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Oskarshamn site investigation

Hydrochemical logging in KLX12A

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August 2006

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Abstract

Hydrochemical logging, or so called tube sampling, has been performed in the core drilled borehole KLX12A. 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 600 m long polyamide tube divided into units of 50 m.

The water content in each tube unit constituted one sample. Every second sample, starting with the uppermost tube unit, was analysed according to SKB chemistry class 3 (isotope options excluded). Samples for isotope determination were collected at the time of sampling and stored in a freezer (tritium and carbon isotopes in a refrigerator); $\delta^{18}O$, deuterium ($\delta^{2}H$), tritium (^{3}H), ^{10}B, $\delta^{37}Cl$ and ^{87}Sr from odd-numbered tube units and $\delta^{34}S$ and carbon isotopes from even-numbered tube units. If these samples will be sent for analysis, the results will be reported in a separate report.

The drill water content remaining in the borehole after drilling was below 20% down to approximately 450 metres. From 450 metres and down, the drill water content increased, reaching a maximum value of 32% in tube unit 545–595 m. The relative charge balance error did not exceed the acceptable limit of ± 5%, except for one sample out of six (7% in tube unit 245–295 m).

Sammanfattning

Hydrokemisk loggning, eller så kallad slangprovtagning, har utförts i det kärnborrade borrhålet KLX12A. 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 600 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 alla tillval). Prover för bestämning av isotoptillvalen togs ut vid provtagningstillfället och sparades i frys (tritium och kolisotoper i kylskåp); δ^{18}O, deuterium (δ^{2}H), tritium (^{3}H), ^{10}B, δ^{37}Cl och ^{87}Sr ur udda enheter, δ^{34}S och kolisotoper ur jämna enheter. Om proven skickas för analys, kommer resultaten att sammanfattas i en separat rapport.

Halten kvarvarande spolvatten i borrhålet efter avslutad borrning var under tjugo procent de första 450 metrarna. Från 450 m och nedåt ökade spolvattenhalten, med en högsta uppmätta halt på 32 % i slangenhet 545–595 m. Det relativa felet i jonbalansen översteg inte den acceptabla nivån av ± 5 %, utom i ett av de sex analyserade proverna (7 % i slangenhet 245–295 m).

Contents

1 Introduction

This document reports the performance and results from the Hydrochemical logging in borehole KLX12A. The Hydrochemical logging is one of the activities performed within the site investigation at Oskarshamn /1, 2/. The work was carried out in accordance with activity plan AP PS 400-06-022. In Table 1-1 controlling documents for performing this activity are listed. Both activity plan and method descriptions are SKB's internal controlling documents. The obtained data from the activity are reported to the database SICADA, where they are traceable by the activity plan number.

Borehole KLX12A is a 602.29 m long telescopic borehole, drilled within the site investigation in the Oskarshamn area. The percussion borehole HLX10 served as the source of flushing water for the drilling of KLX12A. The locations of KLX12A and HLX10 are shown in Figure 1-1.

The borehole KLX12A is not of the so called SKB chemical type; see method descriptions MD 620.003 (Method description for drilling cored boreholes) and 610.003 (Method description for percussion drilling). The cleaning procedures of all equipment used in the borehole, during and after drilling, were performed according to level 1 in the cleaning instructions in MD 600.004 (Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning).

Table 1-1. SKB internal controlling documents for the performance of the activity.

Activity plan	Number	Version
Hydrokemisk loggning i KLX12A	AP PS 400-06-022	1.0
Method descriptions	**Number**	**Version**
Metodbeskrivning för hydrokemisk loggning	SKB MD 422.001	2.0
Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning	SKB MD 600.004	1.0

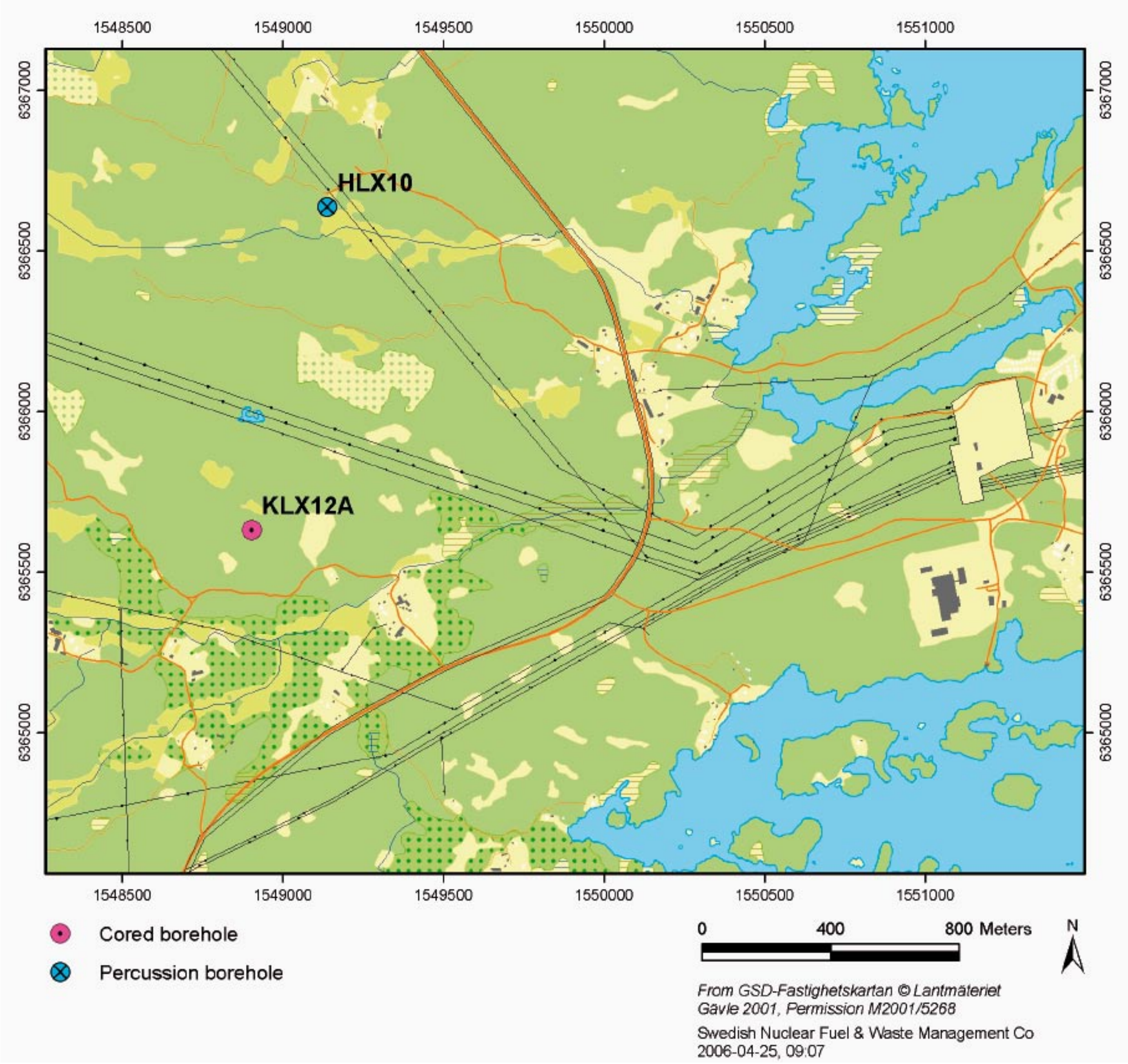

Figure 1-1. *Location of the core drilled borehole KLX12A and the percussion borehole HLX10 within the site investigation in the Oskarshamn area.*

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 KLX12A. The technique used for sampling is fast and simple, also for boreholes of considerable lengths.

The analysis program was carried out according to SKB chemistry class 3 except for optional isotopes. Sample portions intended for isotope analyses were collected at the time of sampling, but have still not been analysed. The samples were stored in a freezer at SKB (except the samples collected for determination of tritium and carbon isotopes; these samples were stored in a refrigerator). If the samples from the activity will be analysed for isotopes, the results from those analyses will be presented in a separate report.

3 Sampling equipment

For the Hydrochemical logging an approximately 600 m long polyamide tube, divided into units of 50 m, was used. The equipment is described in the method description, see Table 1-1.

A schematic picture of the equipment used for the Hydrochemical logging is shown in Figure 3-1. The tube units are connected using metal couplings and manual shut off valves. The external and internal diameters of the tube units are 10 and 8 mm, respectively. The first tube lowered down the borehole has a non-return valve at the bottom to prevent water outflow while lifting the tube units. At the lower end of the tube array, a weight is added in order to stretch the array and thereby prevent fastening.

The water content in each tube unit constitutes one sample, and the volume of each sample is approximately two and a half litres.

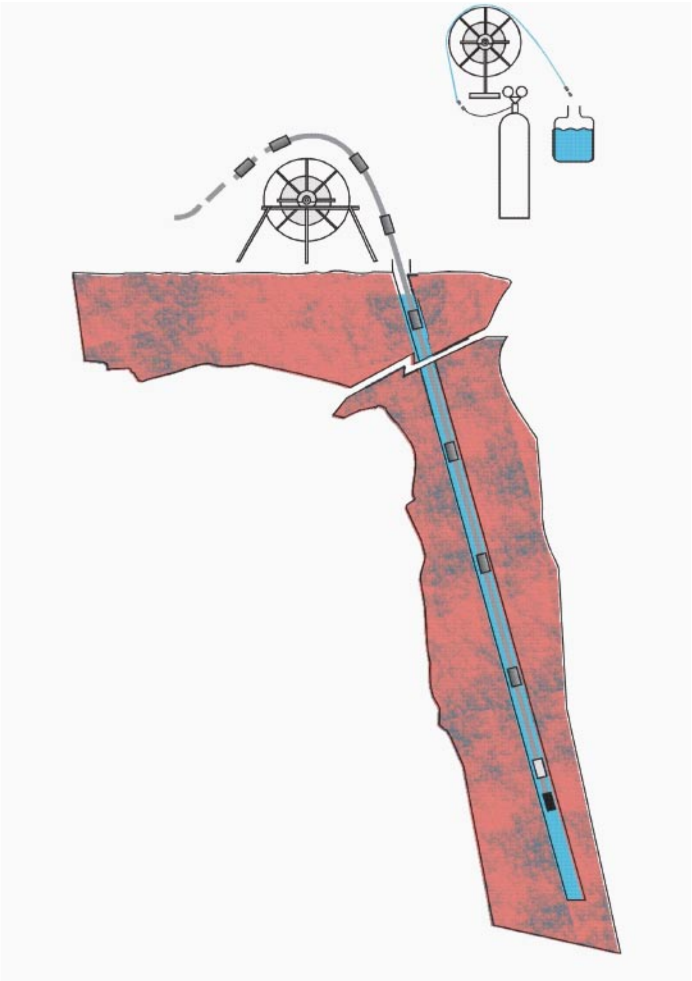

Figure 3-1. *Equipment for Hydrochemical logging in boreholes. At the lower end of the tube array there is a non-return valve and a weight connected. Each tube unit is 50 m long.*

4 Performance

4.1 Hydrochemical logging

The Hydrochemical logging in KLX12A was performed on April 11, 2006 according to the activity plan AP PS 400-06-022 and in compliance with the method description SKB MD 422.001 (cf. Table 1-1).

The equipment was lowered to a length of 595 m of borehole length, in order to avoid potential settled drilling debris at the bottom of the borehole, and thereby decrease the risk of fastening. The tubes were lowered down the borehole at a rate of about five m/minute. The lowering of the tube units started at 10:16 and the lifting of the tubes started at 14:30. The last tube unit was retrieved at 15:36. Pressurized nitrogen gas was used to empty the tube units and the water samples were portioned into sample bottles. Each tube unit represented one sample.

The ground water level measured before and after the Hydrochemical logging was 6.89 and 7.56 m, respectively, below top of casing. As the tube unit at the top of the tube array was lowered to 45 metres of its length, the sampling resulted in a not completely filled tube unit.

4.2 Sample treatment and chemical analysis

An overview of sample treatment and analysis routines of the activity is given in Appendix 1.

An overview showing the samples obtained at the logging occasion is given in Table 4-1. Sample portions intended for isotope analyses were collected at the sampling occasion but not sent for analysis. These samples are stored in a freezer at SKB (except for the samples collected for tritium and carbon isotope determinations which are stored in a refrigerator). If the collected samples intended for isotope analysis will be sent for analysis, the results will be presented in a separate report. The data from the Hydrochemical logging are stored in the database SICADA. The SKB sample numbers are 10967–10978.

The uppermost tube unit was not completely filled, see section 4.1. All other tube units seemed, by visual inspection, to be fully filled with sample water; only small bubbles of gas was observed during lifting. Due to the lack of water in the first tube unit, see above, the volume of archive samples from the uppermost tube unit was reduced.

Table 4-1. Overview of samples collected at the Hydrochemical logging in KLX12A. Filled cells represent collected samples. Dark (blue) filling represents samples sent for analyses, light (yellow) filling represents samples collected and stored in a freezer (tritium and carbon isotopes in a refrigerator) and dashed (purple) cells represent archive samples.

Sample information			Collected sample portions											Archive
Tube unit	Length [m]	SKB no.	Cond., pH, alk.	Major Comp	Uranine	Anions	^{3}H	δ ^{2}H δ^{18}O	δ^{37}Cl	^{10}B	^{87}Sr	δ^{34}S	C-isotopes	Filtered 2×250 mL
12	0 46	10967										🟨	🟨	🟪 ж
11	95	10968	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟨			
10	145	10969										🟨	🟨	🟪
9	195	10970	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟨			
8	245	10971										🟨	🟨	🟪
7	295	10972	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟨			
6	345	10973										🟨	🟨	🟪
5	395	10974	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟨			
4	445	10975										🟨	🟨	🟪
3	495	10976	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟨			
2	545	10977										🟨	🟨	🟪
1	595	10978	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟨			

ж Only ca 200 ml.

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.

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 ± 5% are considered acceptable (in surface waters ± 10%).

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

- General 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 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.

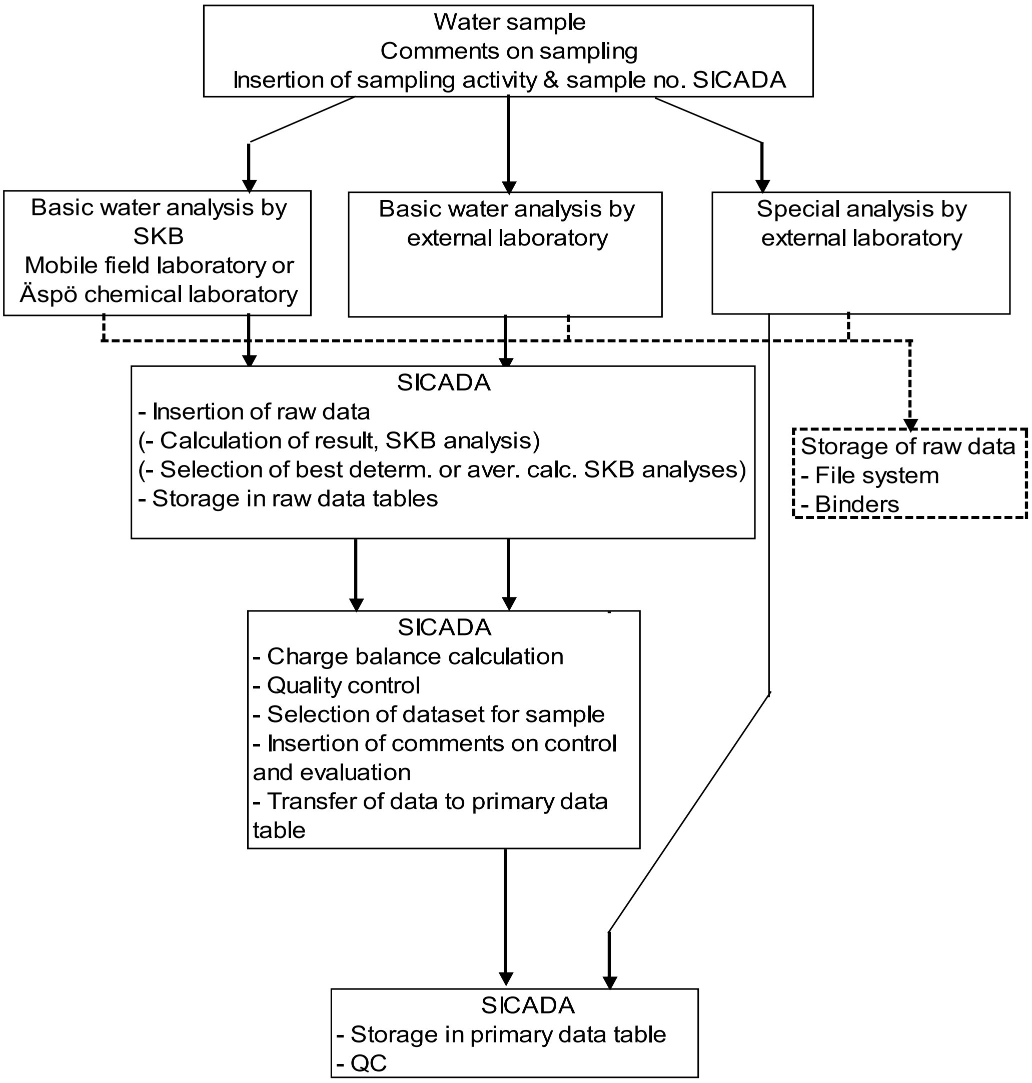

Figure 4-1. *Overview of data management for hydrogeochemical data.*

4.4 Nonconformities

The activity was performed without any deviations from the controlling documents for the activity that can affect the quality of data. Due to problems with lack of water in sampling tube number 12 (0–45 m), the volume of the archive sample was reduced in this section.

5 Results

5.1 Analysis results

The results from the chemical analyses are presented in Appendix 2. The original results are stored in the primary data base (SICADA), and the data in this data base will be used for further interpretation (modelling).

Diagrams showing the drill 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 analyses of pH, HCO_3^- and some of the major constituents (Na^+, Ca^+ and Cl^-) are shown in Figures 5-3 to 5-5, respectively. Sulphate (SO_4^{2-}) analysed by ion chromatography (IC) is compared with sulphate determined as total sulphur using inductively coupled plasma atomic emission spectrometry (ICP-AES) in Figure 5-6. Results are plotted for the mid-length of each tube unit.

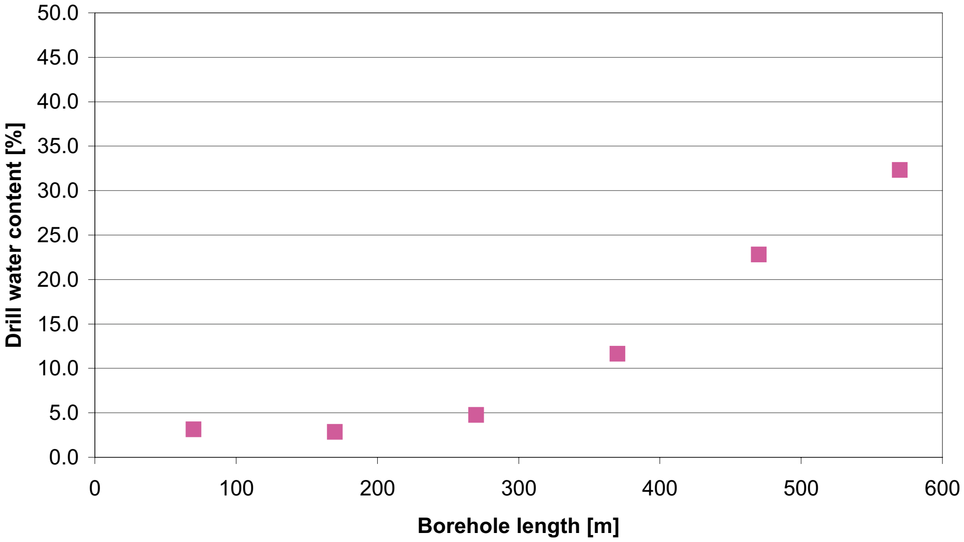

Figure 5-1. *Drill water content remaining at different borehole lengths at the time of the Hydrochemical logging in KLX12A.*

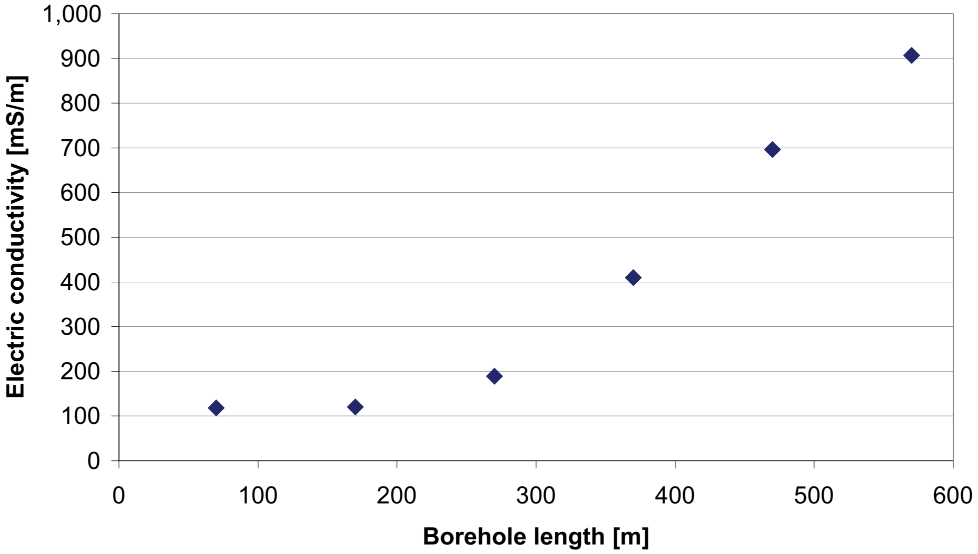

Figure 5-2. *Electric conductivity values along the borehole KLX12A obtained from the Hydrochemical logging in KLX12A.*

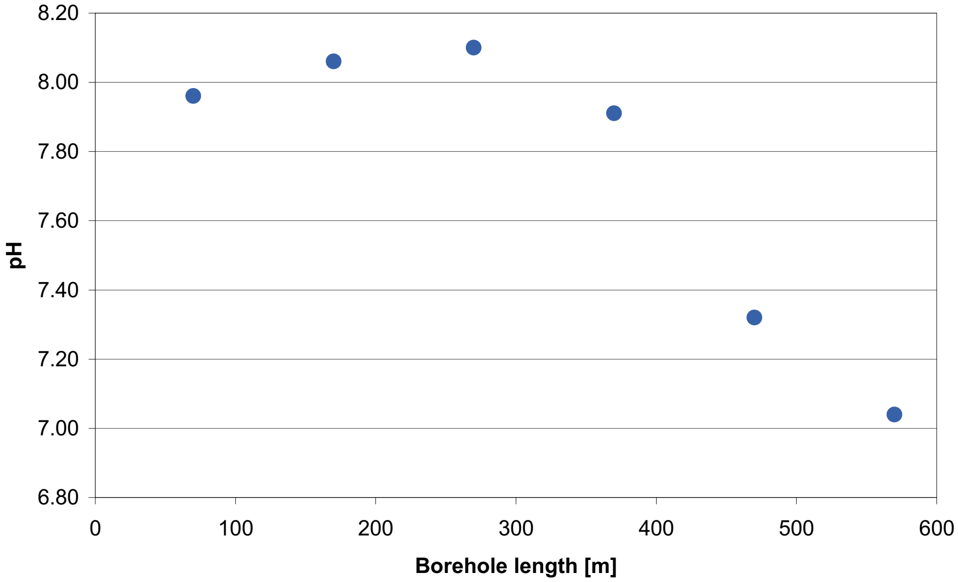

Figure 5-3. *Results from pH measurements obtained from the Hydrochemical logging in KLX12A.*

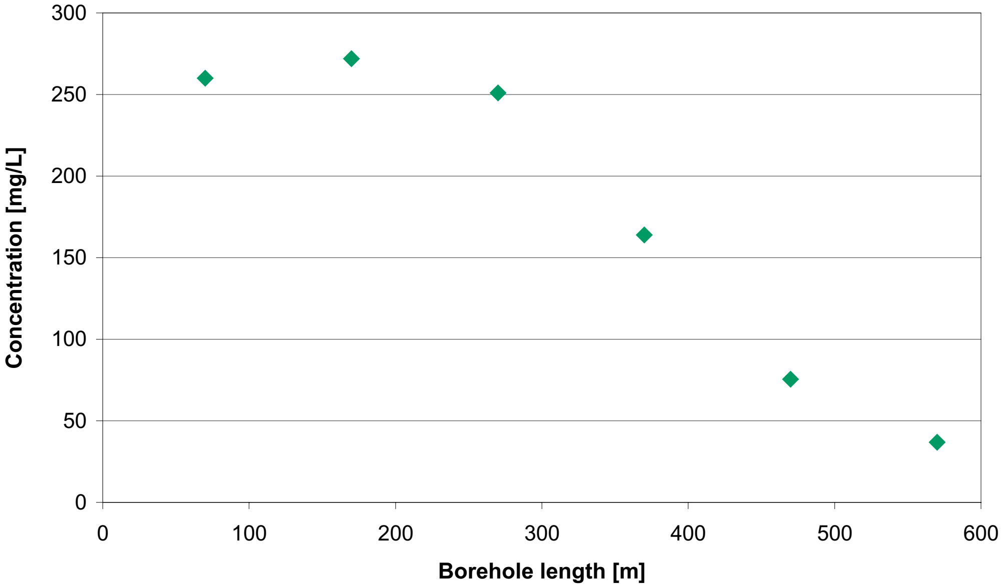

Figure 5-4. *Results from analysis of hydrogen carbonate (HCO_3^-) in water samples obtained from the Hydrochemical logging in KLX12A.*

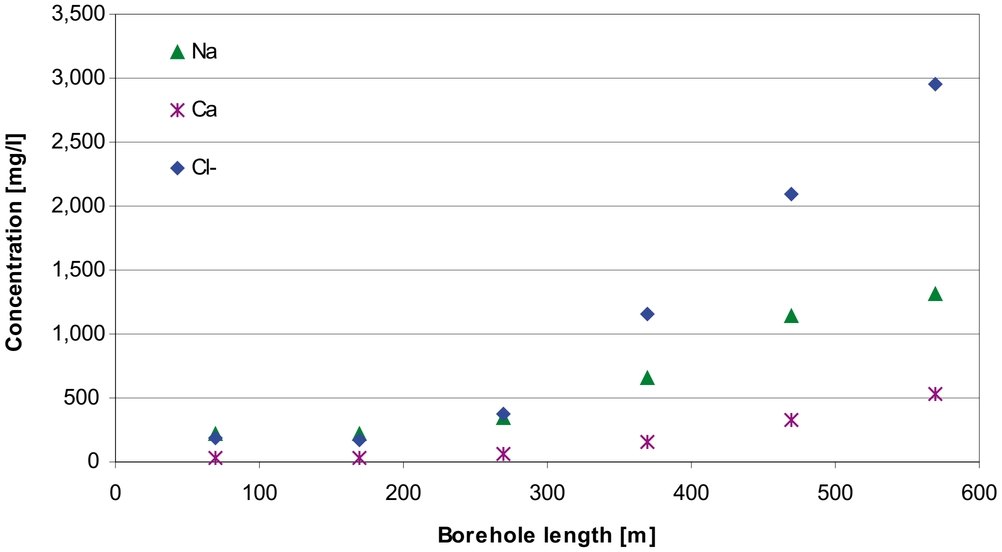

Figure 5-5. *Results from analysis of the constituents Na^+, Ca^{2+} and Cl^- in water samples obtained from the Hydrochemical logging in KLX12A.*

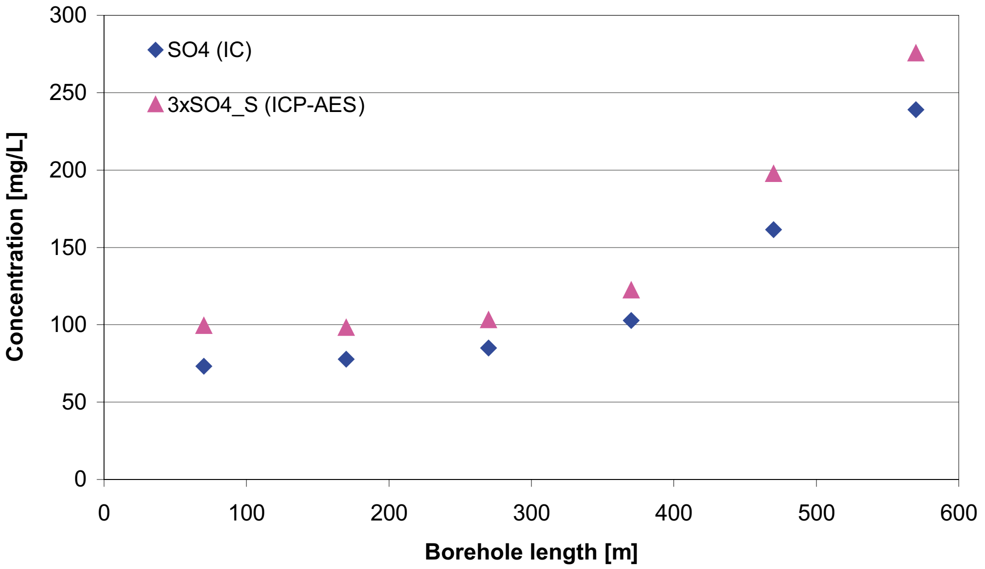

Figure 5-6. *Sulphate (IC) compared to total sulphur (ICP-AES), results from the Hydrochemical logging in KLX12A.*

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 ±5% they are considered acceptable. The errors did not exceed 5% except for tube section 245–295 m, for which the charge balance error was 7%. All of the results concerning anions and cations (except for hydrogen carbonate) from this sample were re-analysed, and found to be correct.

6 Conclusions

The Hydrochemical logging of KLX12A was conducted successfully. The main conclusions that can be drawn from the Hydrochemical logging are:

- The amount of remaining drill water at the time of the Hydrochemical logging was below 20% the first 450 m along the borehole, From 450 m and to the bottom the amount increased, reaching 32% in the lowest section.
- The highest value of electric conductivity and the highest chloride concentration was found in the tube unit from 545–595 m of borehole length. The values were 907 mS/m and 2,960 mg/L, respectively.
- The charge balance error, giving an indication of the quality and uncertainty of the analyses, slightly exceeded the acceptable level only in one of the samples.

No sample was sent to a different laboratory due to lack of sample water. No results were considered unconfident, based on general trends.

7 References

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

/2/ **SKB, 2005.** Platsundersökning Oskarshamn. Program för fortsatta undersökningar av berggrund, mark, vatten och miljö inom delområde Laxemar. SKB R-05-37. Svensk Kärnbränslehantering AB.

Appendix 1

Sampling and analytical methods

Table A1-1. 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	HCO_3^- pH (lab) cond (lab)	Plastic	250	No	No	Titration Pot. meas, Cond. meas	The same day – maximum 24 hours
Anions 2	Cl^-, SO_4^{2-}, Br^-, F^-	Plastic	100	Yes (in connection with analysis)	No	Titration (Cl^-) IC (Cl^-, SO_4^{2-}, Br^-, F^-) ISE (F^-)	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)
Environmental isotopes	δ^2H, $\delta^{18}O$	Plastic	100	No	– –	MS	Not critical (month)
Tritium	^3H (enhanced.)	Plastic (dry bottle)	500	No	–	LSC	
Chlorine-37	$\delta^{37}Cl$	Plastic	500	No	–	ICP-MS	Not critical (month)
Carbon isotopes	$\delta^{13}C$, pmC (^{14}C)	Glass, dark	100×2	No	–	(A)MS	A few days
Sulphur isotopes	$\delta^{34}S$	Plastic	500–1,000	No	–	Combustion ICP-MS	No limit
Strontium-isotopes	$^{87}Sr/^{86}Sr$	Plastic	100	No	–	TIMS	Days or Week
Boron isotopes	$^{10}B/^{11}B$	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP-MS	No limit
Archive samples without acid	–	Plastic	250×2	Yes	No	–	Storage in freeze container

* Suprapur acid is used for conservation of samples.

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
MS	Mass Spectrometry
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
TIMS	Thermal Ionization Mass Spectrometry

Table A1-2. Reporting limits and measurement uncertainties.

Component	Method	Reporting limits or range	Unit	Measurement uncertainty[2]	"Total" uncertainty[3]
HCO_3^-	Alkalinity titration	1	mg/L	4%	< 10%
pH	Pot. meas.	–	–	5%	–
Cond.	Cond. meas.	0.02	mS/m	4%	–
Cl^-	Mohr-titration	> 70	mg/L	5%	< 10%
Cl^-	IC	1–100		6%	10 %
SO_4^{2-}	IC	1	mg/L	10%	15%
Br^-	IC	0.2	mg/L	9%	20%
F^-	IC	0.1	mg/L	10%	20%
F^-	ISE	–		–	
Na	ICP	0.1	mg/L	4%	10%
K	ICP	0.4	mg/L	6%	15%
Ca	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[1] 2	mg/L	10%	20%
δ^2H	MS	2	‰ SMOW[4]	1‰	–
$\delta^{18}O$	MS	0.1	‰ SMOW[4]	0.2‰	–
^3H	LSC	0.8 or 0.1	TU[5]	0.8 or 0.1	Correct order of size
$\delta^{37}Cl$	ICP MS	0.2‰ (20 mg/L)	‰ SMOC[6]	–	–
$\delta^{13}C$	A (MS)	–	‰ PDB[7]	–	–
pmC (^{14}C)	A (MS)	–	pmC[8]	–	–
$\delta^{34}S$	ICP MS	0.2‰	‰ CDT[9]	0.3‰	–
$^{87}Sr/^{86}Sr$	TIMS	–	No unit (ratio)[10]	–	–
$^{10}B/^{11}B$	ICP MS	–	No unit (ratio)[10]	–	–

1. Reporting limits at salinity ≤ 0.4% (520 mS/m) and ≤ 3.5% (3,810 mS/m) respectively.
2. Measurement uncertainty reported by consulted laboratory, generally 95% confidence interval.
3. Estimated total uncertainty by experience (includes effects of sampling and sample handling).
4. Per mille deviation[13] from SMOW (Standard Mean Oceanic Water).
5. TU = Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10^{-18} (1 Bq/L Tritium = 8.45 TU).
6. Per mille deviation[13] from SMOC (Standard Mean Oceanic Chloride).
7. Per mille deviation[13] from PDB (the standard PeeDee Belemnite).
8. The following relation is valid between pmC (percent modern carbon) and Carbon-14 age:
   $pmC = 100 \times e^{((1{,}950-y-1.03t)/8{,}274)}$ where y = the year of the C-14 measurement and t = C-14 age.
9. Per mille deviation[13] from CDT (the standard Canyon Diablo Troilite).
10. Isotope ratio without unit.

Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:
$\delta^yI = 1{,}000\times(K_{sample}-K_{standard})/K_{standard}$, where K= the isotope ratio and ^yI = ^2H, ^{18}O, ^{37}Cl, ^{13}C or ^{34}S etc.

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	Mn mg/L	Li mg/L	Sr mg/L	pH	Drill_ water %
KLX12A	0	45	10967																		
KLX12A	45	95	10968	–0.58	216	3.52	32.8	4.7	260	182	73.1	33.1	0.845	3.52	6.41	1.67	0.127	0.023	0.512	7.96	3.12
KLX12A	95	145	10969																		
KLX12A	145	195	10970	–0.78	220	3.44	30.9	4.5	272	179	77.8	32.7	0.830	3.96	5.55	0.828	0.122	0.023	0.519	8.06	2.83
KLX12A	195	245	10971																		
KLX12A	245	295	10972	6.68	348	3.87	68.4	7.0	251	368	85.1	34.3	1.73	3.68	4.52	0.655	0.177	0.036	1.27	8.10	4.75
KLX12A	295	345	10973																		
KLX12A	345	395	10974	–0.06	663	5.61	161	12.6	164	1,160	103	40.7	5.65	3.10	4.33	0.323	0.332	0.071	3.03	7.91	11.6
KLX12A	395	445	10975																		
KLX12A	445	495	10976	2.57	1,140	7.66	332	17.7	75.5	2,090	161	65.8	10.3	2.75	3.67	2.25	0.693	0.119	6.18	7.32	22.8
KLX12A	495	545	10977																		
KLX12A	545	595	10978	–3.02	1,310	9.58	525	14.3	36.9	2,960	239	91.8	15.1	2.70	3.90	4.08	0.800	0.152	9.78	7.04	32.3

Idcode	Secup m	Seclow m	Sample no.	ElCond mS/m	δ^{2}H dev SMOW	δ^{18}O dev SMOW	^{3}H TU	δ^{37}Cl dev SMOC	^{10}B/^{11}B no unit	^{87}Sr/^{86}Sr no unit	δ^{34}S dev CDT	δ^{13}C dev PDB	^{14}C pmC
KLX12A	0	45	10967								xxx	xxx	xxx
KLX12A	45	95	10968	118	A	A	A	xxx	xxx	xxx			
KLX12A	95	145	10969								xxx	xxx	xxx
KLX12A	145	195	10970	120	A	A	A	xxx	xxx	xxx			
KLX12A	195	245	10971								xxx	xxx	xxx
KLX12A	245	295	10972	189	A	A	A	xxx	xxx	xxx			
KLX12A	295	345	10973								xxx	xxx	xxx
KLX12A	345	395	10974	410	A	A	A	xxx	xxx	xxx			
KLX12A	395	445	10975								xxx	xxx	xxx
KLX12A	445	495	10976	696	A	A	A	xxx	xxx	xxx			
KLX12A	495	545	10977								xxx	xxx	xxx
KLX12A	545	595	10978	907	A	A	A	xxx	xxx	xxx			

A = Results will be reported later.

xxx = Stored in freezer/refrigerator.

ChargeBal % = Relative charge balance eror %.