



Internal information
Minutes

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Minutes from the Geochemistry Experts Meeting

April 1 2008, SKB Blekholmstorget 30, Stockholm

Chairman: Bill Wallin

At the protocol: Birgitta Kalinowski/Bill Wallin

List of participants:

SKB: Anders Ström, Anders Winberg, Ann-Chatrin Nilsson, Bill Wallin, Birgitta Kalinowski, Björn Söderbäck, Eva-Lena Tullborg, John Smellie, Lillemor Claesson Liljedahl, Lotta Hallbeck, Marcus Laaksoharju, Olle Olsson (introduction only)

SKI: Adrian Bath, Bo Strömberg, Georg Lindgren, Hans-Peter Hermansson, Öivind Toverud

SSI: Jinsong Liu, Maria Nordén, Shulan Xu

The aim of the meeting was to present:

- ongoing SDM Site work at both Laxemar and Forsmark
- sulphide data at both Laxemar and Forsmark
- microbiological data on sulphate reduction and geogas levels at both sites
- mineralogical and geochemical evidences for redox transition zone in Laxemar
- uranium concentrations in Forsmark
- a new report (R-07-55) on surface waters and shallow groundwaters at Forsmark

A short outline of the presentations and discussions from the meeting is presented below. In the discussion sections answers are given in italics.

Marcus Laaksoharju, ChemNet

Summary of presentation

SDM Site work:

- Data acquisition and compilation based on data freeze 2.3 including extended DF data from Forsmark (Oct 2007) and Laxemar (Nov 2007).
- Groundwater composition at repository depth at both sites, but especially Laxemar
- Spatial variability of groundwater composition relevant to calibration of flow/transport models, including isotopic data.

The total number of samples for Forsmark 2.3, category 1-3: 44 (+22 category 4 and 107 category 5) and for Laxemar 2.3, category 1-3: 65 (+48 category 4 and 322 category 5)

Forsmark: Groundwater composition to an elevation -150 m is most likely of meteoric origin. Iron reducing bacteria (IRB) activity seems to be dominant as the amount of dissolved Fe²⁺ is high.

Important sulphate reducing bacteria (SRB) activity is found. At repository depth (200-600 m) there are indications of Littorina water input. Dissolved Fe²⁺ content, in lower concentrations than in the shallow water system, is possibly due to occurrence of slowly crystallizing amorphous iron oxyhydroxides. The low dissolved sulphide concentrations (<0.3 mg L⁻¹) are controlled by the precipitation of FeS_(amorphous) linked to SRB activity. Water at greater depths has isotope signatures typically of old water, possibly meteoric water formed before last deglaciation. The highest sulphide concentrations found in the system are due to the competition between the SRB and the simultaneous precipitation of FeS_(amorphous).

Laxemar (indications): Clear evidences of glacial water components at 300-600 m depth, with low Cl concentrations at about 1000-2500 mg L⁻¹. A tendency towards higher salinities in groundwaters from the southern part of the area compared with samples at the same depths from the central parts. Factors of large importance for the evolution of groundwater chemistry are the transmissivities and orientation of the large deformation zones of type EW007, NE0042 (for details se PPT presentations).

Discussion

Adrian Bath: How do Safety assessment SR-Can and SR-Site come together. Requested integration of hydrogeological and hydrogeochemical model.

Good to be clear about different categories. Is there a fundamental difference between the sites as there are more category 1 samples from Forsmark?

-Category 1-3 samples are used for modelling as Laxemar is more complicated to sample than Forsmark. The bedrock is more isolated in Forsmark.

Bo Strömberg asked about the monitoring of the sites. Is only the surface monitored?

-Depth is monitored as well

Maria Nordén asked how the category 5 samples are used.

-They are used to indicate inflow for example, checking trends

Jinsong Liu asked when the samples are categorised: before or after sampling?

-After sampling

Georg Lindgren asked how samples are affected by fractures. Small fractures/ large fractures vs porewater content?

-The interaction between groundwater and porewater was discussed . In large fracturezones pore water composition is affected.

Adrian Bath was concerned about how anomalies in fracture zones are taken into account as there is a tendency to average the fracture system.

-Upconing – indication on stagnant system. Rely on hydrogeology – model feasible

Bill Wallin, Ann-Chatrin Nilsson, Ignasi Puigdomenech

Summary of presentation

Sulphide in Laxemar and Forsmark:

Background: Sulphides can react with the copper canister, which may be a problem especially in association with bentonite erosion. This was brought up in SR-Can.

Sampling: Sulphide levels are high ($>1\text{ mg L}^{-1}$; $>3 \cdot 10^{-5}\text{ M}$) in some borehole sections. In some cases the pumping does not decrease these values. In other borehole sections microbial SO_4^{2-} reduction is enhanced during periods without pumping. During the sampling process the HS^- levels decrease quickly. General: sulphides have increased in some boreholes, in other boreholes there is initially an increase and then decrease, whereas in some boreholes, no substantial change in sulphide values can be observed with time. $\delta^{34}\text{S}$ indicates microbial SO_4^{2-} reduction at both sites. The sulphide data collected during the monitoring campaign will be further evaluated.

Lotta Hallbeck

Summary of presentation 1

Sulphate-reducing bacteria, sulphide and redox in Laxemar and Forsmark

Data on total number of cells and adenosine triphosphate (ATP) are proportional which shows that there are active bacteria in all cored boreholes. Stacked MPN (most probable number) correlates with ATP measurements: Bacteria found at both sites are: heterotrophic methanogens ($\text{org C} \rightarrow \text{methane} + \text{CO}_2$), autotrophic methanogens ($\text{inorg C} + \text{H}_2 \rightarrow \text{methane}$), heterotrophic acetogens, autotrophic acetogens, manganese reducing bacteria (MRB), nitrate reducing bacteria (NRB), SRB, IRB,

No correlation of sulphide versus MPN and SRB, however, there is a correlation of redox and microbes found at both sites. Bacterial populations are sensitive to drainage activities.

Summary of presentation 2

Geogases in Laxemar and Forsmark

Gases detected: CH_4 , CO_2 , N_2 , Ar, He. Nitrogen dominates at all depths at both sites. Helium is the second most frequently occurring gas, with higher levels at Forsmark.

Samplers, often filled with N_2 -gas, which could cause too high levels of N_2 in the samples. Possible to use Ne instead.

Discussion

Adrian Bath: Perturbation of the microbial system results in high sulphide concentrations. **Important to focus on EBS, geosphere and how chemistry is affected.**

-We will look at all data and analyze trends (BW).

Adrian Bath asked about the connection between DOC and sulphide. Possible DOC role at depth?

-There is no obvious connection between DOC and sulphide: sometimes they correlate sometimes not. DOC levels at FM $< 10\text{ mg L}^{-1}$, but in LX the DOC levels vary. Methanogens and acetogens use CO_2 as source of C and H_2 as energy source – i.e. H_2 is needed to use CO_2

Jinsong Liu brought up the possibility that CH_4 could come from the mantle and asked if the sampled data are statistically strong enough to exclude possible higher concentrations of methane at the two selected sites. (Other sites in the Fennoscandinavian shield have much higher concentrations).

-It is possible that CH_4 comes from the mantle, but as we do not have any isotope data we cannot tell where it comes from.

Bo Strömberg asked how confident we are that CH_4 is a limiting factor.

-Anaerobic oxidation of methane is a new finding in marine sediments. There are indications on this in Olkiluoto.

Jinsong Liu continued with the gas issue and discussed the possibility that the high N₂ levels underground could have atmospheric origin. Nitrogen could be trapped within the ice during glaciation and thus contribute to the gas in the deep subsurface.

- Lotta Hallbeck answered that it is widely believed that the nitrogen comes from the mantle of the Earth because in areas not influenced by glaciation there is also high concentration of nitrogen in the groundwater.

-A lot of gas could be trapped from the formation of Earth – contributes to the high concentrations of N₂ in the subsurface.

Further was a discussion of whether NO₃⁻ could cause Cu corrosion or not.

-Comment by Christina Lilja, SKB after the meeting: There are two nitrogen species known to cause stress corrosion cracking on copper: nitrite (NO₂⁻) and ammonium (NH₄⁺). Nitrate (NO₃⁻) is to be considered if it could be a source for nitrite formation by microbes.

-Lotta Hallbeck: It is not likely that high levels are reached as it costs too much energy for bacteria to produce excess amounts of NH₄⁺ and because of that no NO₃⁻ or NO₂⁻ from ammonium oxidation will be present.

Eva-Lena Tullborg, Henrik Drake

Summary of presentation 1

The redox transition zone in Laxemar – mineralogical and geochemical evidences

Oxic conditions: pyrite consumption, calcite leaching and goethite formation was discussed in this presentation. Positive Ce-anomaly. Leaching of U $^{234}\text{U}/^{238}\text{U}=1$, $^{230}\text{Th}/^{234}\text{U}>1$

Stable reducing conditions: calcite and Fe(II)-minerals available along fractures. Negative/no Ce-anomaly. U $^{234}\text{U}/^{238}\text{U}>1$, $^{230}\text{Th}/^{234}\text{U}<1$

Results reveal that the upper part of bedrock characterised by shift from mainly goethite to mainly pyrite, positive Ce-anomalies to slightly negative or insignificant Ce-anomalies, mainly removal of U to mainly deposition of U has been recorded in the fracture samples.

- Oxidising water penetrates to 10-20 m.
- A transition to reducing conditions between 20 and 60 m
- Mainly reducing conditions below 60 m scattered observations of goethite in a few transmissive zones.

Discussion

Bo Strömberg requested redox profile from water conducting fracture into the bedrock at more depths (ELT showed oxidation of pyrite in KLX11F at larger depths than-2 m).

Maria Nordén: Are geochemical and mineralogical observations in good correspondence at both sites.

-The sites have very different prerequisites. In Forsmark we have a thick soil covering and very little rock exposure, whereas the soil cover is significantly thinner and more rock is exposed in Laxemar. The redoxfront is not as distinct in FM as in LX. The mineralogy is also very different.

Bo Strömberg asked why pyrite is used for redox study while biotite is used in SR-Can.

-Pyrite is a more sensitive redox indicator - it reacts rapidly and if it is present in the fracture system it is a good indicator of reducing conditions. Jinsong Liu: how high is the transmissivity at Laxemar?

-The transmissivity at Laxemar varies with depth – between $10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $10^{-9} \text{ m}^2 \text{ s}^{-1}$

Björn Söderbäck, Mats Tröjbom, P-O Johansson

Summary of presentation

This presentation focused on the hydrochemistry in the surface system at Forsmark: A summary of a new report R-07-55

In this report attempts are made to explain why the hydrochemistry looks as it looks in the Forsmark area. This extensive documentation contains multivariate evaluations and models presented in 150 figures. A fifth report, an analogue to the Forsmark report, based on Laxemar 2.3 will be available in May.

The purpose of this report is to give a general understanding of the site and to explain overall patterns as well as anomalies and present a conceptual model that explains the present hydrochemistry in the surface system in the light of the past.

Discussion

Adrian Bath asked why there suddenly is a discharge during Baltic stage

-Due to density turnover

Öivind Toverud requested updated list of published reports

-It has been delivered now.

Bo Strömberg pointed out the need of a coordination geochemistry meeting between ChemNet and the Safety Assessment concerning the corrosion of Cu-canisters

-Such a meeting will be arranged at SKB

Eva-Lena Tullborg , John Smellie, Björn Sandström

Summary of presentation 2

Assessment of elevated uranium concentrations at Forsmark based on data from groundwaters and fracture coatings

Observations made on the U enriched groundwaters – present understanding (SKB 2007 and Laaksoharju 2008):

- Groundwaters with enriched U are generally mildly reducing (Eh between -140 to -200 mV) whilst more reducing groundwaters are low in uranium.
- The groundwaters with enriched U show HCO_3^- content above 50 mg/L with a few exceptions.
- Most of the samples with enriched U contents are of Brackish marine (Littorina) type but low U is also observed, so elevated uranium is not typical for the Brackish marine groundwater type.
- A dominance of U(VI) is measured in the section showing the highest uranium content (~120 mg/L) /Suksi and Salminen 2007/
- Repeated sampling during the monitoring program shows that sections with originally high U contents remain high (or even higher).

Main conclusions

- Speciation-solubility calculations indicate solubility control of the dissolved uranium.
- The highest uranium contents in both fracture coatings and groundwaters are found in fractures (all belonging to deformation zones) at depths between 400 and 650 m.
- The uranium present in groundwaters associated with fracture coatings is dominantly enriched in the oxidised U(VI) state.

- Present studies of the uranium contents and uranium decay series isotopes in both groundwaters and fracture coatings, indicate that part of the uranium has been mobilised during the last 1 Ma.

Discussion

Adrian Bath asked if it is possible to measure radium (U-series)

- No fracture coatings have been measured for radium, but a small number of groundwater samples have been measured.

Adrian Bath asked about the possibility of forming U-Mg complexes (Dong et al, 2008, EST 42:1979-1983).

-Comment by SKB added after the meeting: There is a non-linear correlation between U and Mg in the Forsmark groundwater data. Calcium reaches larger concentrations in the groundwaters and the U-Ca complex could have a larger impact than the U-Mg species. However, the uranium system is relatively complex and both alkalinity and redox levels must be considered when evaluating the influence of the alkaline-earth complexes.