

P-04-219

Oskarshamn site investigation
Hydrochemical logging in KLX04A

Cecilia Berg, Geosigma AB

September 2004

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

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Abstract

Hydrochemical logging, or so called tube sampling, has been performed in the core drilled borehole KLX04A. The method is a fast and simple sampling technique for obtaining information about the chemical composition of the water along an open borehole. The equipment consists of an approximately 1,000 m long polyamide tube divided into units of 50 m.

The water content in each tube unit constituted one sample. Every other sample starting with the uppermost unit, was analysed according to SKB chemistry class 3 (no options included). Samples for isotope determination were collected and stored in a freezer (tritium in a refrigerator) at the time of sampling; $\delta^{18}\text{O}$, deuterium, ^{10}B , tritium, $\delta^{37}\text{Cl}$ and ^{87}Sr from odd-numbered tube units and $\delta^{34}\text{S}$ and carbon isotopes from even-numbered tube units.

The content of flushing water remaining in the borehole after drilling was relatively low (below 5%) the first 500 m of borehole length. The maximum amount of flushing water was found at approximately 700 m where it was 54%. The relative charge balance error did not exceed the acceptable limit of $\pm 5\%$ in any of the ten samples.

Sammanfattning

Hydrokemisk loggning, eller så kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX04A. Metoden är snabb och enkel att använda för att erhålla information om den kemiska sammansättningen hos grundvattnet längs ett öppet borrhål. Utrustningen består av en cirka 1 000 m lång polyamidslang uppdelad i enheter om vardera 50 m.

Innehållet i en slangenhet utgör ett prov. Varannan slangenhet, med start från den översta, analyserades enligt SKB kemiklass 3 (exklusive tillval). Prover för bestämning av isotoptillvalen togs ut vid provtagningstillfället och sparades i frys (tritium i kylskåp); $\delta^{18}\text{O}$, deuterium, ^{10}B , tritium, $\delta^{37}\text{Cl}$ och ^{87}Sr ur udda enheter samt $\delta^{34}\text{S}$ och kolisotoper ur jämna enheter.

Halten kvarvarande spolvatten i borrhålet efter borrning var relativt låg (under 5 %) de första 500 m. Den högsta spolvattenhalten uppmättes omkring 700 m där halten var 54 %. Det relativa felet i jonbalansen översteg inte den acceptabla nivån $\pm 5\%$ i något av de tio analyserade proverna.

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1 Introduction

This document reports on the performance and results from hydrochemical logging in borehole KLX04A, which is one of the activities performed within the site investigation at Oskarshamn /1/. The work was carried out in accordance with activity plan SKB PS 400-04-058 (SKB internal controlling document). In Table 1-1, controlling documents for performance of this activity are listed. Both of the activity plan and the method descriptions are SKB's internal controlling documents. The data is reported to SICADA in field note no Simpevarp 407.

Borehole KLX04A is a 993 m long telescopic borehole, drilled within the site investigation in the Oskarshamn area, Simpevarp. The percussion borehole HLX10 served as the source of flushing water for the drilling of KLX04A. The location of KLX04A is shown in Figure 1-1.

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

Activity plan	Number	Version
Hydrokemisk loggning i KLX04	AP PS 400-04-058	0.1
Method descriptions	Number	Version
Metodbeskrivning för hydrokemisk loggning	SKB MD 422.001	1.0

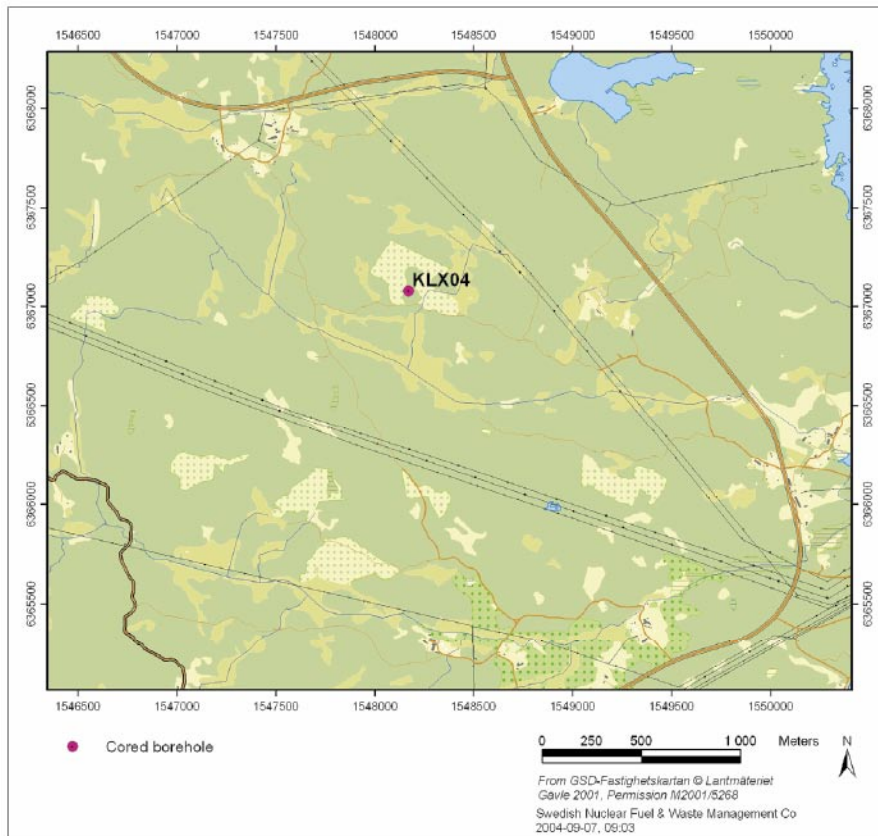


Figure 1-1. Location of the core drilled borehole KLX04A within the site investigation in the Oskarshamn area. (Image by Fredrik Hartz)

2 Objective and scope

Hydrochemical logging was performed in order to obtain an overview of the chemical composition of the water along the open borehole KLX04A. The technique used for sampling is fast and simple, even at great depth.

The analysis program was carried out according to SKB chemistry class 3 except for optional isotopes. Sample portions intended for isotope analyses were collected, but have not been analysed. They are stored in a freezer at SKB (except the sample collected for tritium determination, which was stored in a refrigerator) until further notice. If samples from the activity are analysed for isotopes, the results from those analysis will be presented in a separate report.

3 Sampling equipment

For the hydrochemical logging an approximately 1,000 m long polyamide tube, divided into units of 50 m, was used. The equipment is described in the method description SKB MD 422.001.

A schematic picture of the equipment used for the hydrochemical logging is shown in Figure 3-1. The tube units are connected with couplings. The length of each tube unit is given in Table 3-1. The first tube lowered down the borehole has a nonreturn valve at the bottom to prevent water outflow while lifting the tube units. The external and internal diameters of the tube units are 10 and 8 mm, respectively. The water content in each tube unit constitutes one sample and the volume of each sample is approximately two and a half litres. At the lower end of the tube array, a weight is added to keep the array stretched and to prevent fastening.

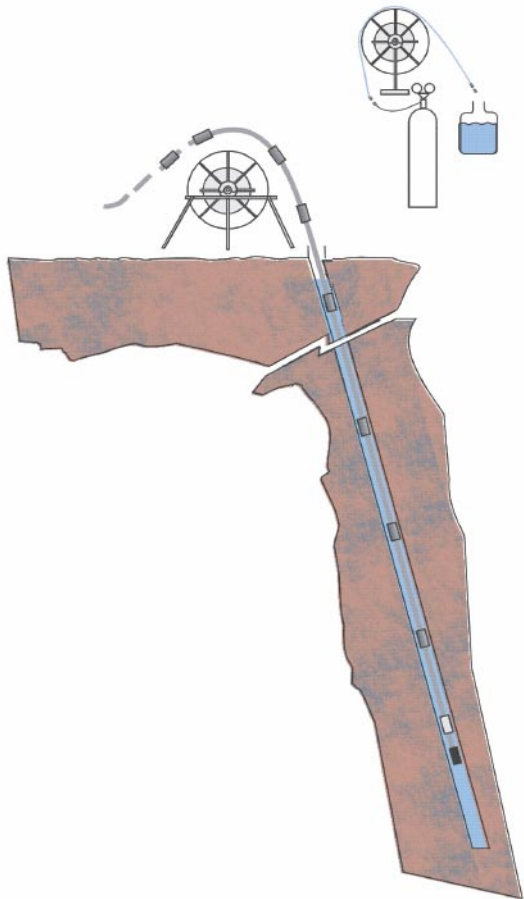


Figure 3-1. Equipment for hydrochemical logging in boreholes. At the lower end of the tube array there is a check valve and a weight connected. Each tube unit is 50 m long.

Table 3-1. Length of tube units used at the hydro-chemical logging in KLX04A.

Unit	Length [m]
1	49.71
2	50.08
3	49.77
4	49.28
5	49.97
6	50.01
7	49.85
8	49.87
9	49.57
10	49.72
11	49.67
12	50.25
13	50.62
14	49.70
15	49.22
16	49.20
17	49.30
18	49.63
19	49.62
20	49.87
Sum:	994.91
Couplings:	2.812
Weight:	0.817
Total tube length:	998.539

4 Performance

4.1 Hydrochemical logging

The hydrochemical logging in KLX04A was performed on July 8, 2004.

The lowering of the tube units started at 14:46. The tubes were lowered down the borehole at a rate of about five metres/minute. The equipment was lowered to a depth of 985 m, i.e. the length of the borehole subtracted by 8 m in order, to avoid drilling debris sedimentation at the bottom of the borehole and thereby decrease the risk of fastening. The lifting of the tubes started at 19:25, and the last tube unit was retrieved at 20:50. The tube unit at the top of the tube array was lowered to 35 m of its length. This resulted in a not completely filled tube unit. Pressurized nitrogen gas was used to empty the tube units and the water samples were portioned into sample bottles. Each tube unit represents one sample.

The ground water levels before and after completed loggings were 12.66 m and 12.47 m, respectively, below the top of the casing.

4.2 Sample treatment and chemical analysis

An overview of sample treatment and analysis routine is given in Appendix 1. The routines are applicable irrespectively of sampling object or sampling method.

An overview showing the samples obtained at the logging occasion is given in Table 4-1. Sample portions intended for isotope analyses were collected but not sent immediately for analysis at the sampling occasion. They are stored in a freezer at SKB (except the sample collected for tritium determination which is stored in refrigerator). The collected samples intended for isotope analysis may be sent for analysis, if so, the results will be presented in a separate report. The data from the hydrochemical logging are stored in the database SICADA in field note no Simpevarp 407. The SKB sample numbers are 7574–7593.

Table 4-1. Overview of samples collected at the hydrochemical logging in KLX04A. Filled cells represent collected samples. Blue filling represents samples sent for analyses, light yellow filling represents samples collected and stored in a freezer (tritium in a refrigerator) and purple dashed cells represent archive samples also stored in a freezer.

Sample information			Collected sample portions											Archive
Tube unit	Length [m]	SKB no.	Cond., pH, alk.	Major Comp.	Uranine	An-ions	³ H	δ ² H /δ ¹⁸ O	δ ³⁷ Cl	¹⁰ B	⁸⁷ Sr	δ ³⁴ S	Carbon isotopes	Filtered 2x250 mL
1	0-35	7574				ω	⊗	⊗			⊗			
2	85	7575												
3	135	7576												
4	185	7577												
5	235	7578												
6	285	7579												
7	335	7580												
8	385	7581												
9	435	7582												
10	485	7583												
11	535	7584												
12	585	7585												
13	635	7586												
14	685	7587												
15	735	7588												
16	785	7589												
17	835	7590												
18	885	7591												
19	935	7592												
20	985	7593												

⊗ filled with sample water from tube unit two
 ω partly filled with sample water from tube unit two

The uppermost tube unit was not completely filled, see Section 4.1. This was the cause for the second tube unit, from the top, as well. During the lifting of the tube array, the water column in the second unit slowly declined. This effect was not observed from unit three and down, i.e. other tube units seemed by, visual inspection, to be fully filled with sample water; only small bubbles of gas was observed during lifting. An over pressure was observed in the tubes from section 585–565 m down to the bottom of the borehole. The highest pressure occurred in the lowest tube unit, i.e. from section 935–985 m. Due to the lack of water in the first tube unit, see above, archive samples from the second tube unit was not obtained. Water intended for archive samples in the second unit were used to fill sample bottles for anions, δD and δ¹⁸O, ³H and ⁸⁷Sr/⁸⁶Sr from the first section (0–35 m).

4.3 Data handling

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

Several constituents are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure of each fifth or tenth collected sample.

All analytical results were 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 from basic water analyses are inserted into raw data tables for further evaluation. The evaluation results in a final data set for each sample. These data sets are 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. Relative errors within $\pm 5\%$ are considered acceptable (in surface waters $\pm 10\%$).

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

- General expert judgement of plausibility based on earlier results and experiences.

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

An overview of the data management is given in Figure 4-1.

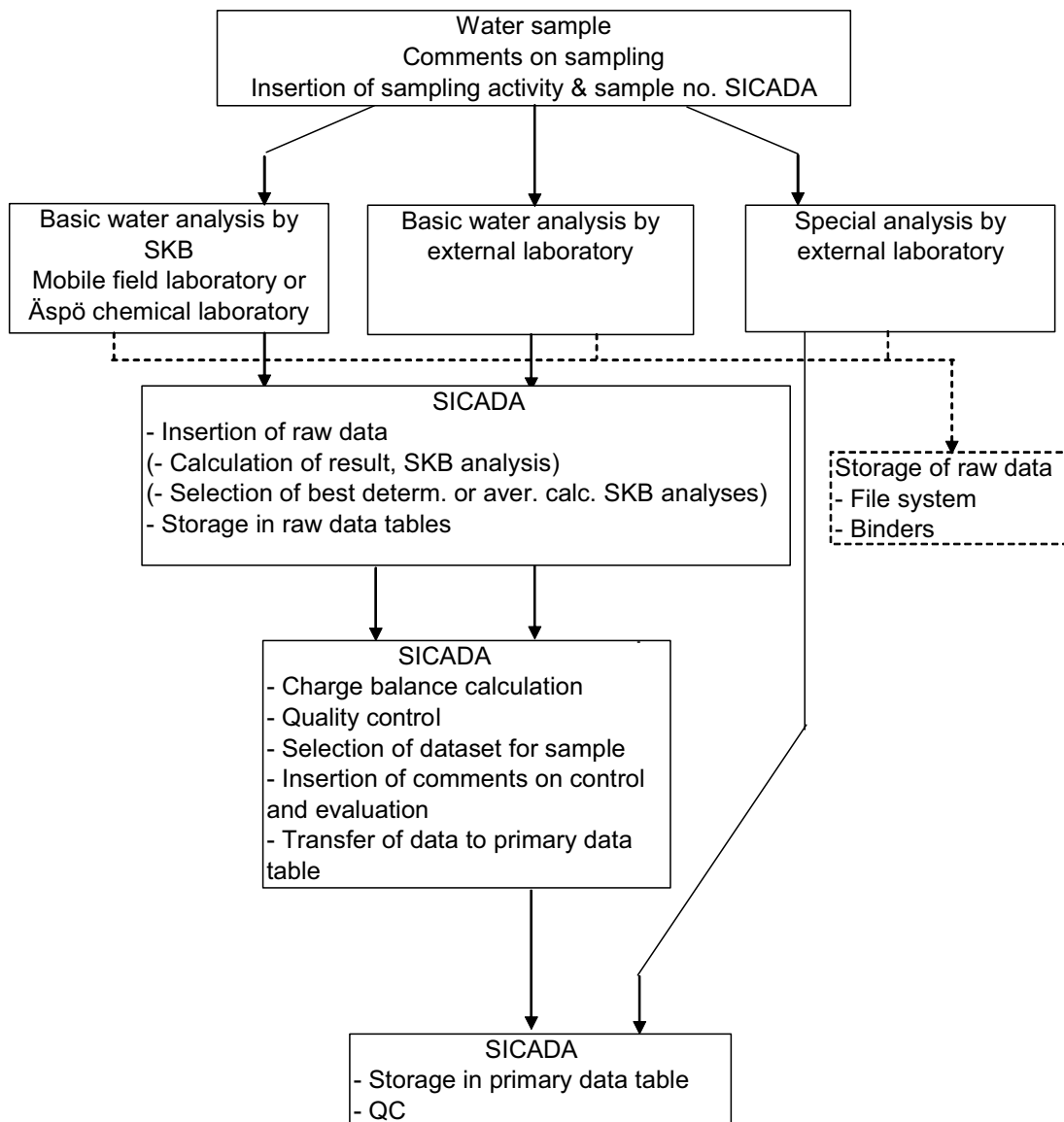


Figure 4-1. Overview of data management for hydrogeochemical data.

4.4 Nonconformities

One deviation from the Activity Plan has been reported. During the portioning of sample water for the first section (0–35 m), the order of priority listed in the Activity Plan was not followed. The amount of water intended to fill archive samples from the second section (135–185 m) was not sufficient to fill all the sample bottles for the first section. After filling all of the bottles to priority 6 ($\delta D/\delta^{18}O$), only approximately 100 mL remained in the tube unit. The remaining water volume was then used to fill the sample bottle for ^{87}Sr instead of the next bottle of priority, i.e. the 500 mL sample bottle for analysis of $\delta^{37}Cl$.

Except for the deviation reported above, the activity was performed without any deviations from the controlling documents for the activity.

5 Results

5.1 Analysis results

Results from the chemical analysis are given in Appendix 2. Diagrams showing the flushing water content and the electric conductivity along the borehole, at the time of the hydrochemical logging, are presented in Figures 5-1 and 5-2. Results from analysis of pH, hydrogen carbonate, major constituents and sulphate are shown in Figures 5-3 to 5-6. Results are plotted for the mid-length of each tube unit. For example, the first tube is plotted at 17.5 m.

Sulphate analysed by using ion chromatography (IC) is compared to sulphate determined as total sulphur using ICP-AES in Figure 5-4. The latter value is somewhat higher than for IC, especially in the upper sections of the borehole.

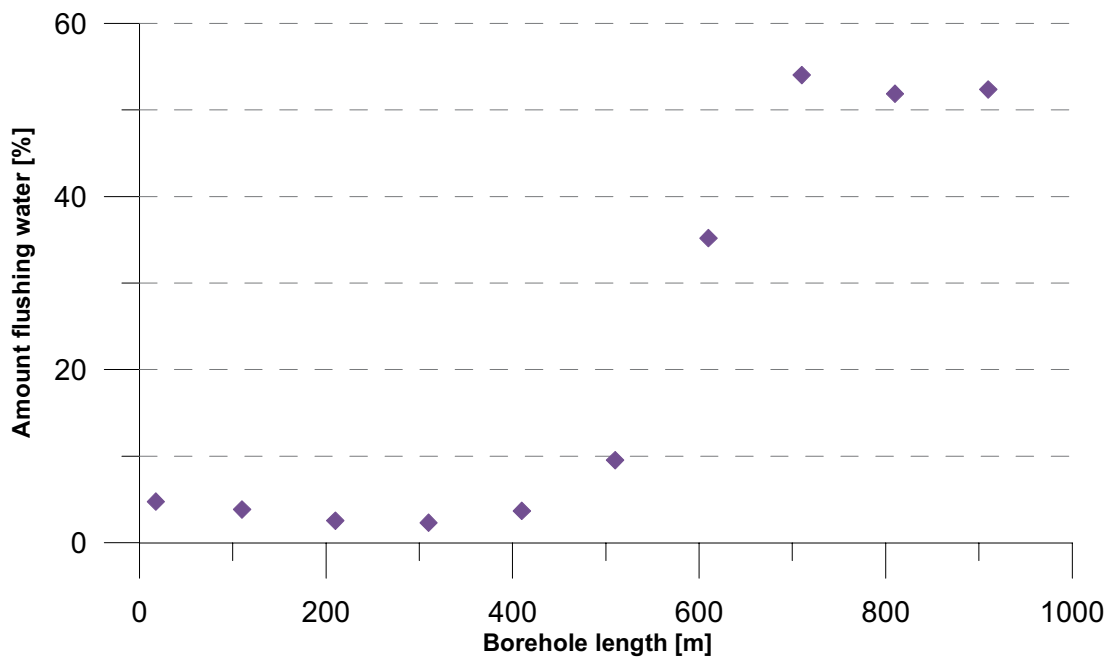


Figure 5-1. Amount of flushing water remaining at different borehole lengths at the time of the hydrochemical logging in KLX04A.

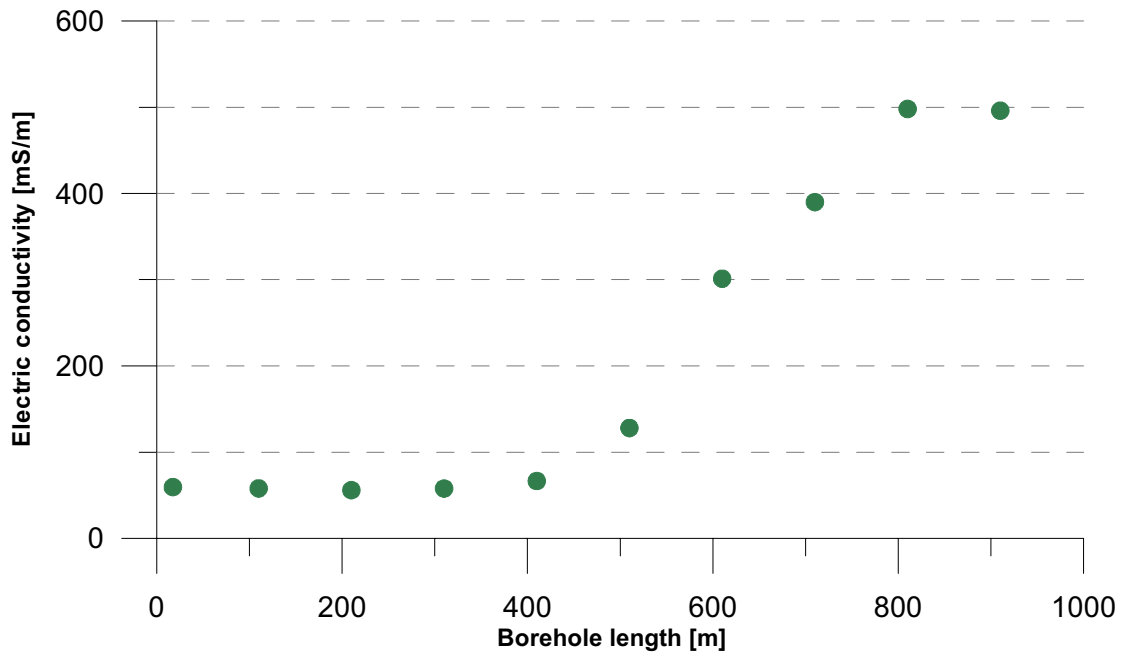


Figure 5-2. Electric conductivity values along the borehole KLX04A obtained from the hydrochemical logging.

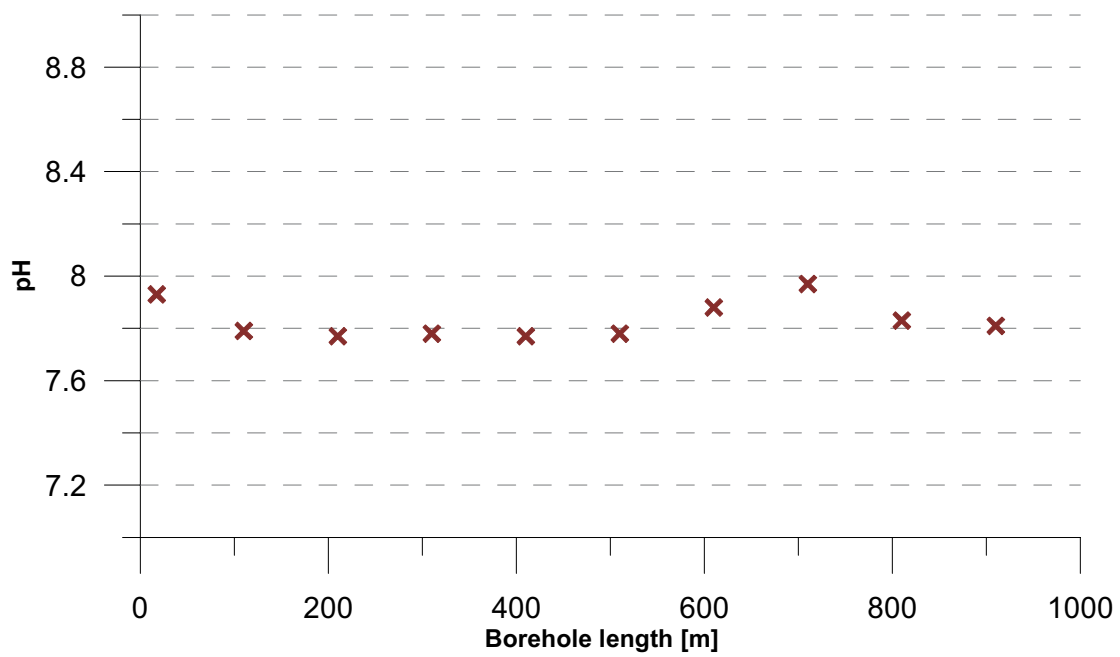


Figure 5-3. Results from pH measurements obtained from the hydrochemical logging in KLX04A.

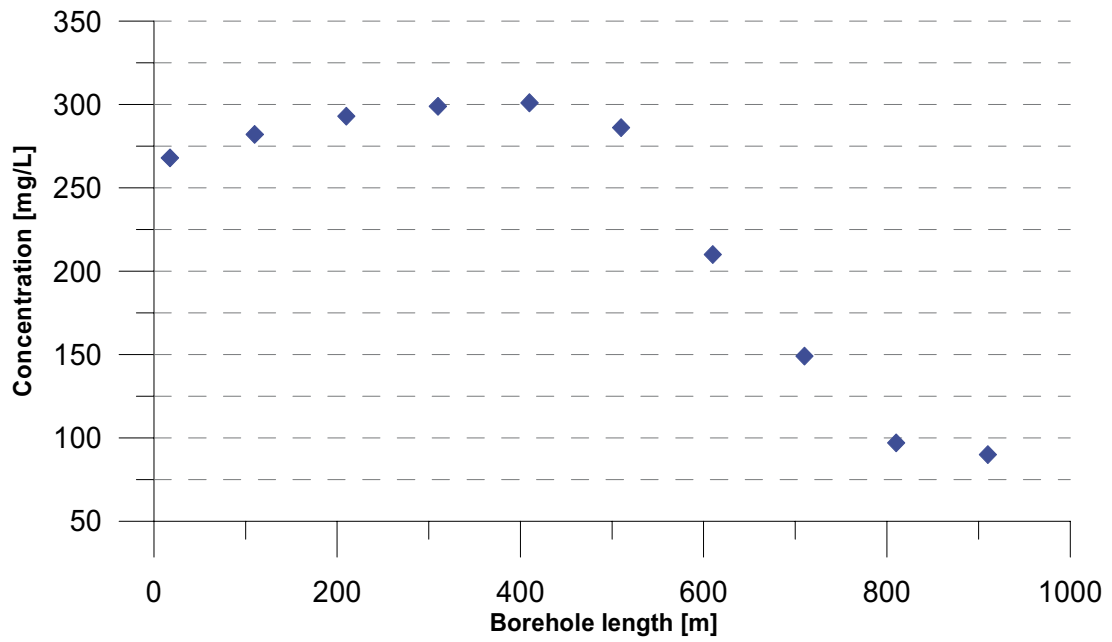


Figure 5-4. Results from hydrogen carbonate analysis of water samples taken at different lengths in KLX04A.

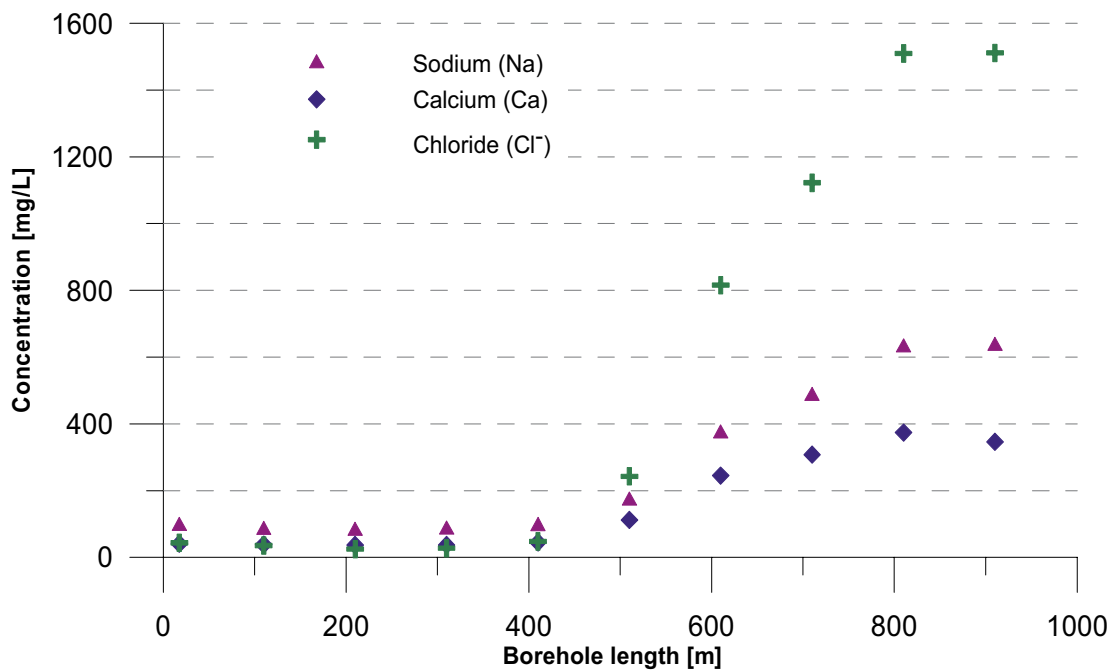


Figure 5-5. Results from analysis of the constituents Na, Ca and Cl⁻ in water samples obtained from hydrochemical logging in KLX04A.

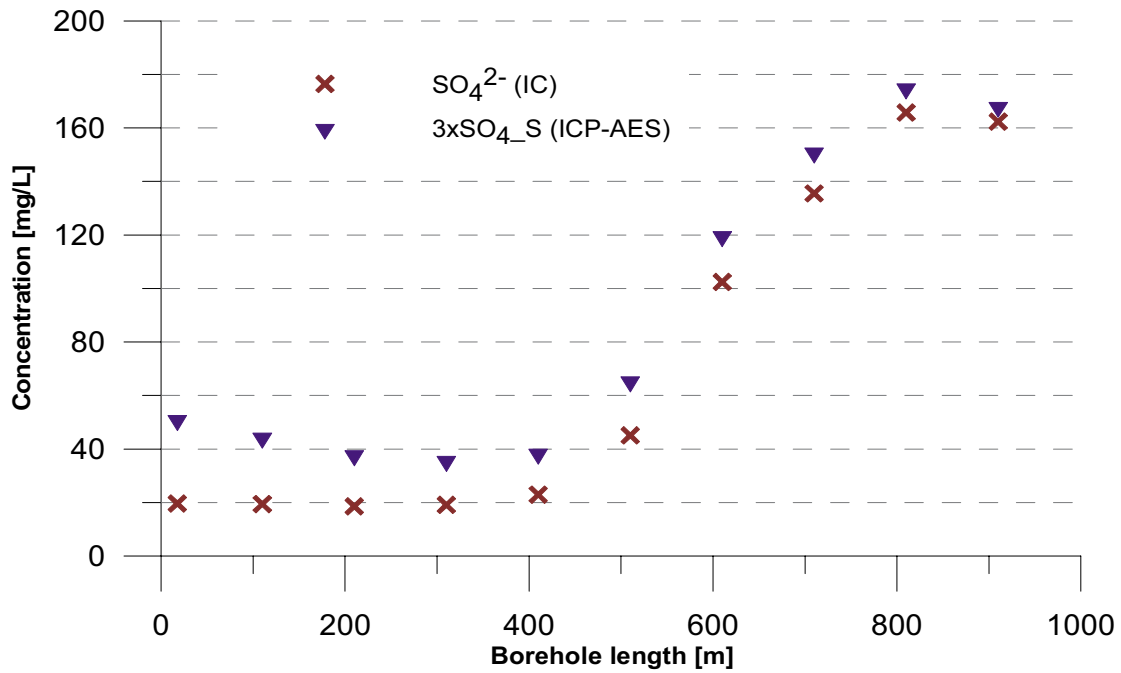


Figure 5-6. Sulphate (IC) compared to total sulphur (ICP).

5.2 Quality of the analyses

The charge balance errors give an indication of the quality and uncertainty of the analyses of major constituents. The relative charge balance errors were calculated for the selected sets of data, see Appendix 2. If the relative errors are within $\pm 5\%$ they are considered acceptable. The errors do not exceed 5% in any case.

6 Conclusions

At the hydrochemical logging in KLX04A, the following chemical conditions were found:

- The amount of flushing water at the time of the hydrochemical logging was below 5% down to 500 m of the borehole length. Below 600 m, there was a steep increase to values of about 50% in the deeper sections.
- The charge balance error, giving an indication of the quality and uncertainty of the analyses, did not exceed the acceptable level in any of the ten samples.
- The electric conductivity and the chloride concentration were increasing only slightly down the borehole. The highest values were 500 mS/m and 1,500 mg/L, respectively (both values from the deepest part measured along the borehole).
- The water composition shows only small variations the first 400 m of the borehole. The changes in the chemical composition below 500 m may partly be due to the significant increase of remaining flushing water.

7 References

- /1/ **SKB, 2001.** Generellt genomförande program för platsundersökningar. SKB R 01-10, Svensk Kärnbränslehantering AB.

Sampling and analysis methods

Table A1-1. Overview of general sample handling routines and analysis methods.

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Anions 1	HCO ₃ ⁻ pH(lab) cond (lab)	Plastic	250	Yes (not in the field)	No	Titration Pot. meas, Cond. meas	Åspö's chemistry lab.	The same day – maximum 24 hours
Anions 2	Cl, SO ₄ , Br, F, I ⁻	Plastic	100	Yes (not in the field)	No	Titration (Cl ⁻) IC (Cl ⁻ , SO ₄ , Br ⁻ , F ⁻) ISE (F ⁻)	Åspö's chemistry lab.	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	Analytica AB	Not critical (month)
Environmental isotopes	² H, ¹⁸ O	Plastic	100	No	-	MS	IFE	Not critical (month)
Tritium,	³ H (enhanced.)	Plastic (dry bottle) Plastic	500	No	-	LSC	Univ. Of Waterloo	Not critical (month)
Chlorine-37	Chlorine-37	Plastic	100	No	-	ICP MS		
Carbon isotopes	¹³ C, ¹⁴ C	Glass (brown)	100×2	No	-	(A)MS	Univ. Of Waterloo	A few days
Sulphur isotopes	³⁴ S	Plastic	500 –1000	Yes	-	Combustion, ICP MS	IFE	No limit
Strontium-isotopes	⁸⁷ Sr/ ⁸⁶ Sr	Plastic	100	Yes	-	TIMS	IFE	Days or Week
Boron isotopes	¹⁰ B	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP – MS	Analytica AB	No limit
Archive samples without acid	-	Plastic	250×2**	Yes	No	-	-	Storage in freeze

* Suprapur acid is used for conservation of samples.

** Minimu □

*** Full name and address is given in Table A1-2.

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
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
GC	Gas Chromatography

Table A1-2. Consulted laboratories, full name and address.

Äspö waterchemical laboratory (SKB)
Analytica AB
Aurorum 10
977 75 Luleå
(Nytorpsvägen 16
Box 511
183 25 Täby)
Environmental Isotope Laboratory
Dep. Of earth sciences
University of Waterloo
Waterloo, Ontario
N2L 3G1 CANADA
Institutt for energiteknik (IFE)
Instituttveien 18
P.O Box 40
2027 Kjeller
NORGE
The Ångström laboratory
Box 534
Se-751 21 Uppsala

Appendix 2

Water composition

Idcode	Secup m	Seclow m	Sample no	Charge Bal %	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	HCO ₃ ⁻ mg/L	Cl ⁻ mg/L	SO ₄ ²⁻ mg/L	SO ₄ -S mg/L	Br ⁻ mg/L	F ⁻ mg/L	Si mg/L	Fe mg/L
KLX04A	0	35	7574	0.2	94.0	3.11	41.1	8.3	267	43.6	19.7	16.6	0.26	2.23	7.45	0.127
KLX04A	35	85	7575	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	85	135	7576	-4.1	81.8	3.04	38.4	7.7	281	35.5	19.5	14.4	<0.20	2.12	7.86	0.237
KLX04A	135	185	7577	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	185	235	7578	-3.6	79.4	3.05	36.8	7.6	293	24.9	18.7	12.2	<0.20	2.02	8.10	0.280
KLX04A	235	285	7579	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	285	335	7580	-3.4	82.6	3.13	37.1	7.5	299	27.5	19.2	11.5	<0.20	2.09	8.31	0.485
KLX04A	335	385	7581	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	385	435	7582	-1.9	93.3	3.09	45.3	7.1	300	47.9	23.0	12.4	0.32	2.12	8.02	0.328
KLX04A	435	485	7583	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	485	535	7584	1.8	170.0	3.32	112.0	6.3	285	243	45.1	21.4	1.66	2.05	7.46	0.396
KLX04A	535	585	7585	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	585	635	7586	-1.0	371.0	4.22	245.0	4.5	210	816	102	39.5	6.40	2.95	5.86	0.576
KLX04A	635	685	7587	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	685	735	7588	-1.3	483.0	5.14	308.0	4.2	148	1,120	136	49.9	8.65	2.85	5.14	0.765
KLX04A	735	785	7589	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	785	835	7590	-1.9	629.0	6.03	374.0	5.3	97	1,510	166	57.9	11.80	2.30	5.02	1.370
KLX04A	835	885	7591	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX04A	885	935	7592	-3.0	633.0	6.23	346.0	5.7	89	1,510	162	55.6	11.30	2.10	5.64	1.930
KLX04A	935	985	7593	-	-	-	-	-	-	-	-	-	-	-	-	-

Mn mg/L	Li mg/L	Sr mg/L	pH	Drill_water %	EiCond mS/m	$\delta^2\text{H}$ dev SMOW	$\delta^{18}\text{O}$ dev SMOW	^3H TU	$\delta^{37}\text{Cl}$ dev SMOC	$^{10}\text{B}/^{11}\text{B}$ no unit	$^{87}\text{Sr}/^{86}\text{Sr}$ no unit	$\delta^{34}\text{S}$ dev CDT	$\delta^{13}\text{C}$ dev PDB	^{14}C pmC
0.191	0.021	0.50	7.93	4.75	59.6	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.217	0.019	0.48	7.79	3.83	58.1	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.234	0.016	0.47	7.77	2.54	56.1	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.241	0.018	0.49	7.78	2.31	58.0	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.234	0.019	0.66	7.77	3.67	66.7	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.223	0.040	1.88	7.78	9.54	128	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.171	0.088	4.3	7.89	35.2	301	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.160	0.118	5.46	7.97	54.1	390	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.197	0.151	6.72	7.83	51.9	498	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx
0.205	0.150	6.25	7.81	52.4	496	xxx	xxx	xxx	xxx	xxx	xxx	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	xxx	xxx	xxx

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
xxx = Stored in freezer/refrigerator
< = result below detection limit
ChargeBal % = Relative charge balance error %