,260	7.69	1,070	21.5	18.7	3,900	160	56.4	17.7	1.49	5.28	2.19	2.37	2.35
KFM10A	298.00	305.14	12543	2006-11-17	-1.32	1,280	9.40	1,050	32.0	31.9	3,880	183	64.8	17.8	1.43	5.38	3.81	4.15	4.11
KFM10A	298.00	305.14	12544	2006-11-20	-0.68	1,330	6.85	1,110	24.7	19.4	3,990	189	66.8	19.8	1.43	5.46	1.91	2.00	1.97
KFM10A	298.00	305.14	12551	2006-11-23	-0.94	1,340	6.33	1,110	23.9	20.7	4,020	196	68.4	17.9	1.43	5.3	1.24	1.43	1.46
KFM10A	298.00	305.14	12552	2006-11-28	-0.69	1,350	6.63	1,130	29.6	20.5	4,050	215	76.3	18.8	1.47	5.64	1.01	1.45	1.43
KFM10A	436.9	437.9	12553	2006-11-30	-2.87	1,240	31.4	661	120	184	3,300	326	116	12.4	_	6.93	10.8	_	_
KFM10A	478.00	487.49	12504	2006-10-12	_	_	-	_	_	148	4,530	-	-	-	_	-	-	_	_
KFM10A	478.00	487.49	12505	2006-10-16	-0.42	1,630	32.5	969	193	155	4,370	469	185	16.5	1.32	6.9	9.18	7.58	7.46
KFM10A	478.00	487.49	12508	2006-10-18	-0.83	1,680	31.4	931	185	160	4,420	479	173	17.8	1.31	6.57	10.1	9.17	8.97
KFM10A	478.00	487.49	12509	2006-10-23	-0.79	1,850	31.1	953	189	156	4,730	494	175	18.0	1.31	6.71	6.88	7.26	7.24
KFM10A	478.00	487.49	12516	2006-10-27	-1.73	1,650	30.1	872	173	157	4,340	462	165	16.2	1.35	6.33	11.7	12.5	12.4
KFM10A	478.00	487.49	12517	2006-10-30	-1.84	1,410	29.1	731	151	169	3,690	400	141	14.0	1.38	6.37	14.7	15.3	15.4

ldcode	Secup m	Seclow m	Sample no.	Mn mg/L	Li mg/L	Sr mg/L	l⁻ mg/L	рН	DOC mg/L	TOC mg/L	HS⁻ mg/L	Drill_water %	ElCond mS/m	NH₄N mg/L	NO₂–N mg/L	NO₃–N mg/L	NO <sub>2</sub> –N+NO <sub>3</sub> –N mg/L	PO₄–P mg/L	P mg/L
KFM10A	298.00	305.14	12520	_	_	_	_	7.50	_	_	_	12.9	916	_	_	_	-	_	_
KFM10A	298.00	305.14	12541	0.255	0.027	10.4	0.077	6.95	8.0	-	0.007	5.4	1,140	0.106	_	_	-	_	_
KFM10A	298.00	305.14	12543	0.367	0.027	10.2	0.069	7.08	4.0	-	0.013	5.3	1,150	0.132	< 0.0002	0.0005	0.0006	< 0.0005	0.0076
KFM10A	298.00	305.14	12544	0.199	0.031	11.0	0.070	7.19	2.8	-	0.024	4.9	1,190	0.074	0.0002	< 0.0003	0.0003	< 0.0005	0.0064
KFM10A	298.00	305.14	12551	0.183	0.033	10.8	-	7.39	1.5	-	0.008	4.8	1,190	0.073	-	-	-	-	-
KFM10A	298.00	305.14	12552	0.186	0.034	11.0	0.074	6.89	2.0	1.6	0.027	4.5	1,210	0.087	0.0003	0.0004	0.0007	< 0.0005	< 0.005
KFM10A	436.9	437.9	12553	1.36	0.044	5.62	-	7.45	-	-	-	3.8	1,030	_	-	-	-	-	-
KFM10A	478.00	487.49	12504	-	-	-	-	7.16	-	-	-	0.5	1,360	_	-	-	-	-	-
KFM10A	478.00	487.49	12505	1.46	0.056	8.88	-	7.34	5.2	-	0.004	1.3	1,310	1.19	-	-	-	-	-
KFM10A	478.00	487.49	12508	1.38	0.056	8.61	0.032	7.35	4.7	-	0.008	1.0	1,330	1.09	0.0006	0.0003	0.0008	< 0.0005	0.0123
KFM10A	478.00	487.49	12509	1.42	0.056	8.80	0.030	7.34	3.5	-	0.013	0.7	1,390	1.17	0.0002	0.0010	0.0011	0.0005	0.0215
KFM10A	478.00	487.49	12516	1.32	0.056	8.25	-	7.31	4.3	-	0.020	1.3	1,300	0.37	-	-	-	-	-
KFM10A	478.00	487.49	12517	1.19	0.049	6.61	0.028	7.13	15	13	0.065	3.6	1,130	0.911	0.0005	0.0003	0.0009	0.0005	0.0104

– = Not analysed.
A = Results will be reported later.
x = No result due to sampling problems.
xx = No results due to analytical problems.
< value = Below reporting limit.</li>
SICADA: water\_elements.

Table A10-2. Trace emelents.

ldcode	Secup	Seclow	Sample	Sampling	AI	As	в	Ва	Cd	Cr	Co	Hg	Ni	V	U	Th	Sc	Rb	Y	Zr
	m	m	no.	date	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
KFM10A	298.00	305.14	12543	2006-11-17	11.3	< 0.5	537	548	< 0.02	0.366	0.094	< 0.002	0.83	0.723	0.43	< 0.04	< 0.08	25.6	0.127	0.027
KFM10A	298.00	305.14	12544	2006-11-20	24.9	< 0.5	577	561	< 0.02	0.371	0.020	< 0.002	0.734	1.220	0.09	< 0.04	< 0.08	25.8	0.091	< 0.02
KFM10A	298.00	305.14	12552	2006-11-28	7.95	< 0.5	605	495	< 0.02	0.322	0.057	< 0.002	1.59	0.602	0.09	< 0.04	< 0.08	27.0	0.024	< 0.02
KFM10A	478.00	487.49	12508	2006-10-18	4.12	1.36	650	84.8	< 0.02	0.663	0.291	< 0.002	5.78	0.208	5.90	< 0.2	< 0.4	49.3	0.272	0.538
KFM10A	478.00	487.49	12509	2006-10-23	24.1	0.78	653	80.5	< 0.02	0.622	0.278	< 0.002	2.86	0.218	6.49	< 0.2	< 0.4	51.2	0.536	0.551
KFM10A	478.00	487.49	12517	2006-10-30	4.74	0.85	554	74.3	< 0.02	0.909	0.220	< 0.002	4.99	0.231	5.58	< 0.2	< 0.4	41.7	1.63	0.785

ldcode	Secup m	Seclow m	Sample no.	Sampling date	Sb ug/L	Cs ug/L	La ug/L	Hf ug/L	Tl ug/L	Ce ug/L	Pr ug/L	Nd ug/L	Sm ug/L	Eu ug/L	Gd ug/L	Tb ug/L	Dy ug/L	Ho ug/L
KFM10A	298.00	305.14	12543	< 0.2	0.146	0.371	0.0092	< 0.004	< 0.03	0.0052	< 0.004	< 0.004	< 0.004	0.0147	< 0.004	< 0.004	< 0.004	< 0.004
KFM10A	298.00	305.14	12544	< 0.2	0.128	0.367	0.0089	< 0.004	< 0.03	0.0052	< 0.004	< 0.004	< 0.004	0.0118	< 0.004	< 0.004	< 0.004	< 0.004
KFM10A	298.00	305.14	12552	< 0.2	0.101	0.362	< 0.004	< 0.004	< 0.03	< 0.004	< 0.004	< 0.004	< 0.004	0.0106	< 0.004	< 0.004	< 0.004	< 0.004
KFM10A	478.00	487.49	12508	< 0.2	0.309	1.22	< 0.02	< 0.02	< 0.03	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
KFM10A	478.00	487.49	12509	< 0.2	0.248	1.31	0.0387	< 0.02	< 0.03	0.0315	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
KFM10A	478.00	487.49	12517	< 0.2	0.275	1.02	0.0599	< 0.02	< 0.03	0.0579	< 0.02	0.0298	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02

ldcode	Secup m	Seclow m	Sample no.	Er ug/L	Tm ug/L	Yb ug/L	Lu ug/L
KFM10A	298.00	305.14	12543	< 0.004	< 0.02	< 0.004	< 0.004
KFM10A	298.00	305.14	12544	< 0.004	< 0.02	< 0.004	< 0.004
KFM10A	298.00	305.14	12552	< 0.004	< 0.02	< 0.004	0.008
KFM10A	478.00	487.49	12508	< 0.02	< 0.02	< 0.02	< 0.02
KFM10A	478.00	487.49	12509	< 0.02	< 0.02	< 0.02	< 0.02
KFM10A	478.00	487.49	12517	0.032	< 0.02	0.0315	< 0.02

– = Not analysed.
A = Results will be reported later.
x = No result due to sampling problems.
xx = No results due to analytical problems.
< value = Below reporting limit.</li>
SICADA: trace\_elements.

Table A10-3. Isotopes (H–, 0–, B–, S–, CI– and C-isotopes).

ldcode	Secup	Seclow	Sample	Sampling	δ²H	³Н	δ <sup>18</sup> Ο	<sup>10</sup> B/ <sup>11</sup> B	δ <sup>34</sup> S	δ <sup>13</sup> C	<sup>87</sup> Sr/ <sup>86</sup> Sr	<sup>14</sup> C	δ³7CI
	m	m	no	date	‰ SMOW	TU	‰ SMOW	no unit	‰ CDT	‰ PDB	no unit	pmC	‰ SMOC
KFM10A	298.00	305.14	12541	2006-11-13	-102.9	< 0.8	-14.0	_	_	_	-	_	_
KFM10A	298.00	305.14	12543	2006-11-17	-102.7	1.6	-13.7	0.2365	25.2	_	0.720619	-	0.16
KFM10A	298.00	305.14	12544	2006-11-20	-102.9	1.2	-13.8	0.2369	25.2	_	0.720394	_	0.20
KFM10A	298.00	305.14	12551	2006-11-23	-98.2	1.1	-13.8	_	_	_	_	_	_
KFM10A	298.00	305.14	12552	2006-11-28	-97.9	1.0	-13.5	0.2374	25.2	XX	0.720237	xx	0.17
KFM10A	436.90	437.90	12553	2006-11-30	-74.5	А	-10.1	_	_	-	-	_	-
KFM10A	478.00	487.49	12505	2006-10-16	-70.2	1.9	-9.1	_	_	_	_	_	_
KFM10A	478.00	487.49	12508	2006-10-18	-76.6	2.1	-9.0	0.2362	24.8	_	0.719559	_	А
KFM10A	478.00	487.49	12509	2006-10-23	-65.1	1.8	-8.9	0.2362	24.2	_	0.719478	_	А
KFM10A	478.00	487.49	12516	2006-10-27	-73.2	3.0	-9.0	_	_	_	_	_	_
KFM10A	478.00	487.49	12517	2006-10-30	-67.3	3.5	-9.3	0.2366	24.0	-10.31	0.720105	32.99	А

- = Not analysed.
A = Results will be reported later.
x = No result due to sampling problems.
xx = No results due to analytical problems.
< value = Below reporting limit.</li>
SICADA: isotopes I.

#### Table A10-4. Isotopes II (U–, Th, Ra– and Rn-isotopes).

ldcode	Secup m	Seclow m	Sample no.	Sampling date	<sup>238</sup> U mBq/L	<sup>235</sup> U mBq/L	<sup>234</sup> U mBq/L	<sup>232</sup> Th mBq/L	<sup>230</sup> Th mBq/L	<sup>226</sup> Ra Bq/L	<sup>222</sup> Rn Bq/L
KFM10A	298.00	305.14	12552	2006-11-28	1.40	0.13	3.80	0.20	0.30	4.72	297
KFM10A	478.00	487.49	12517	2006-10-30	63.77	2.08	238.1	0.04	0.32	1.73	92

– = Not analysed.

A = Results will be reported later. x = No result due to sampling problems.

xx = No results due to analytical problems.

< value = Below reporting limit.

SICADA: u\_th\_isotope\_t, ra\_rn\_isotope\_t

#### Table A10-5. Dissolved gases.

ldcode	Secup m	Seclow m	Sample no.	Sampling date	Ar mL/L	He mL/L	N₂ mL/L	CO₂ mL/L	CH₄ mL/L	O₂ mL/L	H₂ µL/L	CO µL/L	C₂H₀ µL/L	C₂H₄ µL/L	C₂H₂ µL/L	C₃H₅ µL/L	C₃H₅ µL/L	DISS_GAS mL/L H₂O
KFM10A	298.00	305.14	12552	2006-11-28	1.3	3.1	123	0.06	0.06	0.08	< 3.8	< 6.4	0.26	0.13	< 0.06	0.13	0.13	127
KFM10A	478.00	487.49	12517	2006-10-31	7.9	0.33	59	1.5	0.03	0.03	< 2.1	< 3.4	0.3	0.24	< 0.05	0.1	0.11	69
KFM10A	478.00	487.49	12517	2006-10-31	0.76	0.33	65	1.90	0.03	0.05	< 2	< 3.4	0.4	0.28	< 0.05	0.12	0.14	68

– = Not analysed.

A = Results will be reported later.

x = No result due to sampling problems.

xx = No results due to analytical problems.

< value = Below reporting limit.

SICADA: Dissolved\_gases