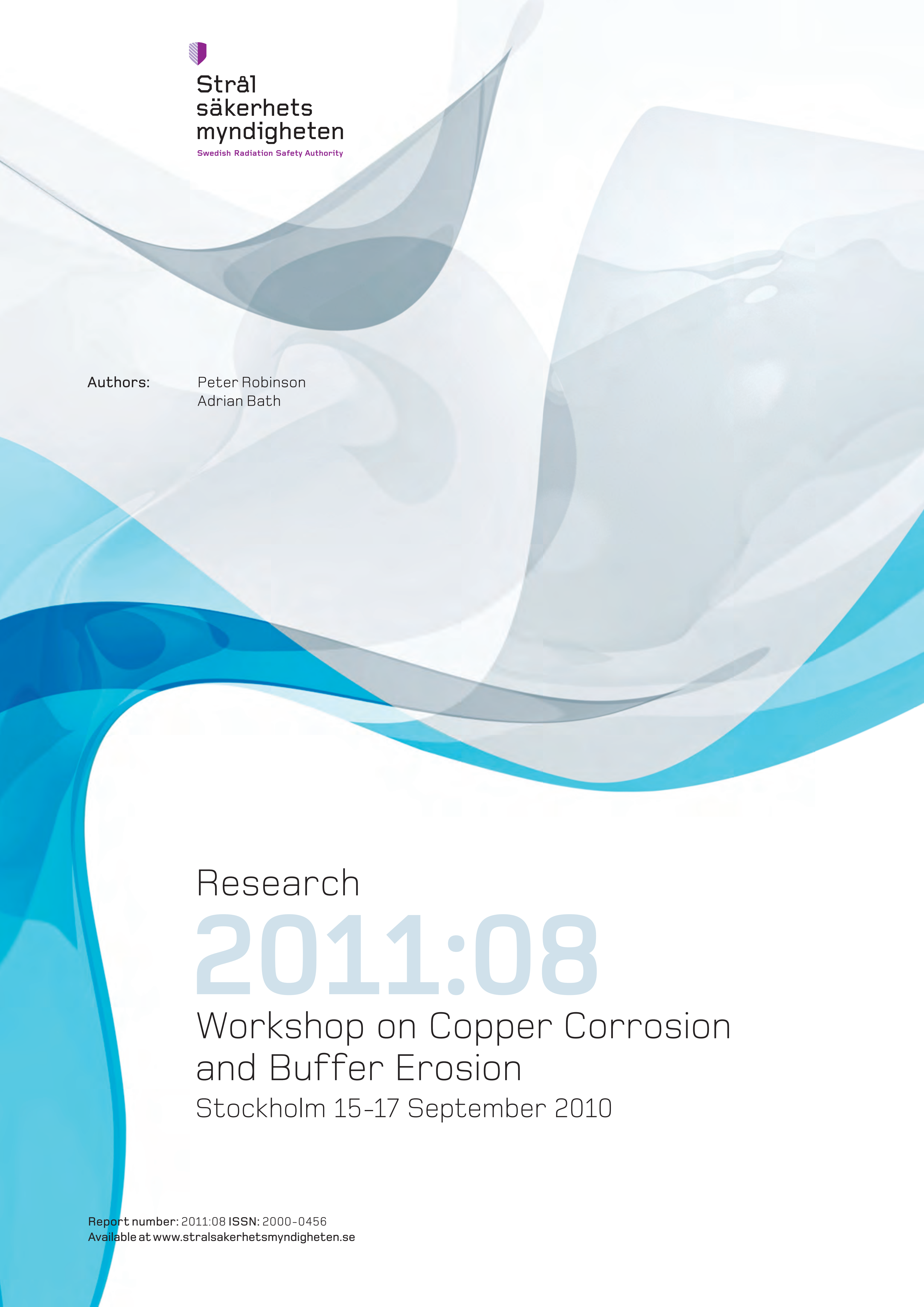

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Research

2011:08

Workshop on Copper Corrosion and Buffer Erosion

Stockholm 15-17 September 2010

Report number: 2011:08 **ISSN:** 2000-0456
Available at www.stralsakerhetsmyndigheten.se

SSM perspective

Background

In SSM:s preparation for reviewing SKB:s license application for disposal of spent nuclear fuel, a series of technical workshops have been conducted. The main purpose of this type of workshops is to get an overall understanding of the state of knowledge on interdisciplinary issues as well as of questions in the research front by inviting several experts. Previous workshops have addressed the overall concept for long-term integrity of the Engineered Barrier System (EBS) the manufacturing, testing and QA of the EBS the performance confirmation for the EBS, long-term stability of the buffer and the backfill and Engineered Barrier System -Assessment of the Corrosion Properties of Copper Canisters.

Objectives

The objective of this workshop was to bring experts in the field of buffer material together with experts in corrosion in order to discuss intersecting issues and issues of coupled processes of buffer erosion and copper corrosion, important for the long-term evolution of the Engineered Barrier System of a deep geological repository.

Results

This report summarizes the issues discussed at the workshop and extracts the essential viewpoints that have been expressed. The report is not to consider as a comprehensive record of all the discussions at the workshop and individual statements made by workshop participants should be regarded as opinions rather than proven facts.

This report includes, apart from the workshop synthesis, extended abstracts for presentations given at the workshop. The participants in the workshop identified a number of issues that not is fully understood and therefore suggested to be dealt with in more detail later on. However, it is necessary to look at these issues in the context of the overall safety case, in particular the key safety functions and threats, and to assess them in a quantitative fashion.

Need for further research

This type of workshop in different specified research questions is likely to continue during the forthcoming review of the SKB license application.

Project information

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Contents

Context of workshop

The workshop was convened to inform and advise SSM about the coupled processes of buffer erosion and enhanced canister corrosion that have been proposed as a potentially detrimental scenario in the long-term evolution of the engineered barrier system of a deep geological repository. It was an extension of the deliberations of SSM's BRITE advisory group on EBS issues and on SKB's approaches to the issues in the forthcoming SR-Site safety case. The workshop was planned to assist and advise SSM in its preparations for review of SKB's license application and SR-Site submission.

The potential for buffer erosion due to a future influx of dilute groundwater that induces bentonite to behave as a sol has been indicated by experiments carried out for SKB. It is generally considered that the most likely source and timing of such groundwater conditions will be the glacial stage of the normal evolution of the repository system, i.e. many tens of thousands of years into the future at least. The workshop considered, however, that potential causes of buffer erosion in the early post-closure period should also be considered.

The main significance of buffer erosion for a safety case is that it would potentially lead to higher rates of corrosion of the copper canister. There are various physicochemical mechanisms that could be implicated in enhanced corrosion but basically they would involve (a) the failure of a diffusion-controlled constraint on corrodant transport to and product transport away from the copper surface, and (b) the viability of microbially-mediated reactions producing higher concentrations of corrodants at or near to the copper surface.

The general issues relating to corrosion had already been the theme for a previous workshop in 2005 (see Report SKI 2006:11), the outcomes of which formed the background for this workshop. Additional background was provided by SKB's interim safety case, SR-Can, and the regulatory authorities' responses to preliminary consideration of the buffer erosion and related corrosion scenario.

Because of its potential significance and recent prominence and with the insights already provided by the BRITE group's review of the scientific case and experimental evidence, the hypothesis that copper is subject to corrosion reaction with pure water under anoxic conditions was included in the scope of the workshop.

The workshop identified a broad number of potential issues and the information required to address the issues, considered their relative significance to EBS performance and to a safety case, and also examined where there might be specific couplings and interdependence between processes that also need to be addressed.

1. Background

1.1. Copper corrosion in the repository environment

A safety principle for the proposed KBS-3 geological repository for spent fuel at Forsmark is that the engineered barriers shall be made of naturally occurring materials. Those materials shall be stable in the long term in the repository environment and shall have long-term properties that are verifiable (SKB, 2006). One of the engineered barriers for containment of the spent nuclear fuel is the copper canister with cast iron insert. SKB states that the primary safety function of the KBS-3 system is to completely isolate the spent nuclear fuel within the copper/iron canisters over the entire assessment period which is one million years (SKB, 2006a).

SKB's SR-Can long-term safety assessment states that the main long-term corrosion process that would affect the copper canisters is general corrosion by dissolved sulphide. It is possible that localised corrosion mechanisms such as stress corrosion cracking might also operate. Sulphide dissolved in pore waters of bentonite buffer surrounding each canister will derive from the dissolution of pyrite present as an accessory mineral in bentonite and from sulphide that is dissolved in groundwaters outside the buffer and diffuses through the buffer towards the canister. An additional source of sulphide will be the reduction of dissolved sulphate, a reaction that is mediated, i.e. accelerated, by the involvement of microorganisms, sulphate-reducing bacteria (SRB). Laboratory tests and underground laboratory experiments have indicated that microorganisms are not active in highly compacted buffer in which the swelling pressure and density exceed certain limits, though recent research has found viable SRB in compacted bentonite capable of very low production of sulphide (SKB, 2006b; Masurat et al, 2010). If the density of buffer were to decrease due to erosion of bentonite, then microorganisms might become more active and stimulate sulphide production adjacent to the canister.

While temperate climate conditions continue, SKB envisages that general corrosion will persist as the main continual process potentially affecting the safety function of the copper canisters. Taking the source of dissolved sulphide in buffer pore water as solely being pre-existing pyrite in the bentonite, and using a simple mass balance estimate, SKB estimate that loss of 0.7 to 3 mm of copper thickness (for the side and top respectively of the canisters) could be attributable to dissolution of all of the pyrite in a bentonite, Deponit CA-N, with a relatively higher pyrite content (SKB, 2006a). A model based on dissolution control of sulphide concentration and diffusive transport of it through the buffer indicates that it would take 160,000 to 3 million years for pyrite dissolution to go to completion.

It is likely that the concentration of dissolved sulphide in the buffer pore waters and in groundwater will have an upper limit that will be controlled by precipitation of iron sulphide, so the local concentrations of ferrous ion will have an influence on that. SKB's expectation is that dissolved sulphide in groundwater at repository depth will not exceed 10^{-5} moles/L (0.33 mg/L of

HS^-) (SKB, 2006a). Taking that concentration of sulphide as being an indicative long-term maximum for sulphide reaching a canister, and using the modelled value of equivalent flow rate for groundwater movement through a fracture intersecting a deposition hole (see Figure 1) which is about 10^{-5} m^3/y (with a range of about 10^{-7} to 10^{-3} m^3/y indicated by the DFN groundwater model) to estimate the maximum flux of sulphide, a general corrosion rate of 10^{-9} to 10^{-6} mm/y is calculated. Thus SKB assert that, even for the most pessimistic parameter assumptions, less than 1 mm of copper thickness will be lost in 100,000 years of continuing temperate climate groundwater conditions. The formula used to estimate the corrosion rate is based on the mass budget for the formation of copper sulphide (see Appendix B in SKB Report TR-06-09).

SKB's SR-Can explicitly considers the potential impacts of permafrost and ice sheet cover at Forsmark in the reference glacial cycle, taking account of a glaciation that affects the site many tens of thousands of years into the future and within 100,000 years. Potential impact on corrosion is considered to relate to increased groundwater flow that would be likely as an advancing or retreating ice sheet occupied the site. Increased water flow would increase the potential flux of dissolved sulphide to the rock-buffer interface at deposition holes where these are intersected by transmissive fractures (the 'Q1' cases). The scenario of particular concern in relation to a future glaciation is the case where the high flow rate of water causes erosion and mass loss of buffer so that the compaction density is reduced and thus advective flow of groundwater to the surface of the canister becomes possible. Moreover the loss of compaction density would allow microbes to become active so that microbial reduction of sulphate to sulphide with SRB would occur in proximity to the canister. SKB state that the availability of methane, CH_4, as the energy source and electron donor for microbial reduction will be the constraint on the activity of SRB (though equally dissolved organic carbon DOC could be the electron donor and constraint).

SKB scope this glaciation scenario of buffer erosion and corrosion by making assumptions about the processes: glacial advance/retreat lasting 40 years during which the flow of groundwater at repository depth would be enhanced by x160. They conclude that significant degrees of buffer erosional loss (i.e. loss of >1200 kg buffer per canister) would occur faster than significant extents of corrosion, so they claim that corrosion would remain the key process albeit with advection and not diffusion controlling transport of corrodants to the canister surface. Their model suggests that, given this scenario and otherwise using the same parameters as the normal evolution model, significant numbers of failed canisters would still not occur for at least 500,000 years after the start of advective loss of buffer (SKB, 2006a).

1.2. Buffer erosion

Buffer erosion refers to the process of buffer material (bentonite) being transported away from the deposition hole in colloidal form by dilute groundwater. The process can also apply to the tunnel backfill, but the main focus of this workshop was on buffer erosion that might occur where a fracture intersects a deposition hole, since this is where the coupling with corrosion is potentially most significant. Physical erosion of buffer material caused by steep hydraulic gradients during resaturation or by shearing of bentonite particles by rapidly flowing groundwater was discussed, but was also not the main focus of the workshop.

Dilute (low ionic strength) groundwater in contact with the buffer is a prerequisite for erosion since it is then that bentonite can lose integrity and form colloids. Such conditions may occur during glacial melting periods if glacial meltwaters penetrate to repository depth. Specifically, calcium is the key control and there is a Critical Coagulation Concentration (CCC) below which erosion may occur.

The issue of buffer erosion has only been recognised relatively recently and so there has been relatively little work on it compared to many other issues. Much of the current understanding is rather speculative. In SR-Can (SKB Report TR-06-09), SKB were unable to rule out this possibility, at least at a small number of deposition holes, and therefore included buffer erosion as part of the reference evolution scenario. Calculations of potential losses of buffer material were made, leading to advective flow conditions in some deposition holes. Enhanced corrosion then led to canister failures.

SSM's BRITE group has recently prepared an overview report on the erosion issue (Apted et al, 2010) and much of the material presented at the workshop relates to that report.

Figure 1 shows the layout envisaged. If the water flowing in the fracture is dilute then there is potential for buffer material to be eroded.

Consideration of buffer erosion requires various aspects to be considered. The geochemistry of the groundwater is crucial. The way this interacts with the bentonite must then be considered, including the position and nature of the interface between the bentonite and the water. The pore water chemistry of the buffer will also play a role. When buffer material is lost, the physical properties of the bentonite are important in determining how the remaining material is redistributed. These were the key topics for the workshop.

Recent work by SKB (Neretnieks et al., 2009) has focussed on the behaviour of the bentonite-water interface. It is envisaged that buffer material expands into the fracture and that its density gradually falls away with distance from the deposition hole. Nearest the deposition hole the bentonite remains a solid, but as the density falls it will be a gel and finally a sol. There are many different forces acting on the bentonite particles: friction, diffusion, gravity, double layer forces and van der Waals forces. Neretnieks et al. (2009) propose a force balance/viscosity model which enables them to predict penetration distance and erosion rates. Table 1 reproduces the key result. It is noted that the lower velocity results are unreliable – because the numerical models are poorly converged and because the penetration distances are large compared to fracture sizes and so could not occur in practice.

Using a regression fit to these results together with a hydrogeological simulation, Hedin calculated the losses from an ensemble of deposition holes and concluded that 50 will see advective conditions by 1 million years, taking this to occur when 1000 kg of buffer material is lost (A Hedin, personal communication, Nov 2009). There remain many uncertainties in this calculation and it is not yet clear what the SR Site reports will conclude.

In addition to the review work undertaken by the BRITE group, SSM have commissioned Quintessa to begin development of an integrated model for erosion and corrosion. The aim of this is to have an independent modelling capability through which various issues can be explored. Another objective is to couple the loss of material through erosion to redistribution in the deposition hole. This will allow consideration of the enhanced corrosion that occurs during erosion, because of reduced density, rather than simply using a threshold on tolerable buffer loss.

Table 1: Calculated rates using the force balance viscosity model for a 1mm fracture (from Neretnieks et al., 2009).

Water velocity in the fracture (m/y)	Erosion Rate (g/y)	Penetration Distance (m)
0.1	11	34.6
0.32	16	18.5
0.95	26	11.5
3.15	43	7.0
31.5	117	2.1
315	292	0.5

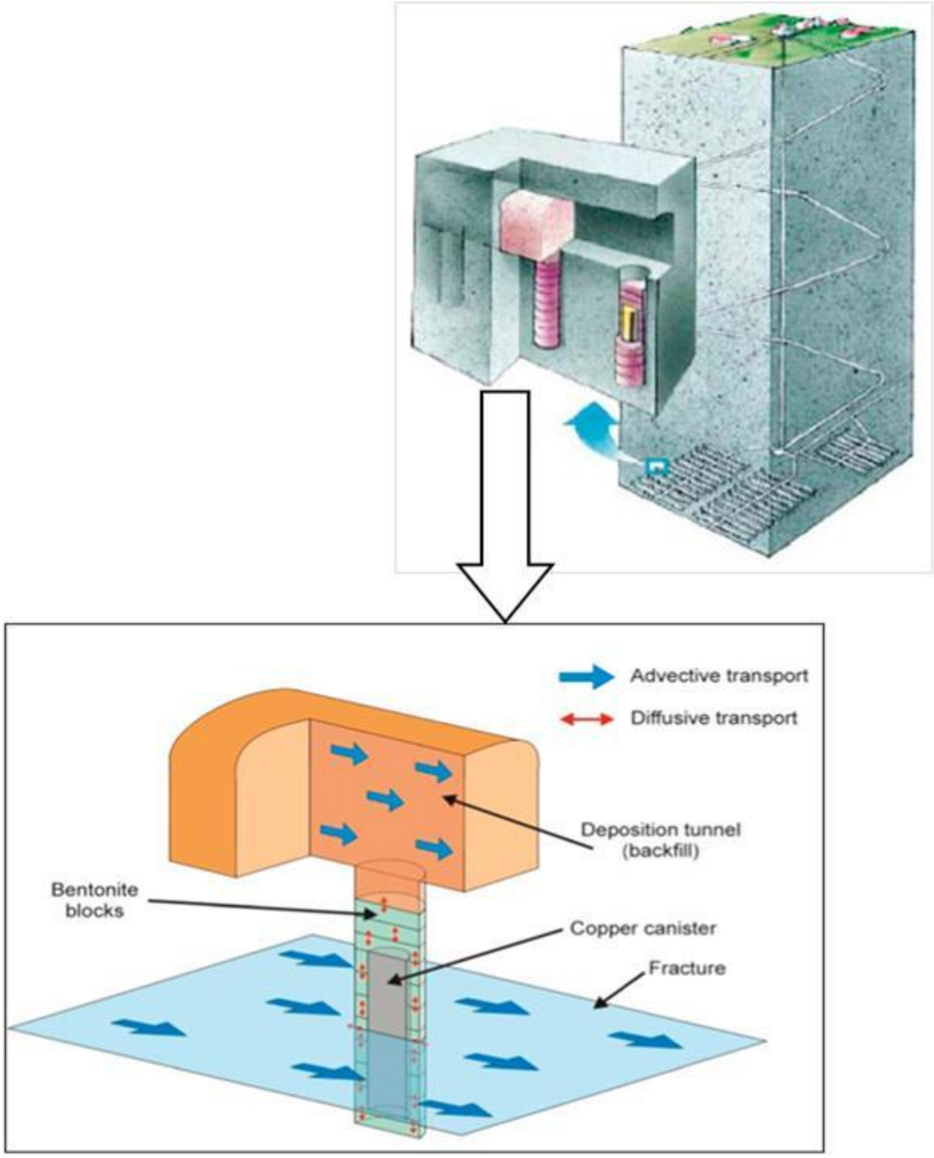


Figure 1: The KBS-3V repository concept, showing a fracture intersecting a deposition hole.

1.3. Near-field geochemical conditions

The geochemical conditions and evolution of groundwaters in the near field, i.e. in rock matrix and fractures at repository depth and adjacent to deposition holes are a large part of the information requirements for understanding and modelling the processes of canister corrosion and potential buffer erosion. The salient features of the presently-observed compositions of groundwaters at repository depth and of the long-time evolution of near-field geochemistry are summarised below.

The schematic time chart in Figure 2 illustrates a hypothetical long-time climate scenario for a repository host area, coupled with simplified indications of how the near-field groundwater composition and the engineered barrier system (EBS) processes affecting buffer and canister might evolve.

Redox and salinity are two of the key hydrochemical variables for near-field groundwaters. After closure of a repository, redox conditions in the EBS will initially change from aerobic to anaerobic as reducing groundwater re-saturates the buffer and backfill and consumes oxygen remaining from the operational period of an open repository.

The present composition of groundwater at Forsmark over the depth range 200-600 m is brackish with chloride (Cl^-) concentrations between 0.09-0.18 M and ionic strength between 0.12-0.24 M. SKB's interprets the origins of this level of salinity as being a mixture in varying proportions of pre-Baltic 'Littorina' brackish water, very old saline water that resides ubiquitously in the Shield bedrock at greater depth, and meteoric fresh waters. The meteoric water component ranges in age from recent post-glacial infiltration to older waters that infiltrated during the last ice age or even earlier. Despite the complexity of sources, groundwater salinities at repository depth are mostly fairly homogeneous although below that the salinity increases slightly with depth. There is a deviation from this vertical trend and lateral homogeneity in the north-west part of the target area where greater salinities of over 0.4 M have been found below 600 m depth.

There are very few analyses for groundwaters below 600 m in the target area, so it is not possible to assess how spatially representative these samples are. Similarly the hydrogeological significance is not evident, though the samples come from the 'footwall' structural domain that is the target host volume and in which the fracturing and faulting intensity is lower than elsewhere. This footwall domain lies to the northwest of a major sub-horizontal fracture zone, ZFMA2, which appears to be a significant groundwater flow path and to have different hydrogeological properties from the rock domains on either side of it.

The above descriptions apply to the compositions of groundwaters that have been sampled as flows from fractures into boreholes. SKB have also extracted and analysed the Cl^- concentrations and stable isotope compositions of pore waters contained in the rock matrix. In drillcores from the relevant rock domains and over the depth range 200-600 m, the Cl^- concentrations of pore waters are between 0.08-0.18 M and are thus more dilute than fracture waters and not at equilibrium with respect to solute exchange between fractures and matrix. Isotopic compositions of these pore waters are consistent with the logic that they have an older origin, pre-dating the last glaciation. The more dilute nature, and possibly differing chemical compositions in other respects, of pore water in rock matrix adjacent to deposition holes is an additional factor to be considered for the modelling of long-time evolution of buffer composition.

The general hydrochemical nature of groundwaters over the 200-600 m depth range is Na-Ca-Cl, with subsidiary concentrations of SO_4^{2-}, Mg^{2+},

HCO_3^- and K^+. The sum of Ca^{2+} and Mg^{2+} is 22 to 62 mM, so the mass budget of divalent cations in present-day groundwater satisfies the requirement for buffer stability. The pH is in the range 6.9 to 8.4. Dissolved SO_4^{2-} is rather variable, in the range 0.3 to 9.6 mM, and reduced sulphur species, predominantly HS^- anion, is $\leq$0.1 mM (other reduced S species, thiosulphate and sulphite, are indicated by speciation modelling to be at around 10^{-12} mM).

Redox is invariably reducing, with the electrode-measured *in situ* Eh in the range -280 to -140 mV vs SHE (based on 13 measurements). Most of this variability of Eh is accounted for by the co-variation of Eh with pH. The measured Eh is consistent with an electrochemical potential calculated on the basis of HS^-/SO_4^{2-} redox equilibrium, whilst the potentials calculated for the $Fe^{2+}/Fe(OH)_3$ equilibrium tend to be rather lower than the measured Eh values; either of these redox equilibria would account for the pH-dependence. The HS-SO_4 redox reaction involves multiple electron transfers so the reaction mechanism in reality is complex. This reaction should, almost certainly, be understood as a biogeochemical process with intermediate oxidation states and involving the mediation of sulphate-reducing bacteria.

These equilibria describe the present state of the system but there are alternative concepts for what drives the biogeochemical redox state in near-field groundwaters and might buffer it against future changes. External inputs of electron donors comprise traces of dissolved organic carbon (DOC) from the biosphere and of dissolved methane from much deep groundwaters. Fe^{II} in ferrous minerals such as chlorite and biotite is fairly ubiquitous in these rocks and probably has its role constrained by reactivity of minerals rather than by mass budget.

The preceding paragraphs describe the redox state of near-field groundwater, but it is possible that redox control in pore water in compacted buffer is rather different due to the mineralogical and biogeochemical environment and possibilities for varying equilibria involving Fe, S and C species. SKB have proposed alternative models for redox control in pore water that involve either pyrite FeS_2 or siderite $FeCO_3$ as the reactive electron donors since both phases occur as accessory minerals in bentonite. It is likely that both phases have a role in varying degrees depending on mineral distributions and also on the nature of the electron acceptor. Dissolved HS^- is an additional electron donor though production of it by SO_4^{2-} reduction within buffer pore water will be constrained depending on the degree to which bentonite compaction has inhibited microbial activity. Other sources of HS^- in buffer pore water are in-diffusion from surrounding groundwater or dissolution of pyrite, which would be flux-limited and rate-limited respectively.

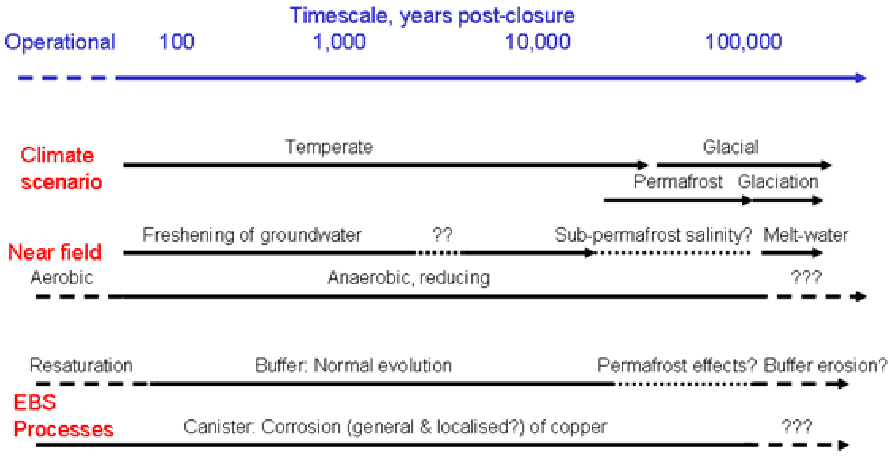


Figure 2: Schematic time chart of a long-time climate scenario for a repository host area, showing how some aspects of the near-field groundwater composition and the engineered barrier system (EBS) processes affecting buffer and canister might evolve

1.4. Long time evolution of near-field conditions

As time advances and temperate climate continues in the normal evolution model for Forsmark, land uplift will continue and groundwaters between surface and repository depth will continue to become fresher due to an increasing hydraulic gradient for meteoric water infiltration and displacement of brackish water. The assumption is that, whilst temperate conditions persist, groundwater flow rates at repository depth will remain roughly similar to what they are at present and that the buffer will remain intact.

If and when, in the far-distant future, the climate switches to a glacial state as described by SKB in the normal evolution scenario in SR-Can, the near-field hydrochemical conditions would be affected by the presence of an ice sheet. There is also a possibility that hydrochemical conditions at repository depth might be affected indirectly by the formation of permafrost in the shallow subsurface. Potential effects of permafrost formation on underlying groundwater compositions have been suggested to be salinization due to ‘freezing out’ of salts from shallow water as it turns to ice, changes of groundwater flow directions due to blocking of infiltration, and upconing of deeper groundwater (SKB, 2006a). There is little evidence from present-day systems for the extent of any of these processes and consequently uncertainty about the likely impact on groundwater compositions at repository depth and the implications for the stability of buffer.

The greatest potential change of hydraulic and chemical conditions in near-field groundwater is believed to occur if Forsmark should be covered by an ice sheet during a future ice age. The enhanced hydraulic gradient for melt-water intrusion and the possibility of circulation of very dilute water to repository depth might be potential causes of buffer erosion and dispersion respectively. How dilute melt water would evolve hydrochemically as it flowed to repository depth under these enhanced hydrodynamic conditions is open to various conceptual models for water-rock reaction and mixing with pre-existing groundwaters. Potential changes of dissolved oxygen, redox, pH and concentrations and relative proportions of cations could influence buffer stability and canister corrosion. Geochemical modelling of oxygen consumption and redox buffering by Fe^{II} minerals has been used to investigate the possibility of oxygen dissolved in melt waters penetrating to repository depth.

In general, the pattern of temporal changes in near-field groundwater compositions through the assessment period for a repository, i.e. from brackish to dilute as land uplift causes meteoric water circulation, then possibly to saline due to overlying permafrost, and then to very dilute as glacial meltwaters flush the system, needs to be considered in terms of potential effects on buffer stability. This cycle for future chemical evolution of groundwater could also include periods when the site is submerged and sea water again infiltrates.

Loss of buffer mass and decreasing compaction due to erosion by dilute groundwater flow through a transmissive fracture intersecting a deposition hole would allow advective water and solute movement to occur in the vicinity of a canister. Transport and mass budgets of corrodants to the canister surface is the issue to be considered for that scenario. Since the groundwater is expected to remain reducing, the main corrodant of concern in that case would be bisulphide, HS^-. Microbes would become viable in buffer that had lost compaction and density, so biogeochemical reduction of SO_4^{2-} mediated by SRB is an issue arising from buffer erosion. Constraints on production of HS^-, and thus on corrosion, might be SO_4^{2-} mass budget and control by groundwater movement as well as electron donors and energy source for the biogeochemical reduction, i.e. fluxes of DOC or CH_4.

2. Summary of Expert Presentations

2.1. Buffer Erosion

A series of expert presentations were given to the buffer erosion group. Abstracts for these are given in an appendix and summaries are presented here. The presentations were:

- Buffer pore water evolution, by David Savage;
- Bentonite rheology and physical erosion, by Göran Sällfors;
- Laboratory evidence for erosion, by David Bennett;
- Ion exchange in the buffer, by Håkan Wennerström;
- Glacial water chemistry, by Randy Arthur;
- Consequences of erosion, by Mick Apted.

2.1.1. Buffer Pore Water Evolution

David Savage described recent and ongoing work undertaken for SSM to look at the way bentonite pore water evolves. He noted a number of features of hydrochemical variations at Forsmark relevant to buffer stability, such as groundwaters being saturated with calcite across all depth ranges studied, which together with mineralogical data indicates that calcite can provide a buffer for calcium ions in solution to mitigate against smectite colloid formation. Pore waters entrained in the rock matrix could be an additional source of divalent cations. However, data concerning cation concentrations and ratios are currently unavailable.

Mineralogical information for fracture fillings at depth at the Forsmark site has been reported in a series of SKB reports and papers. These data show a long history of water-rock reaction, from the Proterozoic to the present, in at least four discrete mineralisation events, ranging from temperatures as high as 250°C for ‘Generations 1 and 2’, to less than 50° for late Palaeozoic to present minerals (‘Generation 4’). This latter generation is characterised by clay minerals and thin precipitates of calcite, but also minor amounts of goethite and pyrite, mainly associated with hydraulically-conductive fractures and fracture zones. Corrensite dominates and is a (Fe-Mg) mixed-layer chlorite-smectite mineral with some swelling properties. Although smectite is reported to occur at all depth levels at Forsmark, it is recorded as being ‘minor’ in abundance in comparison with corrensite, illite, saponite, and mixed-layer smectite-illite. Calcite is also present at all depth levels, but gypsum, dolomite, and siderite are absent throughout the system. Therefore, site mineralogical data show that smectite and calcite occur at all depths in Forsmark fractures, with no evidence for removal/dissolution by previous glacial episodes. This natural analogue implies that these minerals may not have been eroded/dissolved during previous glacial episodes.

He also observed that although SKB emphasise that groundwater compositions at Forsmark can be interpreted by simple mixing relationships alone, thermodynamic activity diagrams show that key parameters (pH, P_{CO2}, Ca/Mg, Na/Ca, SiO_2(aq)) in Forsmark groundwaters may be controlled by reactions involving montmorillonite and saponite clays and calcite present in fracture infills. Therefore available thermodynamic data suggest that repository-depth Forsmark groundwaters are in equilibrium (steady-state) with montmorillonite and saponite and these minerals may control pH, P_{CO2}, Na/Ca and SiO_2(aq) in groundwaters in the near-field. These reactions may thus buffer these parameters in any future intruding glacial meltwaters. This conclusion would not be evident from approaches assuming that mixing is the only process responsible for major element variations. $(Na^+)_2/Ca^{2+}$ activity ratios of most Forsmark groundwaters are <0.05, implying that any clay exchanger in equilibrium with these waters would be >90 % calcium end-member, and thus not in the stability field for sol formation.

The model analysis conducted in 2008-9, reacting MX-80 bentonite at high compaction density in ‘batch’ conditions has been repeated, extending the modelling to 2000 kg m^{-3} density, and introducing typical Forsmark groundwater as the reactant fluid. As demonstrated in a previous study (Savage et al, 2010a), reaction of MX-80 both in pure water and in Forsmark groundwater proceeds to equilibrium extremely rapidly in the suppression of secondary mineral precipitation. However, the incorporation of (equilibrium) mineral growth in the simulations delays attainment of steady-state up to 10,000 years in the case of MX-80 smectite. Therefore modelling of the reaction of montmorillonite in the buffer with Forsmark groundwater shows a trend towards conversion of montmorillonite to saponite, suggesting that the buffer may be partially altered prior to glacial meltwater intrusion.

2.1.2. Bentonite rheology and physical erosion

Göran Sällfors reviewed various potential causes of erosion and the processes that control them. His conclusion was that swelling into small fractures followed by erosion was the most important mechanism.

Clay is a highly complex material and different researchers have different mental images which affect their conceptual models.

The outward movement of bentonite in a fracture is mostly driven by a mechanical swelling process. The swelling pressure is dependent on pore water chemistry.

Clay rheology is affected by shear rate, shear stress, temperature, thixotropy, bentonite composition etc. A range of rheology models are used for different forms of bentonite, whether solid, gel, semi-fluid (sol), fluid, water. Numerous tests on bentonite under a variety of conditions can be found in the literature and these give background information for the choice of model. There is no single agreed set of models available.

Various experimental approaches to measuring clay properties were described

The need to take account of friction between the swelling bentonite and the walls of the fracture was raised. Friction was not taken into account in the Neretnieks (2009) modelling. There is no consensus in the literature on expansion of bentonite into fractures.

The influence of groundwater flow rate on the ability to erode bentonite is key. It can be argued that hydraulic gradients would be greatest when a glacial ice sheet was just to one side of the site, with open sea on the other side. Given typical rates of ice retreat – the time period over which such high gradients might persist would be just 25 years or so. Erosion will also depend on an ability of the water to carry colloids away. Typically 5% (by weight) colloids in water is assumed, which allows a few kg of colloids per year to be transported.

2.1.3. Laboratory evidence for erosion

David Bennett reviewed recent experimental work on buffer erosion.

SKB et al. (Neretnieks, 2009) have conducted some interesting and useful laboratory experiments on bentonite erosion, but only some areas of the bentonite erosion issue are well understood:

- Bentonite blocks may be eroded by dripping or flowing water.

- Piping is likely to occur in pellets and blocks where there are significant hydraulic gradients. SKB argues that piping will only occur early in repository history.
- Bentonite erosion is particularly dependent on the composition of the clay and the salinity and composition of the aqueous phase – but there is not a simple relationship.
- In the long term buffer (and backfill) erosion by dilute groundwaters cannot be ruled out.

Published rates of bentonite penetration into fractures and of bentonite erosion are highly uncertain. For example, some of the bentonite erosion estimates published in Neretnieks (2009) are based on water flow rates that would be unrealistic for a repository, and other estimates are based on numerical modelling in which there was convergence problems.

The experiments performed by SKB et al. (Neretnieks, 2009) do not present convincing evidence for filtration of eroded bentonite colloids (Apted et al., 2010).

SKB's latest Design Premises report (SKB, 2009) explicitly factors buffer mass loss into the design requirements for the buffer. However there is not a lot of scope for emplacing additional bentonite to allow for possible mass loss by erosion.

The key issue, therefore, is how the erosion issue is managed through a combination of improved consequence assessments and the specification of buffer mass and materials, and siting of deposition holes.

There was discussion of the amount of evidence for sealing of piping channels. There is not much experimental evidence for sealing of channels, but it is likely that piping channels will close and reseal once the hydraulic gradients decrease as long as backfill materials with high montmorillonite contents are used (Bennett, 2010). It was noted that significant hydraulic gradients may persist for several tens of years during repository operation.

It was noted that there seems to be no discussion in Finland of rubber sheet water protection measures for the buffer, even though Posiva is keeping both KBS-3V and KBS-3H options open. It was noted that removal of the rubber sheets from around the bentonite buffer rings is one of the most difficult parts of the EBS emplacement sequence.

2.1.4. Ion exchange in the buffer

Håkan Wennerström gave a presentation on ion exchange between clay and external aqueous phases.

He argues that electrostatic effects will dominate, contrary to what has been argued by SKB. This may have the consequence that swelling will be inhibited at high calcium-sodium ratios. This would inhibit erosion but could have other detrimental consequences (e.g. less inhibition of microbes). It might also lead to a less homogeneous buffer material, with consequential impact of diffusion of sulphide.

2.1.5. Glacial water chemistry

Randy Arthur reviewed what is known about glacial meltwaters.

Glacial waters vary in composition as a function of their source, mixing, residence times etc. Compositional changes can occur depending on the season of the year. Physical grinding of rock into rock flour beneath glaciers can affect water chemistry significantly. It is quite common for pyrite and carbonate minerals to be ground up, and for waters beneath glaciers to become anoxic.

Most sampling of glacial melt waters has been done at the snouts of alpine glaciers (these waters may have suffered some interaction with the atmosphere and contamination), but there is some newer data from drilling beneath glaciers, which are of better quality and potentially of greater relevance to the repository situation.

Typically, glacial waters are very dilute, relatively rich in Ca relative to Na, and relatively rich in carbonate relative to sulphate or chloride. The Grimsel glacial water, which has been used as a reference meltwater by SKB, is not typical - it is more sodium rich, poorer in calcium, only of moderate salinity and has an unusually high pH.

For a repository we are most interested in warm based glaciers as these will be present for long periods. Evidence from Antarctica on large, warm-based ice sheets suggests that the waters can be more saline and relatively more sodium rich. Salting out caused by freezing and microbial effects can occur and affect water chemistries (Skidmore et al 2010). Large glaciers have waters that can be very different from those below small valley glaciers. It is not at all easy to identify a ‘typical glacial water’ composition; a wide range of compositions needs to be considered. It was noted that in Scandinavia ice sheets may sit directly on igneous rocks rather than on sedimentary sequences as in Antarctica. It is not clear that data on the chemical compositions of glacial waters from Antarctica can necessarily be directly transferred to the Scandinavian situation.

There could be changes in the chemistry of glacial waters reaching the repository over time and, particularly between one glacial cycles and the next.

In summary, two types of sub-glacial meltwaters exist:

- Those from valley glaciers are extremely dilute Ca-HCO_3-SO_4-type solution (< 500 mg/L TDS).
- Those from larger ice sheets are more concentrated (<10,000 mg/L TDS) Na-Ca-SO_4-HCO_3 type solutions.

Given these bounding meltwater types, buffer erosion could be inhibited for two reasons:

- The dilute meltwaters have low sodium-calcium ratios, favouring non-swelling conditions due to ion-ion correlations.
- The more concentrated meltwaters have higher sodium-calcium ratios, but calcium concentration also increases in these solutions and may exceed the CCC.

The chemical evolution of these waters through water-rock reaction during migration to depth should also be considered.

2.1.6. Consequences of erosion

Mick Apted reviewed the consequences of buffer erosion on various safety functions of the buffer.

The loss of buffer mass as a result of erosion would likely lead to faster diffusion rates prior to the onset of fully advective conditions within a waste deposition hole.

Mass loss by erosion would also cause microbial activity to commence in the buffer prior to the onset of fully advective conditions within a waste deposition hole. This might increase the number of holes where canister failure occurs.

Not much buffer mass loss by erosion would be needed for microbes to become active, and it is possible that microbes might be active in the buffer even without reductions in buffer density.

Figure 3 summarises the key safety functions and when they would be compromised.

Spalling needs to be taken into account; this was not done in SKB’s trial analysis of buffer erosion consequences.

There are considerable uncertainties in SKB’s erosion models. For example there are significant differences between the analyses and models presented by Clay Technology and KTH (Neretnieks, 2009).

A key issue relates to the ability of the buffer to re-homogenise after any piping and/or erosion.

Several factors that require further consideration:
- reconcile the differences between the two models for buffer erosion (the KTH force-balance model and the alternative Clay Technology model)
- determination of the rheological response of buffer to sustained buffer loss (homogeneous or non-homogeneous density change) address potential evolution in current fracture properties and hydraulic gradients, especially during a period of glacial loading and unloading.

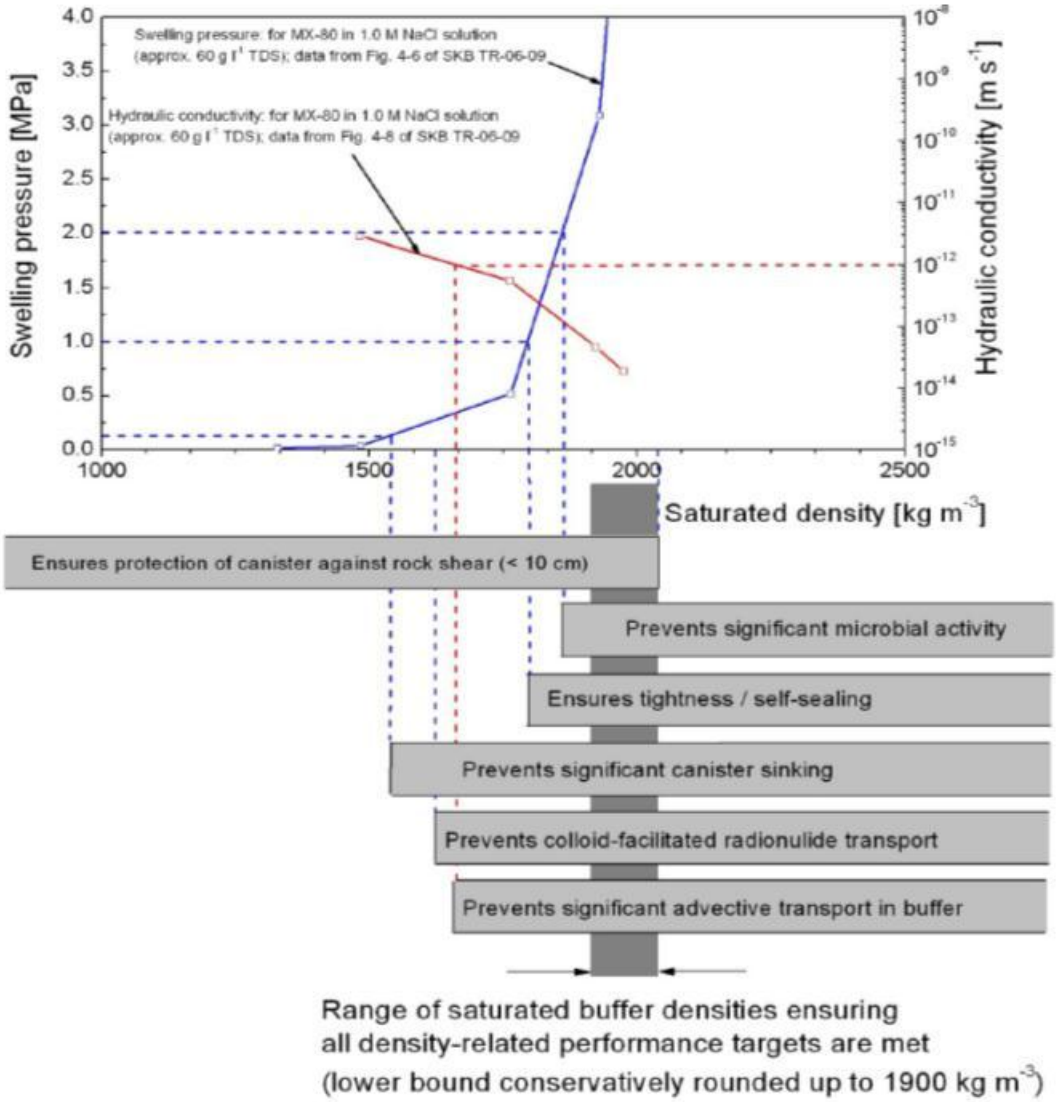


Figure 3: Consequences of reduced buffer density (from 'properties of buffer material' in Posiva Report TKS-2009).

2.2. Copper Corrosion

A series of expert presentations were given to the copper corrosion group. Abstracts for these are given in an appendix and summaries are presented here. The presentations were:

- Overview of copper corrosion in repository environments, by Timo Saario;
- Copper immunity, by Digby Macdonald;
- Sulphide-induced stress corrosion cracking (SCC), by Timo Saario;
- Copper corrosion in anoxic water, by Peter Szakálos and Gunnar Hultquist;
- Corrosion of copper in oxygen-free conditions, by Timo Saario.

2.2.1. Overview of copper corrosion in repository environments

As a background for the workshop, Timo Saario provided an overview of the four relevant mechanisms of corrosion and related processes: general corrosion, localised pitting corrosion, corrosion-assisted creep and stress corrosion cracking (SCC).

During the anoxic conditions that will prevail in the long-term post-closure normal evolution of the system, HS^- and S^{2-} will be the dominant agents for general corrosion of copper. In typical anoxic water compositions, and with no mass transport constraints on the supply of sulphide to a copper surface, general corrosion would proceed at a rate of <0.5 µm/year (King et al, 2001).

For the copper canister emplaced in compacted bentonite, corrosion is, according to SKB, limited by the mass balance and mass transport of sulphide. SKB use a mass balance approach to model the general corrosion reaction with sulphide, concluding that there would be insignificant impact on the canisters for the given hydrochemical conditions and assuming that the buffer remains intact. For a maximum HS^- concentration in buffer pore water of ~1 mg/L, mass transfer calculation indicates a corrosion depth of about 0.33 mm in 10^6 years. A mass balance approach is also used to make a conservative estimate of early general corrosion caused by oxygen occluded in the buffer during manufacture of the compacted blocks until O_2 is used up by oxidation of trace pyrite in the buffer or by the corrosion reaction itself.

There is an ongoing debate about whether a reaction occurs between copper and pure water in anoxic conditions. The putative reaction formula suggests that the products of such a reaction would be a surface film of copper hydroxide and hydrogen:

$Cu + H_2O = Cu_xH_yO_z + H_2$

Further details of this hypothesis and of the experiments to test it were provided to the workshop by Peter Szakálos and Gunnar Hultquist. One aspect of this process is the possibility of absorption of hydrogen by the copper leading to embrittlement. The fundamental basis of the hypothesis and the experimental evidence to test it were the topics of a scientific workshop organised by Kärnavfallsrådet (KAR, the National Council for Nuclear Waste) on 16th November 2009 in Stockholm.

Pitting corrosion is a form of localised corrosion which requires a supply of oxidant in the pits. SKB discounts it using the exclusion principle, i.e. conditions necessary for it to progress to a significant extent will not exist. The 'pitting factor' (PF) is maximum pit depth/depth of general corrosion, i.e. a maximum value for PF of 5 means a maximum pit depth of ca 5 mm for a general corrosion depth of 1 mm.

Creep fracturing would be expected to affect weld areas, if at all, where corners have the highest and most anisotropic stresses. Sulphide at grain boundaries in copper might cause brittle creep fractures. It is recognised that the addition of phosphorus to oxygen-free copper (Cu-OFP) decreases the rate of creep and the risk of brittle creep fracture. There is still a question as to the effect of general corrosion and the in-diffusion of sulphide from pore water, i.e. corrosion-assisted creep.

Stress corrosion cracking (SCC) would also be localised, and could be caused by aqueous species NH_4^+ (ammonium), CH_3COO^- (acetate) and NO_2^- (nitrite). The requirements for SCC to occur are that stress in high enough, e.g. in weld areas, the concentration of the detrimental species is beyond a threshold level and that the ambient electrochemical potential is suitable, oxic or anoxic. SKB and Posiva discount SCC by an 'exclusion principle' argument that the above three requirements will never occur together. This argument is weakened by the potential effects of microbes on the concentrations of detrimental species, despite the experimental evidence from AECL and SKB that microbes cannot be active in pore waters in compacted bentonite. There has been some recent evidence from Japanese researchers that sulphide can induce SCC on copper in sea water (see below). Research work is ongoing to find the minimum sulphide concentration in groundwater that is able to produce SCC in Cu-OFP. Initial indications are that sulphide can enter Cu-OFP through grain-boundary diffusion from saline groundwater with 10 to 200 mg/l S^{2-}.

2.2.2. Copper immunity

Digby Macdonald described a thermodynamic approach to understanding the corrosion/immunity behaviour of copper in various reactions. The Gibbs energy equations for corrosion reactions are used to calculate their 'partial reaction quotients' P. Copper immunity occurs when the value of P for given conditions is greater than the value, P^e, for equilibrium. The variation of log(P) versus pH comprises a 'corrosion domain diagram' in which the line $\log(P^e)$ versus pH for a given temperature defines the boundary between domains in which copper corrosion is possible and in which copper is immune.

Corrosion domain diagrams have been constructed for the reactions of copper with H^+ (i.e. the reaction with pure water), with HS^- and with polysulphide anions. This approach provides a way of illustrating that copper will be active to reaction with water for low values of P, i.e. for low partial pressure p_{H2} and Cu^+ in surrounding solution. It also shows how copper becomes immune as P increases due to slow diffusive mass transport of H_2 and Cu^+ away from the copper surface through intact buffer.

Reduced S species, polysulphides and polythionates, are powerful depassivating agents. Polythionates form at higher redox potential than polysulphides so are more significant in the earlier oxic period. Polythionates are generally more stable at higher pH. The speciation and disproportionation of the S species are conveniently illustrated using Volt Equivalent (VE) Diagrams which plot E^o (volts) versus the oxidation state for sulphur. For repository conditions, the VE diagram separates S species into ones that activate copper, i.e. are corroding towards copper, and ones for which copper has immunity.

VE diagrams are constructed for different values of pH, $[S]_{tot}$ and T to identify the relevant S species for differing repository conditions. The abundances of the polysulphide, polythiosulphates and polythionate species are many orders of magnitude lower than the concentration of HS^-.

To model the full corrosion process, mass transport of S^{2-} and other S species and of Cu^+, H_2, H^+, etc must be coupled.

Using ‘corrosion domains’ to understand whether copper corrosion is or is not possible in pore water under anoxic conditions depends on the starting point for the value of P and the direction of movement in the corrosion domain diagram. Copper is not immune in this environment but the key issues are whether the system is open or closed with respect to H_2 and the kinetics of the reactions.

The implications can be illustrated by reference to contrasting conditions at the Olkiluoto site in Finland and at Forsmark. At Olkiluoto, the natural concentrations of H_2 (up to ~1200 μM H_2 per litre) and the partial pressures, pH_2, are higher in some samples than at Forsmark (up to ~10 μM H_2 per litre). Natural concentrations of Cu in groundwaters at both Olkiluoto and Forsmark are similar at around 10^{-8} M, so the values of log(P) for Olkiluoto groundwaters fall in the field of the corrosion domain diagram where copper corrosion is not possible, whereas for Forsmark, log(P) values are slightly lower and reaction with H_2O is theoretically possible.

2.2.3. Sulphide-induced stress corrosion cracking (SCC)

Timo Saario discussed research in Japan that has produced new evidence that copper is susceptible to sulphide-induced stress corrosion cracking (SCC) in saline waters (e.g. sea water salinity) if sulphide concentration is in or above the range 0.001 to 0.01M (Taniguchi and Kawasaki, 2007). Corrosion cracks were observed in copper in synthetic seawater containing S^{2-} at 320 mg/L and 160 mg/L but not at 32 mg/L.

Processes are hypothesised by which S^{2-} might come into contact with a copper canister surrounded by compacted buffer:

- action of sulphate-reducing bacteria (SRB) on SO_4^{2-} in the buffer (noting that research indicates that SRB may be inactive or have very low activity in compacted bentonite),
- dissolution of trace pyrite in buffer,
- transport in groundwater flow and diffusion through buffers, and
- production from SO_4^{2-} due to SRB action at the bentonite rock interface.

The maximum S^{2-} concentration due to SRB-mediated reduction of SO_4^{2-} is estimated to be 400-500 mg/L at $6.2<pH<7.7$ and increases as pH increases, though maximum S^{2-} will be considerably lower if dissolved Fe^{2+} permits FeS equilibrium to control S^{2-}.

VTT have carried out research for the Finnish Research Programme on Nuclear Waste Management (KYT2010) and SSM on the basis of these processes and have concluded that the flux of S^{2-} and corrosion rate will remain very low whilst solute transport through the buffer remains diffusion-controlled. VTT concluded that the main concern would be an eroded buffer scenario with S^{2-} being transported advectively to the canister surface. VTT have carried out experiments to study the minimum $[S^{2-}]$ that would cause concern in the advection scenario. The experimental set-up positively excluded O_2 and added 10 to 200 mg/L S^{2-} to Finnish saline reference water containing a copper coupon. Measured Eh was around -250 mV and the Cu corrosion potential was around -700 mV; solution conditions remained in the Cu_2S stability field. Examination of copper specimens after experiments suggested that precipitation of copper sulphides might be occurring at susceptible grain boundaries where S^{2-} might be penetrating even in the absence of loading.

How might S^{2-} penetration affect creep and other properties of Cu in the scenarios where $[S^{2-}]$ could exceed, say, 10 mg/L? Work at VTT continues, aimed at establishing the effects of $[S^{2-}]$ on in-diffusion of S^{2-} along grain boundaries and on the effects of in-diffusion on mechanical properties of CuOFP (oxygen-free phosphorus-containing copper).

2.2.4. Copper corrosion in anoxic water

Peter Szakálos and Gunnar Hultquist have been doing experiments on the reaction of copper with water:

$$Cu + H_2O = CuOH_{surface} + H_2$$

for which $\Delta G^o = -228$ to -549 kJ/mole for $pH_2 \geq 1$ mbar at 45ºC depending on the nature of the surface hydroxide layer.

The ΔG^o value depends on the nature of the surface Cu-OH compound. An alternative reaction mechanism is

$$Cu + H_2O = Cu_2O + H_2$$

for which $\Delta G^o = -147$ kJ/mole for $pH_2 = 10^{-9}$ and T = 80ºC. The $CuOH_{surface}$ phase is a precursor of Cu_2O.

The thermodynamic data indicate a propensity for copper to react with water, though the free energy change and driving force for reaction is very low. The kinetics of reaction is an additional matter. The possibility for such a reaction has already been evidenced in industry where copper corrosion in water occurs even where O_2 is aggressively excluded. Experiments seem to show that the reaction can proceed if the system is open so that produced H_2 is continually removed. Otherwise a build-up of hydrogen stops the reaction.

Some further details of the experiments carried out at KTH were given. An experiment has been continuing for 2 years, producing H_2 very slowly which is monitored by quadrupole mass spectrometry. Absorption of H_2 by copper, diffusion of H_2 away from the canister surface through the bentonite, and oxidation of H_2 to H_2O are processes that might maintain pH_2 at a very low value.

2.2.5. Corrosion of copper in oxygen-free conditions

Timo Saario reported on the BRITE advisory group's expert review of the experimental evidence for copper corrosion in water. The hypothesis remains open in the absence of reliable thermodynamic data for the $CuOH_{surface}$ phase. H_2 measurements are not interpretable whilst H_2 retention by metals etc in the experimental system remains unquantifiable and the data for H_2 production do not match with the expected trend. The natural pH_2 in a groundwater system could have a role in changing the reaction rate or suppressing it altogether.

SKB's corrosion experts are trying to replicate the KTH experiments whilst also monitoring $[Cu^+]$ in solution and the voltammetric potential. They report that both lines of evidence indicate that reaction is not occurring. SKB's experimentalists agree that a $CuOH_{surface}$ intermediate might initially be produced, along with H_2, but they consider that these products are not directly related to Cu corrosion but are rather related to reduction of Cu^{II} species (Bojinov et al, 2010).

Experimental work on this unresolved issue is ongoing at VTT with the University of Helsinki, and at Studsvik AB funded by the Finnish KYT programme and SSM.

3. FEPs and information requirements for assessment of corrosion and erosion

One of the main purposes for this workshop was to advise about the information that SSM should expect SKB to provide or that might be obtained from independent research. The required information should enable SSM to scrutinise the conceptual models that are proposed for the processes associated with corrosion and buffer erosion, to consider alternative models, to identify ways in which the various processes might be coupled, and to evaluate the quantitative models of processes and to replicate the calculations to an adequate level.

For assessment of corrosion

- Corrosion process model
  - thermodynamic equilibrium model
  - kinetic model for rate determining process
  - tested for consistency with experimental evidence

- Material properties of copper canisters
  - mechanical and chemical properties
  - manufacturing effects e.g. welds, edges
  - conditioning of copper surface
  - stresses on canister

- Water at surface of canister
  - resaturation of buffer
  - timing of resaturation of buffer
  - model for distribution of water in unsaturated buffer

- Duration of oxic conditions
  - reactions attenuating oxygen in buffer
  - distribution of residual oxygen in backfill, buffer and other voids

- Temperature at canister surface
  - thermal decay versus time
  - thermal conductivity of buffer for different degrees of saturation

- Corrodant concentrations at canister surface
  - speciation
  - biogeochemical production reactions, biofilms, microbes
  - time-dependent variability

- Pore water composition in buffer and adjacent to canister
  - ionic strength and chloride concentration
  - pH, SO_4, etc
  - reactions affecting redox and consuming H_2

- Introduced materials (‘stray’ materials)
  - substances potentially introduced on canister surface or in buffer

- Mass transport to/from canister surface
  - diffusion of corrodants through buffer
  - diffusion of Cu^+ away from canister
  - advection resulting from buffer erosion
  - diffusion of H_2 to/from canister

For assessment of buffer erosion

- Buffer erosion process model
  - backfill erosion model
  - experimental consistency and parameters
  - consistency between alternative models e.g. force balance
  - distribution of mass loss and lowering of density
  - erosion rate
  - relationship of buffer loss to onset of advection

- Physiochemical description of buffer
  - time dependent alteration
  - reactive accessory minerals
  - effects due to permafrost and glacial loading

- Distribution of transmissive fractures intersecting deposition holes
  - fracture apertures
  - effects of spalling in deposition hole annulus
  - calculated groundwater flow velocities at deposition holes

- Groundwater compositions at deposition holes
  - long-term variations of groundwater compositions
  - geochemical conditioning of buffer ion exchange sites
  - divalent cation concentrations versus Critical Coagulation Concentration (CCC)
  - pore water composition in buffer

- Buffer swelling pressure model
  - relationship to pore water composition
  - in relation to compaction density

- Duration of episodes causing erosion
  - external driving forces on hydraulic gradient at repository depth
  - model for sub-glacial meltwater

Uncertainties in the quantification of parameters and the range of variability will be evaluated appropriately. Uncertainties fall into two broad groups: (i) quantifiable uncertainties in physiochemical properties such as thermodynamic data, mechanical properties and correlations and in groundwater compositions and, (ii) conceptual uncertainties and alternative models for the EBS processes and for the long-term evolution of the geosphere system. Some of the information used in corrosion and erosion modelling will be derived by complex routes involving sub-models, simplifications and assumptions. There will be a need for caution about the implications of data biases and correlated uncertainties.

4. Coupled FEPs in corrosion and erosion

There are a number of FEPs that are necessary to describe the coupling between buffer erosion and corrosion of canisters:

- Transport properties of buffer (i.e. diffusive or advective) are coupled with buffer density;

- Swelling properties and buffer density are coupled with mass loss and will affect mechanics of canister-buffer interface;

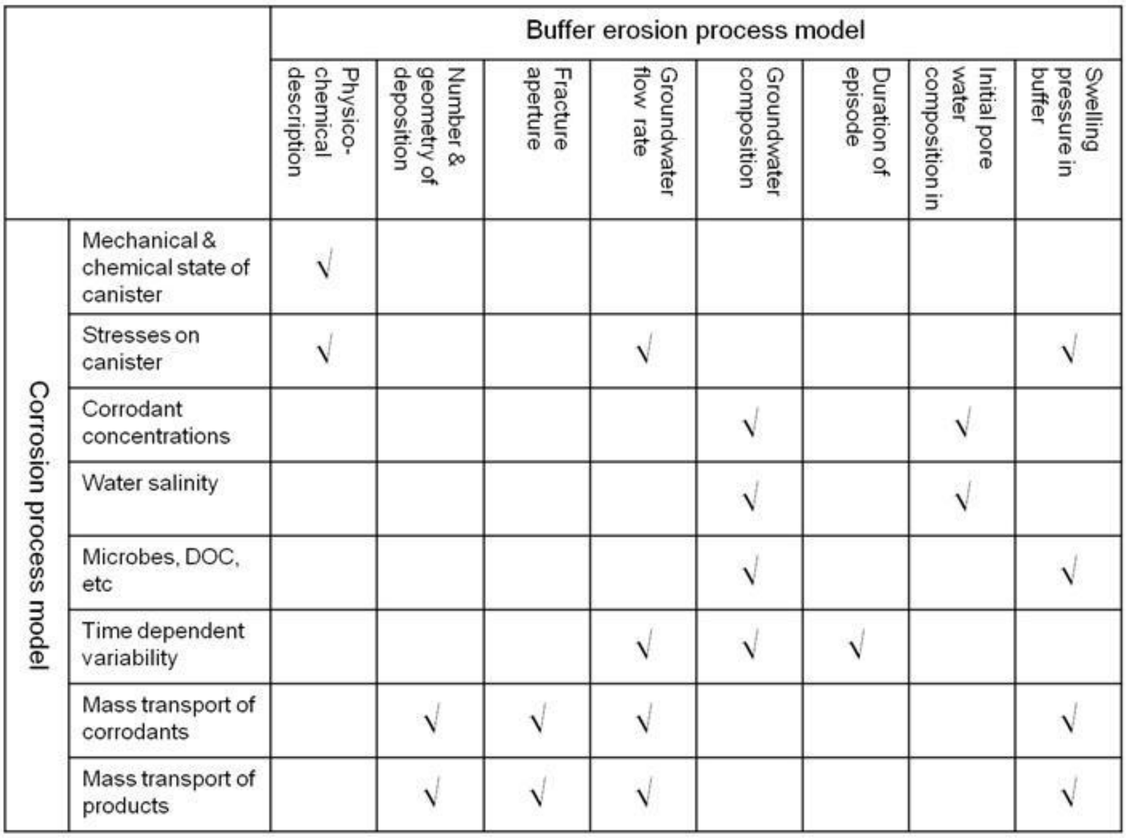
- Thermodynamic activity of water (aH_2O) is coupled with swelling pressure and affects viability of microbial activity in buffer;

- If buffer erosion is caused by sub-glacial hydrodynamics, then loading and stress will be enhanced;

- Buffer erosion by sub-glacial diluted groundwater may be coupled with other biogeochemical changes that could affect corrosion;

- Conditions causing buffer erosion might also erode backfill and ease access of corrodants to tops of deposition holes.

The figure below is a correlation matrix for these processes and models.



		Buffer erosion process model							
		Physico-chemical description	Number & geometry of deposition	Fracture aperture	Groundwater flow rate	Groundwater composition	Duration of episode	Initial pore water composition in buffer	Swelling pressure in buffer
Corrosion process model	Mechanical & chemical state of canister	√							
	Stresses on canister	√			√				√
	Corrodant concentrations					√		√	
	Water salinity					√		√	
	Microbes, DOC, etc					√			√
	Time dependent variability				√	√	√		
	Mass transport of corrodants		√	√	√				√
	Mass transport of products		√	√	√				√

Figure 4. Matrix showing coupled FEPs. The vertical axis contains FEPs for the copper corrosion process model; the horizontal axis shows FEPs for the buffer erosion process model.

5. Issues requiring more information

The scenario of buffer erosion coupled with enhanced copper corrosion has been identified relatively recently and therefore the workshop identified many issues for which SSM may wish to seek more information from SKB or from independent sources. Some of these issues may anyway be addressed directly by SKB in SR-Site but at the time of the workshop they were considered to pose open questions or at least to require clarification about how they are being dealt with in the safety case.

Evolution of buffer

- Understanding the evolution of the buffer must be central to the long-term modelling of canister integrity. Potential alterations of bentonite in the early phase, while temperatures are high and resaturation is occurring, set the starting conditions for the longer-term evolution and performance when erosion may be an issue. Thermal effects might lead to changes in physicochemical and mechanical properties and precipitation of solutes on or near the canister surface.

- Resaturation processes need to be understood sufficiently well, especially with regard to heterogeneous patterns of partial saturation, to underpin the model description of a homogeneously resaturated buffer. Some experimental observations (e.g. SKB's CRT experiment) appear to show "sealing" so that resaturation slows or terminates unless external pressures are increased. This could lead to inhomogeneous density distributions, with consequences for long-term behaviour.

- Alternative models for bentonite properties and behaviour are available to SKB and there is a need to clarify and justify a choice of model and of the conceptual and parameter uncertainties. The ion exchange model presented by Clay Technology does not account for the effects of the electrostatic interactions, which most probably dominate Na^+ versus Ca^{2+} exchange. A more complete analysis might predict decreased clay swelling with respect to glacial meltwater, and increased swelling for increasing salinity.

- SKB have stated in SR-Can that microbes should be eliminated, i.e. should not survive, in buffer with swelling pressure exceeding 2 MPa, whilst acknowledging that further substantiation from additional studies was needed. Recent research has indicated that SRB microbes remain viable in bentonite compacted to a density of 2 g cm^{-3} (equivalent to a swelling pressure in excess of 2MPa), though the level of SRB activity is much lower than in similar experiments with lower compaction densities (Masurat et al, 2010). More experimental results, with tests of reproducibility, of microbial viability and activity are needed over a range of swelling pressures and densities to establish whether microbes are fully eliminated or remain viable but dormant at high swelling pressures. This information will address the question of whether dormant microbes would be reactivated if buffer erosion caused a lowering of swelling pressure.

- Early piping or erosion in the backfill or buffer could impact on their properties. More information about the hydro-mechanical processes that could cause piping and erosion in the early post-closure period will indicate the variability of initial properties of buffer and backfill.

- Buffer properties will evolve due to interactions with groundwater, both initially and in the longer term. Groundwater compositions will change through the temperate climate stage of the normal evolution, in addition to those potential changes that are widely associated with the glacial climate stage. For example, groundwater salinity may increase due to up-coning of deep groundwater. The exchangeable ion populations in bentonite will change and it is possible that some mineral alteration could occur thus affecting the material properties of the buffer.

- During the permafrost episodes of a glacial cycle, there is a possibility that freezing might penetrate to repository depth and therefore affect buffer. How would the disruptive effect of transient freezing couple with response to subsequent dilute groundwater circulation and potential buffer erosion?

- There is some evidence that copper ions released from the canister may diffuse into and interact with the buffer (see below). What are the possible effects, if any, on bentonite properties?

Buffer erosion

- An adequate conceptual understanding, underpinned by experimental observations, of erosion processes is currently not available. Some experiments have been carried out but there is still only a partial understanding of erosion processes. SKB's quantitative modelling of buffer erosion should be consistent with a conceptual understanding. Redistribution of mass in the buffer is the central aspect of buffer erosion but the hydro-mechanical process remains uncertain. Spalling in the annulus of the deposition hole may be an additional complication.

- Groundwater flow rates are a key control on the erosion rate and those that are relevant are at the extreme of the distribution of rates calculated in flow models. The reliability of these extreme predictions needs to be evaluated.

- The initial development and configuration of the bentonite extruded into the fracture is uncertain, particularly the distance to which it extends. There is a strong dependence on fracture apertures and flow velocities that are poorly known, particularly at extremes of parameter distributions where erosion is a potential problem. Channelling and surface roughness may have an effect. At low water velocities, taking account of friction against fracture surfaces, the results may be unpredictable. Different rheological models are needed for the different phases of bentonite, i.e. solid, gel, sol.

- The possible geometrical outcomes of mass loss from the buffer need to be considered systematically. What might the geometry be of the initial volume with less dense buffer? That might be the only consequence, or swelling and erosion might eventually result in a cavity in which the canister surface is exposed directly to groundwater.

- As mass is lost from the buffer, the transport properties will also change. Transport may depend on the degree of homogeneity that is maintained.

- Even if the mass lost in a particular deposition hole is not sufficient to lead to corrosive failure, there may be impacts on its performance during a shearing event.

- The backfill is susceptible to erosion as well as the buffer. There is potential for a loss of confinement in the deposition hole.

- Claims for conservatism in assumptions need to be justified.

- The fate of the non-clay component of the eroded bentonite will probably be ignored on the basis of conservatism; there is a need to confirm that this is satisfactory.

Evolution of near-field conditions

- The geochemical evolution by water-rock reactions of dilute sub-glacial meltwater as it penetrates to repository depth is uncertain. SKB's present model of hydrochemistry is primarily based on mixing of different water components. Dissolution reactions of silicate minerals and calcite and ion exchange reactions will affect the concentrations and relative proportions of divalent and monovalent cations, i.e. Ca^{2+} and Na^{+} in groundwaters exchanging with buffer pore water.

- The basic geochemical model for control of redox conditions at repository depth is fairly well understood, with respect to the attenuation of dissolved oxygen and to the maintenance of reducing conditions due to the S^{2-}/SO_4^{2-} and Fe^{II}/Fe^{III} redox couples.

- The role of other species, dissolved organic carbon, CH_4 and H_2, in biogeochemical controls on redox are less certain. In particular, the way that microbial populations, redox and corrodant concentrations would develop in near-field groundwaters and adjacent to a canister in the buffer erosion scenario has not been considered. Microbially-enhanced corrosion would become significant if sufficient loss of mass and compaction from buffer were to occur.

- The nature of sub-glacial meltwater likely to be present during a glacial melting episode at Forsmark, and its composition if it reaches repository depth, need to be reconsidered.

Copper corrosion

- Some corrosion rates indicated by real-time monitoring in the MiniCan experiments at Äspö HRL have been reported to be much higher than expected (Smart and Rance, 2009; Baldwin and Hicks, 2010). It has been suggested that these high corrosion estimates relative to the rates used by SKB (King et al, 2001) may be due to problems with the measurement technique. The experimental uncertainties and the implications for the significance or otherwise of the high corrosion estimates has yet to be reported.

- There are open questions concerning (i) sulphide-induced stress corrosion cracking, specifically the minimum HS^- concentration that might be active in this respect in saline groundwater, and (ii) the potential effect of general corrosion and in-diffusion of HS^- on the rate of creep and brittle creep fracture. Stress corrosion cracking might occur in a buffer erosion cavity. Since the maximum tensile stress is in the weld area, the worst case might occur if a transmissive fracture were in a deposition hole location corresponding to the location of a weld in the canister.

- If part of the canister surface is exposed, or is surrounded only by low density bentonite then corrosion effects will be focussed there. The size of such a region is therefore significant and should be taken into account.

- Speciation of reduced sulphur has not been fully considered in relation to the rate of copper corrosion. Reduced sulphur has complex speciation comprising polysulphides, polythionates and other polynuclear S species in addition to simple sulphide and bisulphide anions. Polynuclear species may also result as transient products of kinetic processes if the system is perturbed. Although the concentrations of these species, e.g. thiosulphate ($S_2O_3^{2-}$) anion, will probably be many orders of magnitude lower than HS^- and S^{2-}, they are powerful activators of corrosion and therefore might be taken into account in a model for corrosion. SKB have not reported any investigations of $S_2O_3^{2-}$ in groundwater samples, especially those in which anomalous concentrations of HS^- have been found.

- Since pyrite in the buffer is a potential source of dissolved reduced sulphur, there is a question about the mechanism and products of pyrite dissolution. The oxidative dissolution of pyrite is well understood but the mechanism and kinetics of anoxic dissolution are not well established. It can be described as a simple reaction with H^+. It could also be described as an electrochemical process between Cu and pyrite at the copper-buffer interface. There is a question of what corrosion will occur, if any, if pyrite in the buffer is depleted as a source of S^{2-} and there is no significant external source of S^{2-} in groundwater. A mechanistic corrosion model could couple sulphide and anoxic conditions through constitutive equations so that corrosion would be limited either by sulphide supply or by hydrogen removal.

- Sulphide concentration in buffer porewater may be limited by equilibrium with pyrite or iron monosulphide (FeS). Dissolved iron, Fe^{2+}, is also involved in these equilibria and therefore maximum S^{2-} at equilibrium would be inversely proportional to Fe^{2+}. The sources and rates of supply of dissolved iron at various stages of buffer evolution should be considered in modelling of potential variability of sulphide concentrations.

- Corrosion by chloride (Cl^-) was considered, and it is understood that this might become significant at low pH which might be excluded by calcite buffering. Cl^- complexes with Cu^+ and is therefore a general factor to be considered. For example it might be relevant for the proposed anoxic corrosion mechanism.

- The potential for microbes to exist within the buffer (an issue already raised in ‘evolution of buffer’) as density falls may be crucial in determining corrosion rates. They could provide a source of sulphide close to the canister. The viability of microbial activity in backfill may also be significant because that could potentially affect more canisters than the number in deposition holes that are vulnerable to buffer erosion.

- The corrosion model in SR-Can does not take account of the migration of Cu^+ into the buffer where it might be taken up by solid phases thus acting as a ‘sink’ for Cu^+ to drive the corrosion reaction to the right. It was pointed out that analysis of the buffer from the LOT experiment has found that Cu has migrated some distance into the buffer from the canister interface (Karnland et al, 2000). A speculative hypothesis is that experimental corrosion rates might be affected by whether or not buffer material is in contact with copper. In general, if Cu^+ ions migrate into the buffer, there is a question about whether Cu^+ will be immobilised in the buffer or will migrate into the surrounding rock. Uptake of Cu^+ by buffer would be analogous to what happens with steel corrosion in bentonite which is altered to Fe-bentonite (which process has been studied in the EC NF-PRO project; Carlson et al, 2007; Savage et al, 2010).

- After failure, corrosion of the internal iron in the canister will lead to generation of gas and solid corrosion products. Impacts on the release rates of radionuclides need to be considered.

6. Prioritizing and addressing issues

The issues above have been compiled on the basis of the two thematic working groups at the Workshop. They have not yet been prioritised according to their potential impacts on the safety assessment. Prioritisation will need further review, taking into account the most recent developments in SKB’s research on the issues and also the outcomes of independent research sponsored by SSM. It may be that some of the issues raised here are found to be adequately dealt with in SR-Site when it is published in March 2011.

SSM’s priorities in its approach to getting satisfactory resolution of issues should be guided by the following questions:

- Is additional information required to describe the system adequately?

- Are the models for processes providing quantitative estimates of impacts?

- Does this issue threaten to undermine a safety function?

- Are there new safety function indicators suggested?

- Does the issue challenge the validity of simplified conservative approaches?

- Does the issue suggest additional sensitivity to variability and uncertainties in rock or EBS properties?

- Has the full range of conceptual and numerical model uncertainty been explored?

Based on that evaluation, further actions will be required to achieve adequate resolution of the issues. Depending on the nature of the issue, its potential impact on safety and the insights already obtained, some or all of the following approaches will be appropriate:

- Clarifications, additional data (possibly requiring new experiments), new calculations will be sought from SKB;
- Scoping calculations of potential consequences for safety will be carried out independently;
- Information to support qualitative concepts and process understanding, especially with regard to long-term evolution and behaviour, will be sought from analogues in natural or engineered systems;
- ‘What if?’ calculations will be carried out to examine the consequences of worst case scenarios, variant parameter ranges and couplings between processes;
- Rigorous evaluations of conceptual and parameter uncertainties will be applied consistently.

7. Looking Forward to the SR Site Review

The workshop brought together experts on corrosion with experts on engineered barrier systems and repository processes and performance assessment experts. This type of cross-disciplinary team-working will be an important part of the forthcoming review of SR Site. Here we discuss the lessons learnt from the workshop that will help in the review project.

The workshop raised many issues relating to the coupling between erosion and corrosion as well as issues on corrosion and erosion separately. Issues in other areas were also raised, for example microbiology, hydrogeology, hydrogeochemistry, buffer evolution and mechanics. The workshop demonstrated that listing issues in this “bottom up” way (i.e. starting with detailed consideration of features and processes) is relatively straightforward.

In order to attach safety significance to these issues and hence to prioritise them, it is necessary to look at them in the context of the overall safety case, in particular the key safety functions and threats, and to assess them in a quantitative fashion against this “top down” structure. This will be an important part of the SR Site review and the workshop did not attempt to preempt this process. It is clear that the participants at the workshop provide SSM with the necessary expertise to achieve this during the review.

The SR Site review will maintain an “issues register” to track all the issues raised during the review and to record, in due course, how they have been resolved. The experience at the workshop suggests that it will be necessary to engage multi-disciplinary teams to address issues and that they will need to develop an in-depth understanding of SKB's arguments in order to tackle the key issues.

The issue of canister integrity is clearly central to the SKB approach and the issues that relate to it are many, varied and complex. It will be necessary for the review team to first understand and explore the basic structure of the case that SKB submits – this will provide a context in which reviews of detailed technical documents can be undertaken and interpreted.

It will be necessary to develop an independent understanding of the key aspects in some areas in order to determine whether the approach taken by SKB is satisfactory. In some cases this may involve requests to SKB for clarification, for new calculations, for access to data, or even for new experimental work. In other cases, independent modelling will be necessary, to check calculations presented by SKB and to explore issues.

It is to be expected that the review process will be iterative in nature – with sets of issues identified at each stage being subjected to prioritisation before being further explored in the next stage, with the aim of resolving issues progressively. This will require a flexible approach with multi-disciplinary teams being formed to address specific sets of issues at each stage. These teams will need to be given clear guidance in terms of the scope of the work that they are to undertake and the timescales for its delivery.

The "issues register" will need to be available to all members of the review team, to avoid duplication of effort and re-opening of resolved issues.

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Appendix A: Participants

Bjorn Dverstorp (SSM) (part-time attendance)
Flavio Lanaro (SSM)
Jan Linder (SSM)
Georg Lindgren (SSM)
Jinsong Liu (SSM)
Bo Strömberg (SSM)
Shulan Xu (SSM)
Lena Sonnerfelt (SSM) (part-time attendance)

Mick Apted (Intera)
Randy Arthur (Intera)
Adrian Bath (Intellisci)
Richard Becker (Studsvik AB)
Steven Benbow (Quintessa)
David Bennett (TerraSalus)
Gunnar Hultquist (KTH)
Jaakko Leino (STUK)
Ari Luukkonen (STUK)
Digby Macdonald (Penn State University)
Peter Robinson (Quintessa)
Timo Saario (VTT)
Göran Sällfors (Chalmers University)
David Savage (Savage Earth)
Peter Szakálos (KTH)
Håkan Wennerström (Lund University)

Appendix B: Agenda & Workshop Organisation

Wednesday 15th September

09.00-09.15 Introduction and short presentation of participants.
09.15-09.30 Review plan for SR-site, B. Strömberg.
09.30-10.10 Overview of copper corrosion in repository environment, T. Saario.
10.10-10.40 Introduction to buffer erosion, R. Arthur.
11.00-12.00 Site geochemistry and long time evolution, A. Bath.
12.00-12.30 Modelling of integrated buffer evolution and copper corrosion, P.Robinson.
13.30-17.30 Group seminars: corrosion and buffer erosion

Corrosion Group
Copper immunity in Swedish repository environment, D. D. Macdonald.
Sulphide induced SCC of copper, T. Saario.
Corrosion in anoxic pure water, G.Hultquist, P. Szakálos.
Corrosion of copper in oxygen free condition, T. Saario.

Buffer Erosion Group
Buffer pore water chemistry, D. Savage and R. Arthur.
Elastic, plastic and rheological properties of buffer material, G. Sällfors.
Colloid chemistry of buffer erosion, R. Arthur and H. Wennerström.
Buffer property changes after erosion, M. Apted.

Thursday 16th September

09.00-12.00 Continuation of group seminars

Corrosion Group
Information needed from buffer material group in order to better understand copper corrosion, task list.

Buffer Erosion Group
Information needed on hydrogeology, hydrogeochemistry, and glaciology in order to better evaluate the buffer erosion processes, task list.

13.00-14.00 The coupling between corrosion, buffer erosion and hydrogeology, A. Bath and P. Robinson.
14.00-15.00 Joint session and presentation of task lists prepared in working groups.
15.20-17.00 Group seminars: corrosion and buffer erosion.

Corrosion Group
Critical issue list with respect to corrosion and SR-site.
Task list from buffer erosion group, how should issues be treated?

Buffer Erosion Group
Critical issue list with respect to buffer/backfill
Task list from the corrosion group, how should issues related to hydrogeology, hydrogeochemistry and glaciology be treated?

17.00-18.00 Presentation of critical issue lists from working groups.

Friday 17th September

9.00-12.00 Group seminars, corrosion and buffer erosion.

- The aims with this last session are:
- To define what can be done to resolve issues raised by working groups.
- To define responsibilities writing chapters in the workshop report.
- To start writing workshop report.

Appendix C

1. Overview of copper corrosion in repository environment

Spent nuclear fuel in Finland and Sweden will be disposed in deposition holes excavated in granitic bedrock at a depth of about 400 to 500 m. The release of activated products is prevented by a multi-barrier concept. A copper canister with 50 mm wall thickness will be the main corrosion shield, expected to last un-perforated for over 100,000 years.

There are several different corrosion mechanisms that in principle may threaten the integrity of the copper canister. Likewise, there are several different scenarios which may expose the copper canister to these corrosion phenomena. During the years, most of the corrosion related concerns have been satisfactorily dealt with, leaving a few to be further researched.

This presentation gives an overview of the corrosion related issues with regard to the integrity of the copper canister, as well as the main approaches developed by the share holders to ensure the integrity for the duration needed. A more detailed description of the few remaining ongoing corrosion related research items is also included.

The mechanisms dealt with are 1) general corrosion, b) pitting corrosion, c) stress corrosion cracking and d) corrosion assisted creep. In the area of general corrosion, the effect of oxygen remaining in the repository after closure has been rather adequately dealt with by a mass-balance based approach. Likewise, the general corrosion produced by the sulphide transported in the groundwater flow (maximum 1-3 mg/l in Finland and Sweden) can be shown by mass-balance calculations to be insignificant for the canister safety.

Recently, a new general corrosion mechanism of copper has been proposed, involving oxidation of copper by water under anoxic conditions. Szakálos et al. [1] have proposed that copper reacts with water under anoxic conditions producing a copper hydroxide film, and that a major part of the hydrogen liberated in the process enters copper, possibly making it mechanically brittle. There is an ongoing debate on this issue at the moment and therefore further evidence is needed before any decisive conclusions can be made. At present, at least two independent research projects are being conducted to investigate the plausibility of the hypothesis and possible consequences thereof.

Pitting corrosion is a form of localised corrosion, where a local area becomes more anodic than the surrounding area and thus dissolution occurs more rapidly in this local area, generating a pit. Severity of pitting can in general be described by the so-called pitting factor PF, i.e. the ratio of maximum pit depth to that of general corrosion. Oxygen (in principle any oxidising agent) is considered a pre-requisite for pit propagation. A decrease in dissolved oxygen concentration (because of the limited amount of air/O_2 available in the repository) would result in less Cu dissolution and an increase in the pit pH, both of would eventually tend to cause the pit to stop propagating. In the latest published analysis of the copper canister case [1], using pitting factors to assess the depth of localized corrosion (realistic PF = 2, conservative PF = 5), the predicted depth of localized corrosion remains at less than 2 mm.

Creep (slow deformation) of the copper canister does occur in the repository. When resaturation takes place, bentonite swelling forces the copper canister to yield until it becomes supported by the inner cast iron canister. Also, in case of a sudden shear movement (e.g. as a result of an earth quake) some of the canisters may be affected and would accommodate part of the remaining stress by creep. In early days, with the oxygen free copper, Cu-OF) some data sets showed what was then called brittle creep fracture, i.e. creep ductility of clearly less than 10 %. The phenomenon was attributed to presence of sulphur at the grain boundaries. Addition of small amount of phosphorus (40 … 60 ppm) resulted in CuOFP with superior creep properties, and disappearance of the brittle creep fracture phenomena. The remaining question which may need an answer is, with the very long time in question (possibly tens of years for bentonite swelling), will the brittle creep phenomena appear again or not. To answer this question convincingly, either reliable micromechanical modelling approaches or long term creep tests are possibly needed.

Creep is a mechanical degradation phenomenon, which may be enhanced by corrosion processes. The data sets used for safety analyses regarding creep of copper canisters have been measured in laboratory air, not in corrosive environment representative that of the repository. Creep tests of CuOFP under conditions representative of the early oxic period are ongoing to answer this question.

The main SCC agents for CuOFP known to exist in the repository and to be produced by bacterial activity are ammonia, acetate and nitrite. The approach chosen by the operators (SKB and Posiva) is to prove that the necessary ingredients for SCC to occur, i.e. high enough stress, high enough potential and high enough concentration of the aggressive species do not co-exist ever in the repository. This is called the decision tree-method (or fault tree-method). The method has shown to be promising and there seems to be some consensus at the moment that SCC under oxic conditions would not threaten the integrity of the copper canisters in the repository. If one were to look for the weakest link in the argumentation it may the microbe models used to predict the evolution of the microbe populations in time, as to the knowledge of the author they have not been calibrated by any set of experiments.

In 2007 a new Japanese research showed that also sulphides can cause SCC in pure copper under anoxic high chloride water conditions [2]. Sulphides may come to contact with the copper canister surface through three different processes: 1) transport via groundwater flow, 2) production at the bentonite/rock interface via sulphate reducing bacteria (SRB) and further transport and 3) through SRB activity within bentonite (pyrite reduction). In the groundwater sulphide concentrations are typically relatively low, 1-3 mg/l. The maximum value that can be formed through SRB activity at the bentonite/rock interface can be high (in the range 400 to 500 mg/l), causing a high diffusion gradient through the bentonite. The sulphide concentration that forms because of SRB activity within bentonite is known to some extent as a function of bentonite density. According to experimental findings sulphides may form within the bentonite even in fully compacted bentonite. In scenarios where the density of bentonite locally decreases (e.g. early piping, bentonite erosion by glacial melt waters) the access of sulphide to the copper surface will be much easier.

A relatively large effort is ongoing to experimentally determine whether CuOFP base material is susceptible to SCC in presence of sulphides when exposed to a representative anoxic groundwater. Furthermore, if the material is susceptible, what would be the minimum concentration of sulphide needed for SCC to occur (within 0 to 100 mg/l concentration range). Within the same effort, also a diffusion model is being developed allowing the three above described different scenarios to be considered. The first results have indicated evidence for a new degradation mechanism involving in-diffusion of sulphide from groundwater to grain boundaries in CuOFP ahead of a crack tip [3].

1. P. Szakálos, G. Hultquist and G. Wikmark, (2007). Corrosion of Copper by Water. Electrochemical and Solid-State Letters, 10 (11) C63-C67.
2. N. Taniguchi and M. Kawasaki, 2007, Influence of Sulphide Concentration on the Corrosion Behaviour of Pure Copper in Synthetic Sea Water, 3rd Int. Workshop on Long-term Prediction of Corrosion Damage in Nuclear Waste Systems, Pennsylvania State University, May 14-18, 2007.
3. E. Arilahti, T. Lehtikuusi, M. Olin, T. Saario and P. Varis, Sulphide induced stress corrosion cracking of CuOFP in groundwater, 4th International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems, Brugge, Belgium, June 29-July 2, 2010.

2. Site Geochemistry and Long Time Evolution

Adrian Bath
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In the long term, the geochemical conditions at repository depth will progressively dominate the chemical processes in the engineered barriers. Whilst there are many generic aspects of Fennoscandian crystalline rock groundwater geochemistry that provide a useful framework to understand the general conditions, there is a substantial database for Forsmark that identifies site-specific characteristics that will affect how the engineered barrier system performs with regard to backfill and buffer evolution and copper corrosion. Site-specific features and their interpretation in terms of past evolution and susceptibility to change are also checks on models of long time evolution in the system.

Present geochemical conditions at repository depth at Forsmark

The major geochemical parameters for groundwaters at Forsmark, pH, redox, major cationic and anionic solutes and overall salinity, have 'typical' values and ranges. Ionic compositions are indicative mainly of the post-glacial hydrogeological history of submergence and pre-Baltic sea water intrusion followed by re-emergence and fresh water infiltration, resulting in a dominantly brackish water composition over the depth range 200-600 m. The deeper part of the brackish water volume has its salinity derived from much older deeper groundwater. Spatial variations of water compositions in the target volume are mostly small except for increasing salinity in the deeper northwest part of the target volume.

pH measurements are in the range from 7 to 8.5 and redox conditions at repository depth are reducing, as expected, with dissolved oxygen invariably undetectable though there are few direct measurements of DO and Eh in the target volume. Eh values are between -280 and -140 mV vs SHE and correlate with pH, reflecting the controlling redox couples. pH and redox are established as water infiltrates in relatively shallow bedrock, the main reactions being calcite dissolution, silicate weathering, organic C oxidation and perhaps oxidative pyrite dissolution. Deeper bedrock minerals also provide buffering capacity for future perturbations such as the intrusion of dissolved oxygen.

Potentials calculated for the $Fe^{2+}/Fe(OH)_3$ and HS^-/SO_4^{2-} couples are close to measured Eh, suggesting that these are the main geochemical redox reactions with HS^- concentrations being limited by FeS precipitation. However anomalous HS^- concentrations have been measured in some brackish groundwaters and SKB think that FeS seems to be less active at this site. These redox reactions are influenced by microbiological mediation, so reaction kinetics as well as conventional equilibria may be significant for HS^- concentrations in near-field groundwaters around deposition holes. Therefore, in addition to geochemical fluxes of SO_4^{2-} and Fe^{2+}, microbial populations and other biogeochemical factors such as dissolved organic carbon will affect near-field production of HS^-. Other reduced species that would be potential corrodants towards copper could be similarly affected. SKB's analyses indicate large spatial variations of microbial populations that may be linked to varying propensity for these reactions, but the degree of localised significance in relation to the normal geochemical processes is unclear.

Secondary minerals in transmissive fractures are indicative of long-term groundwater geochemistry and are also geochemical sources of redox-active solutes for present and future waters. The general distribution at repository depth is chlorite >> calcite >> hematite ~ clays ~ goethite ~ pyrite; pyrite decreases below about 300m. The assemblage is consistent with the redox equilibria indicated by solute couples.

Groundwater diffusing into the EBS is the source of cations that will progressively re-equilibrate with the exchange ions in bentonite in buffer and backfill. The water is brackish (ionic strength ~0.2 M) and has a Na^+-Ca^{2+}-Cl^- composition (mNa^+/mCa^{2+} = 1.5 to 3.8; mCa^{2+}/mMg^{2+} = 2.2 to 74). There are sufficient divalent cations relative to monovalent to maintain bentonite swelling pressure. Long time evolution of the groundwater system will cause dilution. There is a question about how the relative proportions of cations and other parameters such as pH will change as groundwater at repository depth evolves from dominance by old seawater to being predominantly fresh water.

Water contained in the pores of the rock matrix is more or less consistently more dilute than mobile groundwater in fractures at similar depth, though this effect is diminished in the structural domain containing the target volume. These differences have been due to the slow rate of diffusive exchange between waters in matrix and fracture. The potential long-term influence of matrix water on near-field geochemistry is an additional consideration.

Long time evolution of geochemical conditions

There are several issues of long time evolution and the potential effects of episodic changes of environmental conditions on geochemical conditions in near-field groundwaters. Shorter term perturbations of near field conditions will also be caused by the repository and by introduced materials; for example, enhancement of dissolved organic C in the near field would likely stimulate microbial activity and related redox reactions such as sulphate reduction.

Long time evolution under present temperate (or warming) climate will cause the progressive dilution of groundwater as noted above. In the very long term, i.e. many tens of 1000’s of years at least, of the normal evolution a change to a glacial climate may occur. This scenario would influence groundwater firstly by the development of permafrost as a barrier to normal diffuse fresh water infiltration and groundwater discharge, and secondly by development of an ice sheet that might cause enhanced infiltration of dilute melt water for relatively short periods. Permafrost conditions potentially have much longer duration than the transient hydraulic intrusion of glacial melt water (as suggested by the conceptual model for sub-glacial hydraulics).

It is hypothesised that permafrost formation causes salinization of underlying groundwater due to 2-phase fractionation of solutes when ice freezes out from shallow groundwater. There is a paucity of data for the effects of this process on groundwater compositions, and there is also slender evidence so far that any such bulk salinization is likely to occur. SKB continues to research this issue and the potential significance of permafrost on groundwater movement and freeze-out salinity for buffer stability remains uncertain.

The significance of a future episode of glacial melt water intrusion has been considered in three respects: that dissolved oxygen in the ‘pulse’ of melt water might penetrate to repository depth, that the enhanced hydraulic gradient will increase groundwater fluxes at repository depth, and that there will be a rapid freshening of groundwater composition at repository depth. The first would affect copper corrosion whilst the latter two scenarios would be significant for buffer stability and erosion. There have been several modelling studies of the capacity and rate for dissolved oxygen to be attenuated by geochemical redox reactions in the bedrock between surface and repository. They indicate a very low probability that oxygen might pass through both the rock and buffer barriers to reach the canisters, involving extreme hydraulic conditions and lack of geochemical attenuation. Glacial melt water would be very dilute but would react with bedrock during downwards flow in a similar way to the geochemical evolution of normal fresh water infiltration. There is a question about the extent and nature of those geochemical reactions for the relatively greater flux of melt water infiltration. A combination of faster flow rate and unmodified dilute composition for water in bedrock around deposition holes would be potentially a cause of buffer erosion.

Alongside those main scenarios for long time evolution of hydraulic and geochemical conditions at repository depth, there are other aspects of changing hydrogeological conditions and groundwater compositions that should also be considered. For example, there are possibilities that microbial populations and the rates of biogeochemical reactions might be affected by changing groundwater compositions especially with respect to redox-active solutes including organic carbon.

3. PA Modelling of Copper Corrosion, Integrated with Buffer Evolution

Peter Robinson and Steven Benbow
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Quintessa is developing an integrated (systems level) model for copper corrosion that accounts for the evolving buffer when buffer erosion occurs. Initial planning for the work has been completed and preliminary calculations have begun. The presentation will summarise what is planned and demonstrate results of initial calculations.

The work that is described is assumed to be the first stage in a longer term modelling study in which the interactions between processes that affect canister corrosion are fully investigated.

The models are intended to form the basis of more detailed models that can be developed in subsequent years. They will include an initial representation of all relevant physical processes, but with some processes represented in more detail than others. This will allow investigation of sensitivities to the processes that are modelled, allowing identification of the processes that impact most on the key performance measures of the EBS, which will help to focus modelling developments in future work.

Two scenarios will be considered in this work: a base case scenario in which the buffer is assumed to remain intact; and a scenario in which bentonite erosion takes place. Variant cases for each scenario can be considered to investigate sensitivities. In the latter scenario, the bentonite erosion processes will be represented in a simplified way, by imposing a predetermined erosion rate (mass loss rate) on the bentonite with redistribution of the bentonite within the buffer at a controllable rate. In future work this could be replaced by a more chemically-based representation of the erosion processes and a more mechanistic representation of the bentonite redistribution process whilst keeping the remainder of the model the same.

The modelling will be undertaken with Quintessa’s QPAC general purpose modelling software together with relevant modules. This collection of components has previously been referred to as QPAC-EBS.

The key output of interest from the modelling will be the degree of corrosion of the surface of the copper canister and its spatial profile. In particular, conditions that lead to the potential for regions of enhanced corrosion will be of interest. The following issues will be explored in both scenarios:

- The role of sulphide originating in the buffer, specifically considering solubility limits and the role of pyrite, which will provide information on the importance of homogeneity control in the initial pyrite concentration and its potential to lead to uneven corrosion;
- The role of sulphide supply in groundwater (either in addition to or instead of buffer sulphide), taking account of natural groundwater concentrations, flow rates, and diffusion within buffer, where geometric consideration will lead to

higher corrosion nearer the fracture plane, particularly on the up-stream side; and
- The role of sulphate reducing bacteria (SRB).

For the scenario where the buffer is allowed to erode, the following additional issues will be investigated:

- The potential for transport of sulphide to the canister (or part-way to the canister) by advection, including
  - the impact of redistribution of buffer material;
  - the geometry of any cavity in the buffer; and
  - the relationship with the SKB performance criterion of 1200 kg loss of buffer material.
- The impact of changed buffer diffusivity (characterised by the relationship to buffer density); and
- The effect of SRB in the presence of cavities or reduced density buffer.

Details of the representation of the features and processes that will be included in the model will be described.

Some questions where input from workshop participants is sought will be listed at the end of the presentation.

4. Geochemical Constraints on Buffer Pore Water Evolution and Implications for Erosion

David Savage
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Recent work carried out for SSM on this topic has shown that currently-available models for bentonite pore water evolution are inadequate in describing all key processes, which ideally should include kinetic silicate mineral hydrolysis and growth, in addition to clay ion exchange, clay edge site protolysis, and trace mineral equilibration (Savage et al., 2010). Goals for this project in 2010 include:

- Can the conclusions reached in 2008-9 for pure water and a high-pH fluid be extended to real (Forsmark) groundwater compositions?
- What evidence is there for water-rock reaction and mineral stability in:
  - mineral assemblages in fractures at Forsmark?
  - Forsmark groundwater chemical compositional data?
- What implications are there from the above for reactions in the EBS?

Mineralogical information for fracture fillings at depth at the Forsmark site has been reported in a series of reports and papers summarised by Sandström and co-workers (Sandström et al., 2008; Sandström and Stephens, 2009). These data show a long history of water-rock reaction, from the Proterozoic to the present, in at least four discrete mineralisation events, ranging from temperatures as high as 250°C for ‘Generations 1 and 2’, to less than 50° for late Palaeozoic to present minerals (‘Generation 4’). This latter generation is characterised by clay minerals and thin precipitates of calcite, but also minor amounts of goethite and pyrite, mainly associated with hydraulically-conductive fractures and fracture zones. Corrensite dominates and is a (Fe-Mg) mixed-layer chlorite-smectite mineral with some swelling properties. It has recently been identified as a major product of the interaction of Tono granite with groundwater (Sugimori et al., 2008). Although smectite is reported to occur at all depth levels at Forsmark by Sandström and co-workers, it is recorded as being ‘minor’ in abundance in comparison with corrensite, illite, saponite, and mixed-layer smectite-illite. Calcite is also present at all depth levels, but gypsum, dolomite, and siderite are absent throughout the system.

Although SKB emphasises that groundwater compositions at Forsmark can be interpreted by simple mixing relationships alone (e.g. Laaksoharju et al., 2008), a number of thermodynamic activity diagrams have been constructed here to evaluate the possible control of key aqueous species (pH, PCO_2, Na/Ca) by water-rock reactions. Mineral stabilities in the system $CaO\text{-}MgO\text{-}K_2O\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O\text{-}CO_2$ and $Na_2O\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O\text{-}CO_2$ are summarised in Figure 1 and Figure 2, respectively.

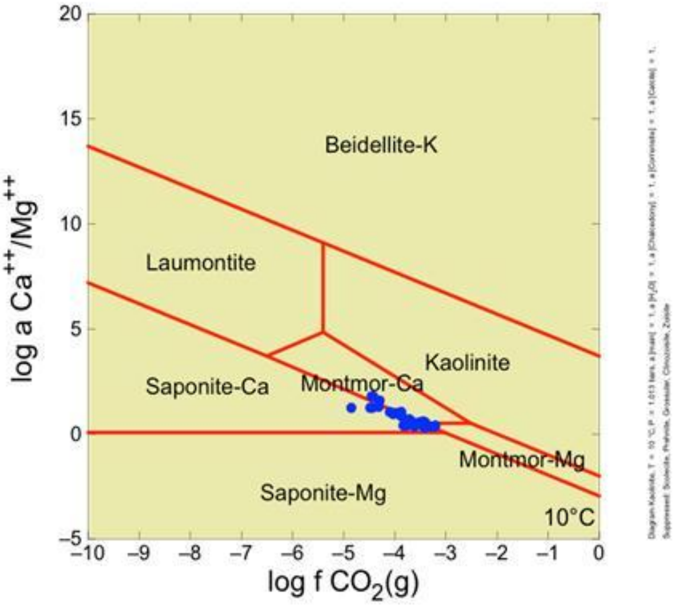

Figure 1. Mineral stabilities in the system CaO-MgO-K2O-Al2O3-SiO2-H2O-CO2 at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A. Bath , pers. comm..). Data suggest control of Ca/Mg, PCO2 (and pH), by montmorillonite-saponite coexistence.

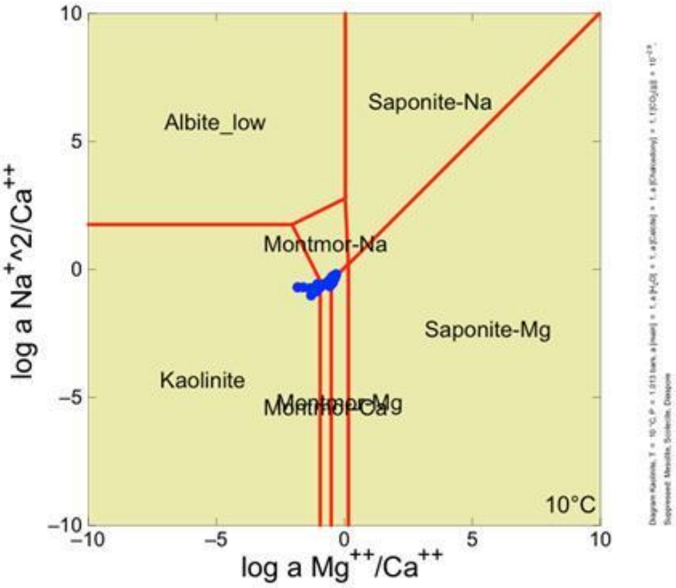

Figure 2. Mineral stabilities in the system Na2O-CaO-MgO-Al2O3-SiO2-H2O-CO2 at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A. Bath, pers. comm..). This suggests control of Na/Ca ratios by montmorillonite-saponite coexistence. This reaction could buffer Na/Ca in glacial meltwaters during intrusion to depth during glacial periods.

Figure 2. Mineral stabilities in the system Na_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2 at 10 °C. Blue dots represent compositions of groundwaters from repository depth at Forsmark (A. Bath, pers. comm..). This suggests control of Na/Ca ratios by montmorillonite-saponite coexistence. This reaction could buffer Na/Ca in glacial meltwaters during intrusion to depth during glacial periods.

Data in these figures show that minerals present in Forsmark fracture fills (montmorillonite, saponite, calcite, chalcedony) could be important as controls of the activity ratios of erosion-relevant cations in groundwater (Na, Ca, Mg), as well as other important near-field parameters, such as pH, PCO_2, and $SiO_{2(aq)}$. This control may also be extended to future periods of glacial meltwater intrusion. Na/Ca is in the range 3-9.5 as defined by montmorillonite-saponite coexistence.

The model analysis conducted in 2008-9, reacting MX-80 bentonite at high compaction density in ‘batch’ conditions has been repeated this year, extending the modelling to 2000 kg m^{-3} density, and introducing typical Forsmark groundwater (Table 2.1 in Auqué et al., 2006) as the reactant fluid. As demonstrated in the previous study (Savage et al., 2010), reaction of MX-80 both in pure water and in Forsmark groundwater proceeds to equilibrium extremely rapidly in the suppression of secondary mineral precipitation. However, the incorporation of (equilibrium) mineral growth in the simulations delays attainment of steady-state up to 10,000 years in those cases using thermodynamic data for montmorillonite derived from the ‘Vieillard’ model (Vieillard, 2000). Data estimated by Wolery (Wolery, 1978) suggest more rapid equilibration, in the order of 1000 years. Further work is necessary to examine the effects of the introduction of the kinetics of growth of secondary minerals on these equilibration times.

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5. Bentonite rheology and physical erosion

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Loss of bentonite, or physical erosion of bentonite, requires a good understanding of a number of physical properties and phenomena among others:

- Soil properties and material behaviour under vastly different conditions and water contents.
- Modes for bentonite loss
- Aperture width and continuity
- Expansion and supply of bentonite from the deposition hole
- Flow of water and chemistry of the flowing water
- Flow regime on a larger scale, gradients and duration

These areas were dealt with and are summarized below.

Soil properties and material behaviour under vastly different conditions and water contents

Bentonite properties as a soil at water ratios up to its liquid limit have been extensively researched during the last few decades and are fairly well known. Most important properties from a barrier point of view are hydraulic conductivity and swelling pressure. For a number of different bentonite material these properties have been determined and are usually given as functions of bulk density, and data can be found in numerous reports by SKB.

For higher water ratios, bentonites are often classified as gels, sols (or semi-liquid state) or liquids, depending on water ratios and then flow properties for the sol or liquid are more appropriate to determine. On this subject the knowledge is not as complete as for the bentonite in solid state. However, the best and most comprehensive results are given by Birgersson et.al (2009). Reasonable and fairly reliable results have been presented for water ratios up to, say 30. For even higher water ratios some results exists, even if they might be considered as less accurate. To complicate the problem further, not only the measuring technique will influence the results, but also the chemistry (ions and their concentrations) will play an important role for the properties. Other variables which will have a great impact on the flow properties are temperature, clay mineral etc. numerous examples and recommendations will be given in the final report.

Modes for bentonite loss

Bentonite can be lost either due to expansion from the deposition hole, sinking due to gravity or expansion accompanied by erosion of dilute bentonite solutions. Pure expansion cannot very well be a factor as the amount of bentonite in the deposition holes are large compared to the total volume of fractures surrounding the repository. The same is true for loss due to gravity and thus the only possible mode for substantial loss would be expansion of the bentonite in combination with erosion caused by flowing water on a larger scale in the surrounding fractures. This emphasizes that a sound understanding of the mechanisms involved for expansion of the bentonite, especially for high water ratios, constitutes crucial knowledge. In this context a sound understanding and data on swelling pressure, hydraulic conductivity and its interaction with the fracture walls are essential.

Aperture width and continuity

A presumption for flow of water in the fractures are that these have a certain width and are continuous or at least form a continuous network. A lot of work has been devoted to determining aperture width and the flow conditions associated with that. Without going into details it has been found that typical fracture widths in Forsmark are in the order of 50 to 100 or 200 µm. The extent of their continuity has to a certain extent been investigated by a number of pumping test, revealing a comparatively low permeable rock mass.

Expansion and supply of bentonite from the deposition hole

In a dry hole, where the canister and the surrounding bentonite have practically no access to water, no swelling will take place, and thus no erosion will occur. The bentonite is restrained from swelling due to high negative pore pressures. However if water is available, the bentonite will swell, but the process is time delayed as water then must flow into the very low permeable bentonite. This process is well understood and can be readily modeled based on traditional geotechnical parameters. This has been done by Birgersson et al. (2009). However when swelling into a fracture the interaction with the fracture wall must be taken into account, and crucial for the results are the assumption of wall friction and also the width of the aperture. It is fair to say that for rather high densities the wall friction is well understood and can be measured, while it for very high water ratios, perhaps above 10, is very difficult or maybe even not possible, to measure the effect of wall friction. Birgersson et.al. also model the swelling process and thereby arrives at an estimate of the rate of supply of bentonite, due to swelling, as a function of hydraulic conductivity, swelling properties, aperture width and wall friction. A completely different approach is taken by Neretnieks et al. (2009), where a semi-theoretical approach is adopted and leads to far more extensive swelling out into even small fractures. More knowledge is needed regarding particularly flow properties for bentonite sols and possible interaction with the walls in the apertures. The extent of swelling resulting from the two different approaches is very different and almost contradictory.

Flow of water and chemistry of the flowing water

It has been discussed elsewhere how the chemistry of the water affects the properties of the gel/sol. There seems to be a consensus of that severe erosion might only take place when the flowing water contains only small amounts of ions, often referred to as glacial melting water. These effects are also dealt with elsewhere. Also important to take into account is the water ratio, or expressed as the bentonite concentration of the gel/sol which is assumed to be eroded, as the concentration as such influences the amount of bentonite mass which can eroded.

Flow regime on a larger scale, gradients and duration

The above mentioned conditions with flowing glacial melt water will be present during and for some period after glaciations. In between the chemistry of the water will most likely be such that the bentonite also at high water ratios will be contractive and not particularly susceptible to erosion by water flowing with moderate velocities. Moreover, gradients high enough to generate flow of such magnitudes that substantial erosion might occur will probably only be present when the ice front is in the vicinity of the repository. Speculations and conclusions need to be drawn regarding how long these periods might be.

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6. Bentonite erosion – A review of laboratory evidence

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The Swedish Nuclear Fuel and Waste Management Company, SKB is preparing to apply for a licence to dispose of spent nuclear fuel. SKB is proposing that spent nuclear fuel should be disposed of according to the KBS-3 concept. According to the KBS-3 concept, after 30 to 40 years of interim storage, spent nuclear fuel would be placed in cylindrical copper canisters and these would be disposed of at a depth of 400 to 500m in crystalline bedrock. The copper canisters would be placed within a bentonite clay buffer. Tunnels leading to the waste deposition holes and other excavations would be backfilled and sealed, using a bentonite-based backfill and cement-based tunnel plugs.

One concern is that groundwater pressure gradients and flows might cause piping and or erosion of the bentonite-based barrier materials. Piping can lead to the formation of hydraulically conductive channels in bentonite-based engineered barriers, and may lead to erosion. Piping erosion could also hamper engineered barrier emplacement and may necessitate physical measures to be put in place during repository operations to protect the bentonite materials from water inflows. Bentonite chemical erosion, when the bentonite is in contact with very diluted groundwater, might under certain circumstances lead to significant loss of mass from bentonite barriers. Significant erosion might cause the buffer not to fulfil its safety functions. For example, the hydraulic conductivity of the buffer might rise above 1E-12 m/s, and this could allow increased transport of corrosive species (e.g., sulphide) to the canister and cause more rapid canister corrosion.

An assessment has been made by SSM's BRITE advisory group of recent experiments and modelling work on buffer erosion conducted by SKB and its contractors (Apted, M., Arthur, R., Bennett, D., Sällfors, G., Savage, D. and Wennerström, H., 2010, Buffer erosion: An overview of concepts and potential safety consequences, SSM Report 2010:XX).

SKB's work has shown that bentonite may be eroded in the form of colloids or larger particles. Bentonite may be eroded as a result of chemical processes that lead to bentonite swelling into fractures in the host rock and the formation and dispersion of colloids or, if flows are fast enough, as a result of shearing at the bentonite-water interface. Bentonite erosion is particularly dependent on the composition of the clay and the salinity and composition of the waters present.

The results of SKB's R&D program indicate that buffer erosion may occur if the clay buffer is exposed to flowing water having low concentrations of calcium (or other divalent/trivalent cations), and if NaCl concentrations do not exceed 25mM (SKB 2009).

Some of SKB's experiments are of a problem-scoping nature and represent the early stages of research into bentonite erosion. Some of the experiments go further, are relatively more refined, better focussed and constrained but, in total, the range of experiments conducted to date is limited, and only some areas of the problem have been addressed. For example, further work would be needed to properly understand the role of dissolved Ca in preventing erosion of Na-rich clays.

Some of SKB’s experiments have highlighted processes that are not accounted for in current conceptual models - e.g., the effect of dispersed bentonite on water flow. There are also some questions over how relevant the experiments conducted so far are to the repository system. For example, unlike in SKB’s experiments, in the repository environment real fractures will be rough, will have various orientations, intersections and asperities, and on average may be approximately ten times narrower than considered in the experiments.

Bentonite penetration distances into fractures could, therefore, be smaller than calculated in some of the simulations discussed SKB, but there is no real experimental evidence to confirm this. There is also no convincing experimental evidence that the accessory minerals in commercial bentonite will form effective filters, as postulated by SKB (2009).

In conclusion, some interesting and useful experiments have been performed on bentonite erosion, but as yet only some areas of the topic are well understood. Bentonite erosion depends on clay composition and water salinities and compositions – but there is not a simple relationship and further research may be necessary. The estimates of bentonite penetration into fractures and of bentonite erosion provided by SKB to date (SKB 2009) are highly uncertain. It appears that at this stage the possibility of buffer erosion cannot be eliminated and that the issue needs to be managed via a combination of further research, improved consequence assessments, specification of appropriate ‘rules’ for buffer installation, selecting appropriate buffer materials with high smectite contents, and identifying suitable locations for deposition holes in the disposal facility.

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7. Ion exchange in clay buffer

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Potentially the bentonite clay buffer protecting the canisters can erode when exposed to flowing water. It is difficult to predict the electrolyte composition of the water and its composition is likely to vary during a period of 100 000 years. The main ions expected to affect the physical properties of the clay are the cations of sodium, calcium and possibly magnesium. Since the clays are highly charged anions play a minor role. There will be a cation exchange between the clay buffer and the aqueous solution in contact with the clay. The swelling and then also indirectly the rheology of the clay depends on the ions composition. It is thus relevant to consider the exchange in relation to the problem of clay buffer erosion.

There are two different views on how to describe the ion exchange between a charged swelling material, like a clay, and an aqueous solution. One is based on model of a chemical equilibrium, using an equilibrium constant K. This presupposes the dominance of short-range forces between ions and the material. This is the approach chosen in the SKB report TR-09-35 and also in reports from Clay technology. The other view is that the dominant effect in swollen systems is due to electrostatics. In this case the immediate ion environment is very similar to that in solution, while there is a difference in the long-range electrostatic interactions. The parameters determining the exchange are in this case, apart from bulk concentrations, the charge density on the clay particles and the degree of swelling. It is my (HW) clear opinion that the electrostatic effects dominate the ion exchange in a swollen clay system and a proper description of the phenomena has to take this as a starting point of the description of the phenomenon.

The most commonly used model of electrostatics in highly charged systems is based on the Poisson-Boltzmann equation. (For a comprehensive description of the theory see: The Colloidal Domain. Where… by Evans & Wennerström, 2nd ed Wiley 1999). In this model one assumes that the ion distribution is determined by the value of the electrostatic potential

$$c_i(\vec{r}) = c_i(bulk)\exp\{-z_i e\phi(\vec{r})/kT\} \qquad (1)$$

using the bulk solution as the reference point for the electrostatic potential. For a system of two parallel charged surfaces one obtains a position dependent ratio of the concentrations of calcium and sodium and

$$\frac{c_{Ca}(x)}{c_{Na}(x)} = \frac{c_{Ca}(bulk)}{c_{Na}(bulk)}\exp\{-e\phi(x)/kT\} \qquad (2),$$

where we have used x as the coordinate in the perpendicular direction. Note the following:

i) If $|e\phi/kT| \le 1$ there is only a minor preference for calcium, but if $|e\phi/kT| > 1$ there can be order of magnitude effects.

ii) The potential can be seen as having two components so that $\phi(x) \equiv \{\phi(x) - \phi(midplane)\} + \phi(midplane)$. The first part describes the distribution of ions within the clay, while the second accounts for the difference in potential between clay and bulk. Knowing the latter one can, within the PB description, determine the swelling pressure and the chemical potential of the different ions.

The ratio of the calcium versus sodium content in the clay is in the Poisson-Boltzmann description given by

$$\frac{n_{Ca}}{n_{Na}} = \frac{c_{Ca}(bulk)}{c_{Na}(bulk)} \frac{\int \exp(-2e\phi / kT) dx}{\int \exp(-e\phi / kT) dx} \qquad (3)$$

showing that there is a strong preferential uptake of divalent relative to monovalent ions when the potential is large. This occurs for highly charged clay systems when there is a low net salt concentration in the bulk. Such conditions might be found in melt-waters from glaciers. Note from eq.(3) that the ratio of the ion content is typically clearly higher than the ratio of the activities as given by the ratio of the mid-plane concentrations.

For the highly charged clay systems the PB theory doesn't give a reliable description of the force between the surfaces, i.e. the swelling pressure. The deficiency of the mean field description also affects the accuracy of the description of ion exchange. However, in this case there is only a quantitative error and the equations presented above provide a reasonably accurate description. The presence of calcium ions affects the swelling pressure of the clays. It is theoretically estimated and also supported by experimental observations (see SKB reports) that for calcium to sodium ratios $n_{Ca} / n_{Na} \geq 10$ the swelling pressure can be zero. As a consequence buffer erosion is not likely to occur, but one might also loose the beneficial consequences of a finite pressure. This could include decreased inhibition of microbial growth and decreased self-healing after a mechanical damage (earthquake?). One might also find that if the initial water supply is rich in calcium the buffer will not swell to form a compact uniform protection of the canisters. If deswelling is induced at a later stage, for example during a deglaciation period, one can possibly obtain a microscopically more inhomogeneous clay buffer. If this occurs there are quantitatively significant changes in the diffusional transport of anions like the sulphide ion.

8. Chemistry of subglacial meltwaters: An evaluation of potential impacts on buffer erosion

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Colloidal montmorillonite sols could form if the bentonite buffer in a KBS-3 repository for spent nuclear fuel should expand into a fracture and come into contact with dilute glacial meltwaters that have migrated to repository depths from the surface of a warm-based ice sheet. Conditions favoring the formation of such sols are of interest because it is generally believed that significant erosional mass losses of the buffer would not occur unless sols form.

Montmorillonite sols are stable under two limiting conditions:

1. if the concentrations of divalent cations in the colloidal system are below a threshold “critical coagulation concentration” (CCC) consistent with DLVO theory and the Shulze-Hardy rule, or

2. if monovalent cations occupy a significant fraction of ion-exchange sites in these clay minerals.

The exchangeable cations Na^+ and Ca^{2+} are particularly important with respect to these conditions because they tend to be the most abundant monovalent and divalent cations in Swedish groundwaters. With regard to the first condition above, it can be noted that the CCC for Ca^{2+} has been determined to be approximately 1 mM. With regard to the second condition, it can be noted that montmorillonite sols have been observed to become unstable if the equivalent fraction of Ca^{2+} on exchange sites ≥ 0.9. This behavior has been attributed to the effects of ion-ion correlations, which are not accounted for in DLVO theory and which can strongly increase the net attraction between colloidal particles having high surface charge and divalent counterions in the electrical double layer.

The above two conditions were evaluated in relation to the chemistry of meltwaters that have been sampled in various studies of the supraglacial, proglacial and subglacial regions of warm-based Alpine glaciers and ice sheets. The analytical data considered include mean concentrations, or ranges in concentrations, of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (HCO_3^-, SO_4^{2-} and Cl^-). Most of the waters were sampled from proglacial environments and may therefore represent complex mixtures of subglacial, englacial and supraglacial meltwater components. A few samples of subglacial meltwaters sampled directly from boreholes drilled into the Haut Glacier d’Arolla in Switzerland were also considered, as well as samples of snowmelt and supraglacial streamwaters associated with this glacier. An analysis of an “interacted glacial meltwater” that was sampled in host rocks of the Grimsel Test Site in Switzerland was also included in the evaluation. This so-called “Grimsel water” is of interest because it was used in SR-Can to represent the chemistry of glacial meltwaters that could come into contact with the buffer over a 25,000 year interval of the 120,000 year reference glacial cycle.

The aqueous speciation of the meltwater samples noted above was evaluated at 0°C using the Geochemist’s Workbench geochemical modeling software package and a supporting thermodynamic database ("thermo.dat"). Calculated results include the molarity of "free" (i.e., uncomplexed) Ca^{2+}, which can be compared directly with the CCC for this cation. The second condition of sol stability noted above was evaluated based on mass-action constraints for the ion-exchange reaction,

Ca^{2+}(solution) + $2Na^{+}$(montmorillonite) = $2Na^{+}$(solution) +
Ca^{2+}(montmorillonte),

which can be represented by:

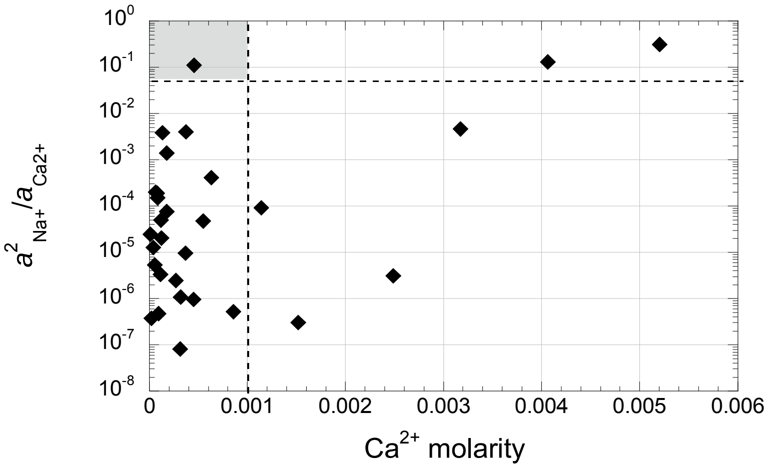
$$K_{GT} = \frac{X_{Ca} a^2_{Na^+}}{X^2_{Na} a_{Ca^{2+}}},$$

where K_{GT} denotes a selectivity coefficient consistent with the Gaines-Thomas convention, X_{Ca} and X_{Na} refer to the equivalent charge fractions of Ca^{2+} and Na^{+} occupying exchange sites on montmorillonite, and a_{Na^+} and $a_{Ca^{2+}}$ stand for the activities of Na^{+} and Ca^{2+}, respectively. If it is assumed that Na^{+} and Ca^{2+} are the only exchangeable cations involved in the reaction such that $X_{Na} = 1 - X_{Ca}$, the above equation can be re-arranged to give:

$$X_{Ca} + \frac{1}{X_{Ca}} = 2 + \frac{a^2_{Na^+}}{K_{GT} a_{Ca^{2+}}}.$$

The selectivity coefficient, K_{GT}, = 4.5 (at ≈ 25°C), and is effectively independent of the density of montmorillonite-water systems. Thus, for $X_{Ca} \geq 0.9$, which would tend to favor the stability of montmorillonite gels rather than sols, $a^2_{Na^+}/a_{Ca^{2+}} \leq 0.05$.

The results of the speciation calculations are summarized in the figure below. Noting that montmorillonite sols are unstable under conditions lying to the right of the vertical dashed line (Ca^{2+} molarity ≥ CCC = 1 mM) or below the horizontal dashed line ($a^2_{Na+}/a_{Ca2+} \leq 0.05$), it can be seen that sols are stable only over a small range of conditions indicated by the shaded region in the figure. The single meltwater plotting in this region is a jöhkulhlaup (outburst flow) sample from Casey Station, Antarctica, and is believed to be unrepresentative of subglacial environments due to the effects of $CO_2(g)$ degassing and concomitant precipitation of carbonate minerals. The available evidence considered to date thus suggests that glacial meltwaters, including Grimsel water, should inhibit, not promote, buffer erosion. Although most of these solutions are extremely dilute with Ca^{2+} concentrations well below the CCC, they also have very low values of the activity ratio, a^2_{Na+}/a_{Ca2+}, which should drive ion-exchange reactions toward the condition $X_{Ca} \geq 0.9$ and thus stabilize montmorillonite gels due to attractive forces arising from the effects of ion-ion correlations.



The above conclusion is based on a bounding analysis in which it was simply assumed that colloidal montmorillonite particles equilibrate with glacial meltwaters having a fixed composition, and that these solutions do not interact with the host rock as they migrate toward a KBS-3 repository. The analysis should be extended to consider a more realistic model of reactive-transport processes that are likely to occur near the leading edge of bentonite as it expands into a fracture, and equilibrium and kinetic constraints on possible meltwater-rock interactions.

9. Impacts of Buffer Erosion on Long-term Safety Functions

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Mass loss from sustained buffer erosion leads to a lowering of buffer density. Many of the safety functions of buffer are directly related to maintaining a certain threshold buffer density. In this regard, SKB made a presentation in November 2009 to SSM and its BRITE advisory group that linked SKB 'force-balance' model for buffer-erosion with specific data on fracture properties at the Forsmark site. The SKB approach assessed the likelihood, in terms of number of deposition sites possibly intersecting fractures capable of sustaining buffer erosion, that sufficient buffer mass might occur to lower the buffer density to the point that transport of dissolved species across the buffer would change from diffusion-control to advection-control.

This analysis extends the SKB approach to examine how additional key safety functions of the buffer might be compromised by sustained mass loss/ lowering of buffer density. In particular, rates of buffer-mass loss over a period of 10^5 years (approximately one glacial cycle) sufficient to compromise the safety functions of "ensures tightness and self sealing by buffer" and "prevent significant microbial activity" were evaluated.

Based on SKB 'force-balance' model and reported Forsmark data, there may be a limited number of waste package positions at the Forsmark site that would be lead to compromising the buffer safety functions of "transition to advection-control", "ensures tightness and self sealing by buffer" and "prevent significant microbial activity" for a period of 10^5 years. This analysis has also identified several factors that require further consideration:

- The differences between the two SKB models for buffer erosion (the KTH force-balance model and the alternative Clay Technology model) should to be more fully explored by SKB, with an effort to reconcile or place into context these differences
- The rheological response of buffer to sustained buffer loss into a fracture, and whether there would be a homogeneous or non-homogeneous density change, should be discussed by SKB.
- The potential evolution in current fracture velocities and apertures to alternative values, especially during a period of glacial loading and unloading, should be addressed by SKB.
- An analysis extended the previous SKB approach of linking the KTH 'force-balance' model for buffer erosion to site-specific fracture data from Forsmark to examine how key safety functions
  - "transition to advection-control",
  - "ensures tightness and self sealing by buffer",
  - "prevent significant microbial activity"

  of the buffer might be compromised by sustained mass loss/ lowering of buffer density over a period of 10^5 years (approximately one glacial cycle).

Based on this analysis there may be a limited number of waste package positions at the Forsmark site that would be lead to compromising the buffer safety functions.

Several factors that require further consideration by SKB:

- Reconcile the differences between the two SKB models for buffer erosion (the KTH force-balance model and the alternative Clay Technology model),
- Identify knowledge about the rheological response of buffer to sustained buffer loss (homogeneous or non-homogeneous density change),
- Address potential evolution in current fracture properties, especially during a period of glacial loading and unloading.

10. Is Copper Immune to Corrosion When in Contact With Water and Aqueous Solutions?

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Sweden's SKB-III plan for the disposal of high level nuclear waste (HLNW) is partly predicated upon the condition that copper, the material from which the canisters will be fabricated, is thermodynamically immune to corrosion when in contact with pure water. In the immune state, corrosion cannot occur because any oxidation process of the copper is characterized by a positive change in the Gibbs energy, rather than a negative change, as demanded by the Second Law of Thermodynamics for a spontaneous process. Accordingly, "immunity" is a thermodynamic state that must be characterized upon the basis of thermodynamic arguments. This immunity postulate was adopted, because of the occurrence of deposits of native (metallic) copper in various geological formations similar to those in Sweden throughout the World. Thus, it was reasoned that, during the anoxic period, when all of the oxygen that was present during the initial oxic period, due to exposure to air upon placement of the waste, had been consumed and the redox potential, E_h, had fallen to a sufficiently low value copper would become thermodynamically immune and corrosion would not occur, even over geological times, provided the environment remained conducive to that condition. In that case, dispersal of the waste due to a corrosion-induced failure was deemed to be impossible.

The issue of copper immunity has developed into one of considerable controversy within both the scientific and lay communities in Sweden, because direct experimentation has failed to achieve resolution. Thus, experiments by Hultquist et. al. [1-3] have reported detection of hydrogen when copper metal is exposed to pure water, while other experiments appear to refute those claims [4-6]. The experiments were all carried out to the highest scientific standards using hydrogen detection techniques that were more than adequate for the task and each group reported internally-consistent results that, nevertheless, differed from group to group. While the work reported in Refs. 1 to 6 is of great scientific interest, it is perhaps moot, when viewed in light of the environment that is present at Forsmark, the site of the initial HLNW repository in Sweden.

Thermodynamic Data for Copper and Sulfur Species

The initial task in the present investigation was to review various databases and the literature for thermodynamic data. Of particular interest was assessing the consistency of the data from one database to another. High consistency was expected, because the Gibbs energies of formation, the third law entropies, and the heat capacity are commonly taken from a common source. Of course, that does not ensure accuracy, because the original measurements themselves may have been in error. A better assessment method is to compare predicted phenomena with direct experiment, by first making sure that the phenomenon that is being predicted was not used for the original derivation of the data. For example, common comparisons include calculated and observed solubility, acid/base dissociation, volatility, and electrode potentials. However, to do this effectively for all species in the database is an enormous task that is well beyond the scope of the present work. Instead, this approach is being used to assess the data for only those species for which we have doubts of appropriate accuracy. Since this task is on-going, the results will be reported in the next report.

The second objective of this task was to develop a more comprehensive database for the polysulfide and polythiooxyanions by carefully reviewing the more recent literature than that included in the older databases. This proved to be highly successful, as we were able to locate several recent papers that reported thermodynamic data for a variety of partially oxidized/reduced sulfur species, including the polysulfides, polythiosulfates, and the polythionates (Table 1).

Table 1: Thermodynamic data for polysulfides and polythiooxyanions taken from the literature.

Species	**$\Delta_f G^o$ /kJmol^{-1}**	**$\Delta_f H^o$ /kJmol^{-1}**	**S^0 /J.K^{-1}.mol^{-1}**	**Cp^0 /J.K^{-1}.mol^{-1}**	**Source**
S_2^{2-}	77.685	13.040	28.451	-221.635	Kamyshny et. al.[7]
S_3^{2-}	71.564	6.600	9.000	-222.744	Kamyshny et. al.[7]
S_4^{2-}	56.394	9.000	100.000	-226.000	Kamyshny et. al.[7]
S_5^{2-}	66.666	21.338	139.000	-227.395	Kamyshny et. al.[7]
S_6^{2-}	68.189	13.300	139.000	-227.395	Kamyshny et. al.[7]
S_7^{2-}	80.951	16.500	139.000	-227.395	Kamyshny et. al.[7]
S_8^{2-}	88.272	23.800	171.000	-228.540	Kamyshny et. al.[7]
S^{2-}	85.973	33.095	-14.602	-137.154	NBS[4], Helgeson[13]
$S_2O_3^{2-}$	-518.646	-648.52	66.944	-237.631	Shock[8], NBS[10]
$S_4O_6^{2-}$	-1040.253	-1224.238	257.316	-109.153	Shock[9], NBS[10]
$S_2O_4^{2-}$	-600.567	-753.538	92.048	-207.684	Shock[9], NBS[10]
$S_2O_5^{2-}$	-790.876	-970.688	104.600	-200.199	Shock[9], Kivialo[15]
$S_2O_6^{2-}$	-969.037	-1173.194	125.520	-187.730	Shock[9], Kivialo[15]
$S_2O_7^{2-}$	-795.090	-1011.101	188.334	-75.969	Williamson[11]
$S_2O_8^{2-}$	-1114.868	-1344.763	244.346	-103.318	Shock[8], NBS[10]
$S_3O_3^{2-}$	-827.187	-951.400	118.001	-198.747	Williamson[11]
$S_3O_6^{2-}$	-957.360	-1167.336	138.072	-180.243	Shock[9], Kivialo[15], Rossini[16]
$S_4O_3^{2-}$	-957.384	-1085.099	138.323	-163.272	Williamson[11]
$S_5O_3^{2-}$	-1030.080	-1159.700	164.004	-118.441	Williamson[11]
$S_5O_6^{2-}$	-955.337	-1175.704	167.360	-162.782	Shock[9], Kivialo[15]
$S_6O_3^{2-}$	-1074.377	-1205.201	192.037	-69.505	Williamson[11]
$S_6O_6^{2-}$	-1196.975	-1381.000	321.323	156.185	Williamson[11]
$S_7O_3^{2-}$	-1104.774	-1236.401	221.413	-18.224	Williamson[11]
HS^-	12.082	-16.108	68.199	-93.618	Shock[8], NBS[10], Helgeson[13]
HS_2^-	11.506	-267.902	-742.317	-195.115	Williamson[11]
HS_3^-	20.510	-352.402	-1023.862	-185.042	Williamson[11]
HS_4^-	27.714	-394.401	-1156.822	-180.285	Williamson[11]
HS_5^-	33.017	-419.601	-1227.058	-177.772	Williamson[11]
HS_6^-	36.228	-436.299	-1261.765	-176.530	Williamson[11]
H_2S(a)	-28.6	-39.706	125.5	183.667	Plyasunov[14]
$H_2S_2O_4$(a)	-616.66	-733.455	213.384	155.905	Shock[9]
$HS_2O_4^-$	-614.471	-749.354	152.716	56.282	Shock[9], Williamson[11]

H_2SO_3(a)	-537.86	-608.898	232.212	0.000	NBS[10]
$H_2S_2O_3$(a)	-535.576	-629.274	188.280	114.724	Shock[9]
HSO_3^-	-527.613	-626.219	139.746	-5.304	Shock[8], NBS[10]
H_2SO_4(a)	-744.526	-909.392	20.083	-176.410	NBS[10]
HSO_4^-	-755.67	-889.1	125.52	22.589	Shock[8], NBS[10]
HSO_5^-	-637.440	-775.630	212.129	154.047	Shock[9]
$HS_2O_3^-$	-532.132	-643.918	127.612	15.095	Shock[9]
SO_3^{2-}	-486.546	-635.55	-29.288	-280.022	Shock[9], Phillips[12]
SO_4^{2-}	-744.361	-909.602	18.828	-264.944	Shock[8], NBS[10]
SO_2(a)	-300.555	-323.005	161.921	311.612	NBS[10], Shock[8]
SO_3(a)	-525.637	-635.591	-28.995	0.000	NBS[10]
$HS_2O_5^-$	-998.490	-1218.799	-31.229	-532.911	Williamson[11]
$HS_2O_6^-$	-1073.389	-739.798	1929.134	6013.290	Williamson[11]
$HS_2O_7^-$	-1372.589	-1253.798	1311.266	3950.056	Williamson[11]
$HS_2O_8^-$	-1510.289	-1253.798	1875.687	5834.817	Williamson[11]
$HS_3O_3^-$	-471.386	-718.899	-295.549	-1415.549	Williamson[11]
$HS_4O_3^-$	-477.382	-760.898	-384.233	-1711.690	Williamson[11]
$HS_5O_3^-$	-480.179	-786.098	-427.308	-1855.527	Williamson[11]
$HS_6O_3^-$	-481.378	-802.801	-447.236	-1922.074	Williamson[11]
$HS_7O_3^-$	-481.974	-815.001	-454.085	-1944.945	Williamson[11]

Corrosion Domain Diagrams

Consider the most basic corrosion reaction in the copper/water system:

$$Cu + H^+ = Cu^+ + 1/2H_2 \qquad (1)$$

The change in Gibbs energy for this reaction can be written as

$$\Delta G = \Delta G^0 + 2.303RTlog\left(f_{H_2}^{1/2} a_{Cu^+}/a_{H^+}\right) \qquad (2)$$

which, upon rearrangement yields

$$log\left(f_{H_2}^{1/2} a_{Cu^+}\right) = \frac{\Delta G - \Delta G^0}{2.303RT} - pH \qquad (3)$$

where ΔG^0 is the change in standard Gibbs energy; i.e., the change in Gibbs energy when all components of the reaction are in their standard state with the fugacity of hydrogen, f_{H_2}, and the activity of cuprous ion, a_{Cu^+}, being equal to one. At equilibrium, $\Delta G = 0$, and designating the equilibrium values of f_{H_2} and a_{Cu^+} with superscripts “e” we may write

$$P^e = f_{H_2}^{e,1/2} a_{Cu^+}^e = 10^{-\left(\frac{\Delta G^0}{2.303RT} + pH\right)} \qquad (4)$$

where P^e is termed the "partial equilibrium reaction quotient". We now define the partial reaction quotients, P, for non-equilibrium conditions as follows

$$P = f_{H_2}^{1/2} a_{Cu^+} \tag{5}$$

The condition for spontaneity of Reaction (1) then becomes $P < P^e$ and immunity is indicated by $P > P^e$.

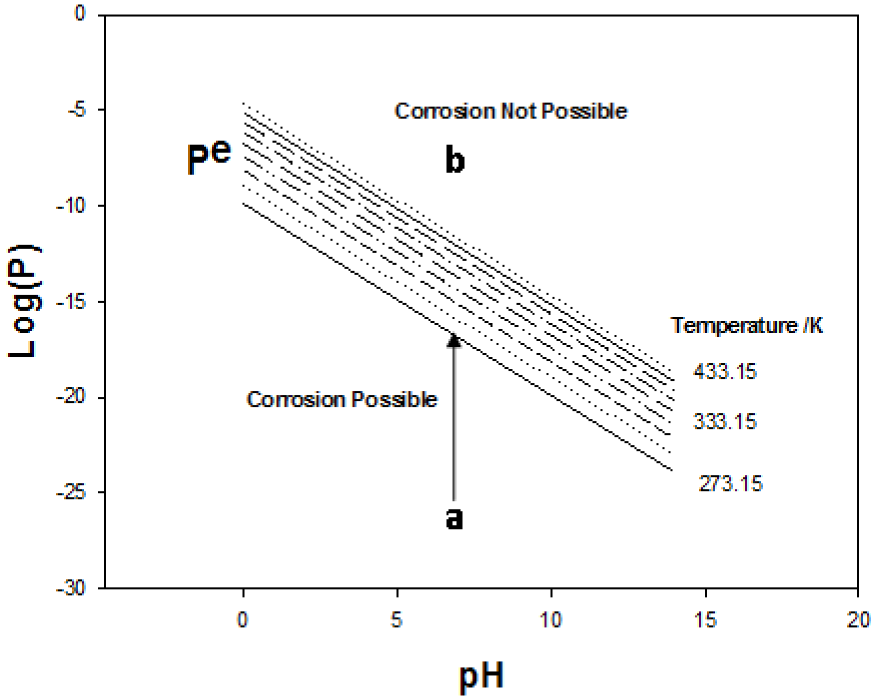

Figure 1: Corrosion domain diagram for copper in water as a function of temperature.

The quantity P^e has been calculated for Reaction (1) using Equation (4) and is plotted as a function of pH in Figure 1. These plots divide the log(P) versus pH domain into regions of immunity (upper region) and corrosion (lower region). These plots clearly demonstrate that whether copper is immune (thermodynamically stable) depends sensitively upon the value of P, which is a property of the environment, and hence upon the initial conditions in the system. Thus, if P is small (e.g., at Point a, Figure 1), $P < P^e$ and the corrosion of copper is spontaneous as written in Equation (1). On the other hand, if the system is located at Point (b), Figure 1), $P > P^e$ and corrosion is not possible, thermodynamically, and hence the metal is "immune". Returning now to the case described by Point a, we note that as the corrosion reaction proceeds, the concentration of Cu^+ and the fugacity of hydrogen at the interface will increase, particularly in a medium of restricted mass transport, such that P will steadily increase with time until it meets the value of P^e at the corresponding temperature. At this point, the metal may be classified as being "quasi-immune"; "quasi" only because transport of Cu^+ and H_2 away from the canister surface, through the bentonite overpack must be matched by corrosion, in order to maintain $P = P^e$ at the metal surface. Accordingly, the corrosion rate ultimately becomes controlled by the diffusion of Cu^+, H^+, and H_2 through the adjacent bentonite overpack. Thus, we conclude that, for any system starting at a point below the P^e versus pH for the relevant temperature, copper metal is not thermodynamically immune and will corrode in the repository at a rate that is governed by the rate of transport of the corrosion products away from the metal surface and of reactants (H^+) to the surface. Of course, this rate is readily predicted by solving the diffusion equation, if the diffusivities of Cu^+ and H_2 in bentonite are known.

As noted above, for any system whose initial conditions (value of P) lie above the relevant P^e versus pH line, copper is unequivocally immune and corrosion cannot occur as it would violate the Second Law of Thermodynamics. It is evident, that the conditions for immunity may be engineered in advance by doping the bentonite with a *Cu(I)* salt and a suitable reducing agent to simulate hydrogen, such that the initial conditions lie above P^e versus pH. It is suggested that cuprous sulfite, Cu_2SO_3, might be a suitable material. Of course, the dopant will slowly diffuse out of the bentonite and into the external environment, but it might be sufficiently slow that the conditions of immunity may be maintained for a considerable period. Thus, in a "back-of-the-envelope" calculation,

$$t = L^2/D \tag{7}$$

we choose L = 10 cm and $D = 10^{-9}$ cm^2/s to yield a diffusion time of 10^{11} seconds or 316,456 years. At a time of this order, the value of P at the canister surface will have been reduced to P^e and corrosion will have initiated at a rate that is determined by the transport of Cu^+ and H_2 through the bentonite overpack. It is important to note that the above calculation is only a rough estimate and that a more accurate value can be obtained by solving the diffusion equation with experimentally determined values for the diffusivities of Cu^+ and H_2. The important point is that immunity may be maintained for a sufficiently long period that the more active components of the HLNW will have decayed away.

The analysis presented above is restricted to the corrosion of copper in contact with pure water. However, ground water is far from pure and a common contaminant is bisulfide ion, HS^-. This species arises from dissolution of sulfide minerals in the host rock of the repository, from dissolution of pyrite in the bentonite, and even from the decomposition of organic (plant) material. It is fair to conclude that bisulfide, and other sulfur-containing species are ubiquitous in groundwater environment at concentration ranging up to a few ppm, at least. It is also well-known that sulfide, including bisulfide, activates copper by giving rise to the formation of Cu_2S at potentials that are significantly more negative that the potential for the formation of Cu_2O. Thus, in the presence of bisulfide, the lowest corrosion reaction of copper may be written as

$$2Cu + HS^- + H^+ = Cu_2S + H_2 \tag{8}$$

for which the change in Gibbs energy is written as

$$\Delta G = \Delta G^0 + 2.303RTlog\left(f_{H_2}^{1/2}/a_{HS^-}.a_{H^+}\right) \tag{9}$$

As before, we define an equilibrium value of P as

$$P^e = f_{H_2}^{e,1/2} / a_{HS^-}^e \tag{10}$$

where

$$f_{H_2}^{e,1/2} / a_{HS^-}^e = 10^{-\left(\frac{\Delta G^0}{2.303RT} + pH\right)} \tag{11}$$

Values of P^e versus pH are plotted in Figure 2 as a function of temperature for temperatures ranging from 0°C to 160°C in steps of 20°C. Again, P^e versus pH divides the diagram into two regions corresponding to spontaneous corrosion (lower region) and immunity (upper region). The reader will note that the P^e values for the lines are more positive than those for the Cu-pure water case by a factor of about 10^{27}, demonstrating that immunity is much more difficult to achieve in the presence of bisulfide.

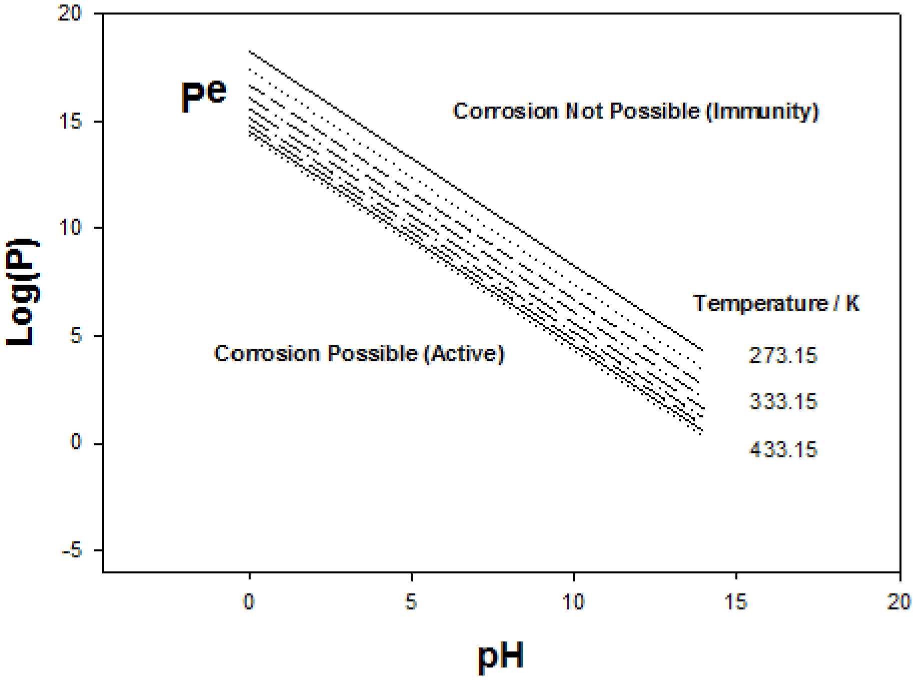

Figure 2: Corrosion domain diagram for copper in water + HS- as a function of temperature.

In order to illustrate the difficulties posed by small amounts of bisulfide in the environment, we note that if [HS-] = 10^{-12}M (3.3 x 10^{-8} ppm) and $p_{H2} = 10^{-6}$ atm (0.02 ppb), the environment is characterized by a log (P) value of -10.854, which lies well below P^e in Figure 2. Accordingly, under these conditions, copper cannot be considered to be immune. Noting again that immunity is achieved only if $P > P^e$, it is evident that the desired immune condition could only be achieved by having extraordinarily low concentrations of HS^- and/or extraordinarily high partial pressures of hydrogen. For example, the following two sets of conditions are predicted to yield immunity, $[HS^-]$ and p_{H_2} combinations of 3.3 x10^{-10} ppm and 10^{-6} atm (about a factor of 10^5 greater than the actual value from Forsmark) and 0.033 ppm and 10^{10} atm, respectively. In the first case, the concentration of HS^- is orders of magnitude lower than the sulfide concentration in ground water (a few ppb to a few ppm), particularly in the presence of bentonite, which commonly contains pyrite, FeS_2. In the second case, the required partial pressure of hydrogen (10^{10} atm) is impossibly high to be achieved and maintained practically in the repository. Accordingly, the prospects for achieving immunity of copper in a repository in which the ground water contains a significant concentration of bisulfide must be judged as being remote or even non-existent. Of course, these thermodynamic predictions can be easily checked by experiment and experiments to do so should be performed at the earliest opportunity.

It is likely that a great variety of partially oxidized/reduced sulfur species will exist in the repository, due to the initial oxidation of pyrite during the initial oxic period (first 100 years or so after resaturation of the buffer by groundwater) or due to the action of Sulfate Reducing Bacteria (SRBs) acting upon sulfate present in the ground water or as Gypsum in the bentonite. These species are expected to include the polysulfides, H_2S_x, HS_x^-, S_x^{2-}), polythiosulfates ($H_2S_xO_3$, $HS_xO_3^-$, $S_xO_3^{2-}$), and the polythionates ($H_2S_xO_6$, $HS_xO_6^-$, $S_xO_6^{2-}$) amongst others. Corrosion Domain Diagrams for copper in the presence of these species with log (P) being typical of repository conditions have been derives and an example is shown in Figure 3.

$$\mathbf{6Cu+S_3(-2a)+2H(+a)=3Cu_2S+H_2(g)}$$

$$\log\left(\frac{p_{H2(g)}}{a_{S3(-2)}}\right)=\frac{-\Delta G^0}{2.303RT}-2pH$$

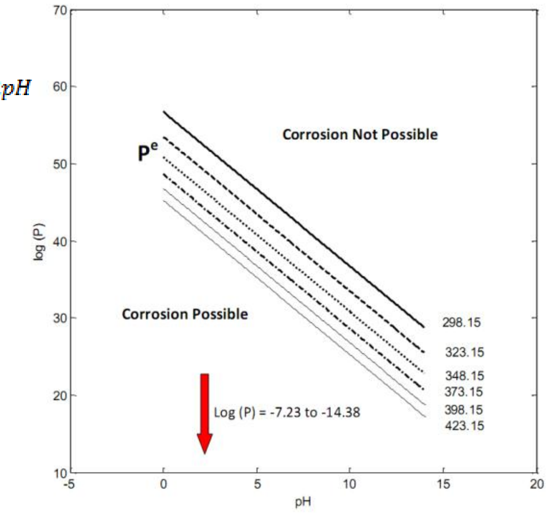

Figure 3: Corrosion Domain Diagram for copper in the presence of the polysulfide, S32-.

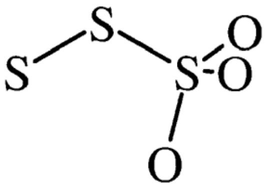

Figure 4: Structure of the trithiosulfate anion.

Note that log(P) for the repository lies well below log(P^e) for any of the temperatures considered, and hence S_3^{2-} is considered to be a powerful activator of metallic copper. In fact, the same conclusion is arrived at for all of the polysulfides (H_2S_x, HS_x^-, S_x^{2-}), polythiosulfates ($H_2S_xO_3$, $HS_xO_3^-$, $S_xO_3^{2-}$), and the polythionates ($H_2S_xO_6$, $HS_xO_6^-$, $S_xO_6^{2-}$), with the exception of $S_xO_3^{2-}$, $x \geq 3$. Thus, the CDD for Cu in contact with $HS_3O_3^-$, Figure 4, shows that this species is a powerful activator of copper. The value of log(P) for the environment is estimated to be -0.47, indicating a very large driving force in terms of ΔG for the corrosion process. On the other hand, higher members of the polythiosulfate homologous series, $S_xO_3^{2-}$, are predicted not to activate copper, as shown by the CDD plotted in Figure 5, for example. In this case, the value of log(P) for the environment lies well above log(P^e) for the activating reaction. The origin of this loss in activating ability by the higher polythionates remains unknown, but it is postulated to lie in the electron density on the terminal sulfur atom versus that on the three oxygen atoms (Figure 4). Thus, if the electron density is concentrated on the oxygen atoms, the trisulfate anion is postulated to adsorb with the three oxygen atoms adjacent to the metal with their orbitals overlapping with those of the metal, thereby forming a chemical bond. In this configuration, the sulfur is remote from the surface and hence does not have the opportunity to react to form Cu_2S. On the other hand, if the electron density is concentrated on the terminal sulfur atom, the sulfur is in intimate contact with the surface and hence can readily form Cu_2S though rupture of the terminal S-S bond and formation of Cu-S bonds at the surface. Resolution of this issue will require Density Functional Theory (DFT) calculations to ascertain the electron densities on the atoms of both those entities that do and do not activate copper; e.g., dithiosulfate ($S_2O_3^{2-}$) and trithiosulfate ($S_3O_3^{2-}$), respectively.

Volt-Equivalent Diagrams

It is well-known that sulfur is a powerful thermodynamic activator of copper, nickel, and iron through the formation of solid sulfide phases at more active electrochemical potentials than those at which the oxides form, in some cases, by as much as several hundred millivolts. Sulfur is also characterized as having the richest chemistry of any element in the periodic table, except for carbon, and as having the greatest range of oxidation states (-2 to +8), including fractional oxidation states. This richness in chemistry is exploited by nature in biological systems for the metabolism of sulfate, for example, by *Sulfate Reducing Bacteria* (SRB), or by *Thiobacillus Thiooxidans* (TT) in the oxidation of elemental sulfur to sulfate (including concentrated sulfuric acid). Sulfur, in the presence of water and oxygen (air), is also oxidized by UV radiation to sulfuric acid in an abiogenic process [17], the mechanism of which is little understood. In any case, these processes all proceed through sulfur compounds differing in oxidation state as they progress in the *S(-II)* to *S(VI)* or *S(VI)* to *S(-II)* directions. As our work on CDDS, summarized above, demonstrates, various, but not all, sulfur species activate copper and hence their presence in the groundwater at Forsmark raises the specter of their representing a corrosion threat to copper canisters in the repository. In some cases the energy gained by reduction of sulfate is used to directly oxidize a metal as in the case of *Thiobacillus Ferrooxidans* (*Acidithiobacillus ferrooxidans*), but the author knows of no instance where this occurs for copper, which is generally toxic toward micro-organisms. This aerobic species is known to live in pyrite deposits, which is a component of bentonite. It is important to note that the processes that they affect must be thermodynamically viable in the environments of interest and that the bacteria themselves simply act as powerful catalysts. Thus, for SRBs to reduce sulfate to sulfide, the change of Gibbs energy for the reaction $SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O$ must be negative and must not require the bacteria to be so. This is because of the path-independence requirement of equilibrium thermodynamics. The transition of sulfate to sulfide, as affected chemically or biochemically (with bacteria as catalysts) is best viewed as occurring through a series of intermediates, as follows:

$$SO_4^{2-} \rightarrow S_xO_y^{2-} \rightarrow S_x^{2-} \rightarrow S^0 \rightarrow S^{2-} \tag{12}$$

with the oxidation of sulfide to sulfate occurring via the reverse sequence. Thus, the reaction sequence from left to right can be viewed as discrete reduction in y and increase in x (actually, increase in x/y) and hence a discrete reduction in the sulfur oxidation state.

$$\mathbf{4Cu+HS_3O_3(-a) =2Cu_2S+SO_3(-2a)+H(+a)}$$

$$\log\left(\frac{a_{SO3(2-)}}{a_{HS3O3(1-)}}\right) = \frac{-\Delta G^0}{2.303RT} + pH$$

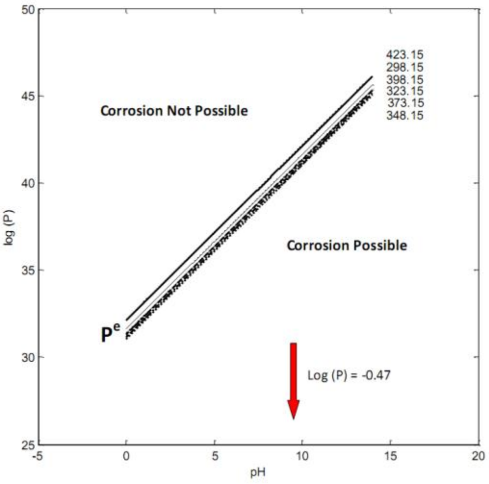

Figure 5: Corrosion Domain Diagram for copper in the presence of $HS_3O_3^-$.
Note that this species is a powerful activator of copper.

Equation (12) shows that there are several homologous series of sulfur compounds that are of interest when discussing the rich chemistry of this element. They are:

- Polythionates: $S_xO_6^{2-}$; sulfur oxidation state (z) = $10/x$ ($z < 6$), ranging from z = 5 ($S_2O_6^{2-}$, which does not appear to have been synthesized) to 1.67 for $S_6O_6^{2-}$
- Polythiosulfates: $S_xO_3^{2-}$; sulfur oxidation state (z) = $4/x$ ($z < 4$), ranging from z = 2 ($S_2O_3^{2-}$, “thiosulfate”) to 0.57 for $S_7O_3^{2-}$.
- Elemental sulfur, S^0, z = 0.
- Polysulfides: S_x^{2-}; sulfur oxidation state (z) = $-2/x$ ($z < 0$), ranging from -2 (x = 1, S^{2-}) to -0.167 (x = 6).

The objectives of the present work are to:

- Develop a rational basis for classifying the chemistry of the various sulfur species with regard to differences in thermodynamic affinities, as determined by their electrochemical reduction potentials and their oxidation states; and
- To ascertain whether an explanation of the abilities of the various sulfur species lies within the thermodynamics of the S-H_2O system.

$$\mathbf{6Cu+S_4O_3(-2a)=3Cu_2S+SO_3(-2a)}$$

$$\log\left(\frac{a_{SO3(-2)}}{a_{S4O3(-2)}}\right)=\frac{-\Delta G^0}{2.303RT}$$

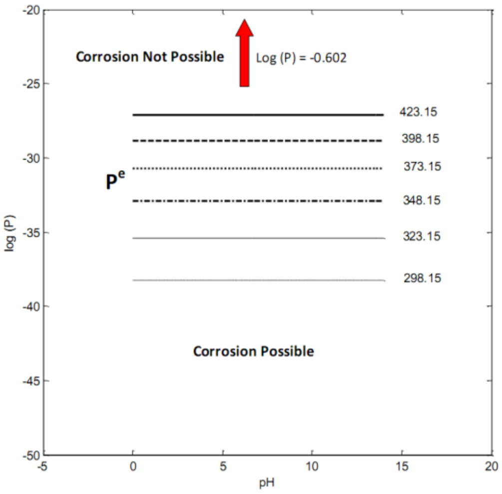

Figure 6: Corrosion Domain Diagram for copper in the presence of $S_4O_3^{2-}$.
Note that this species is predicted not to activate copper.

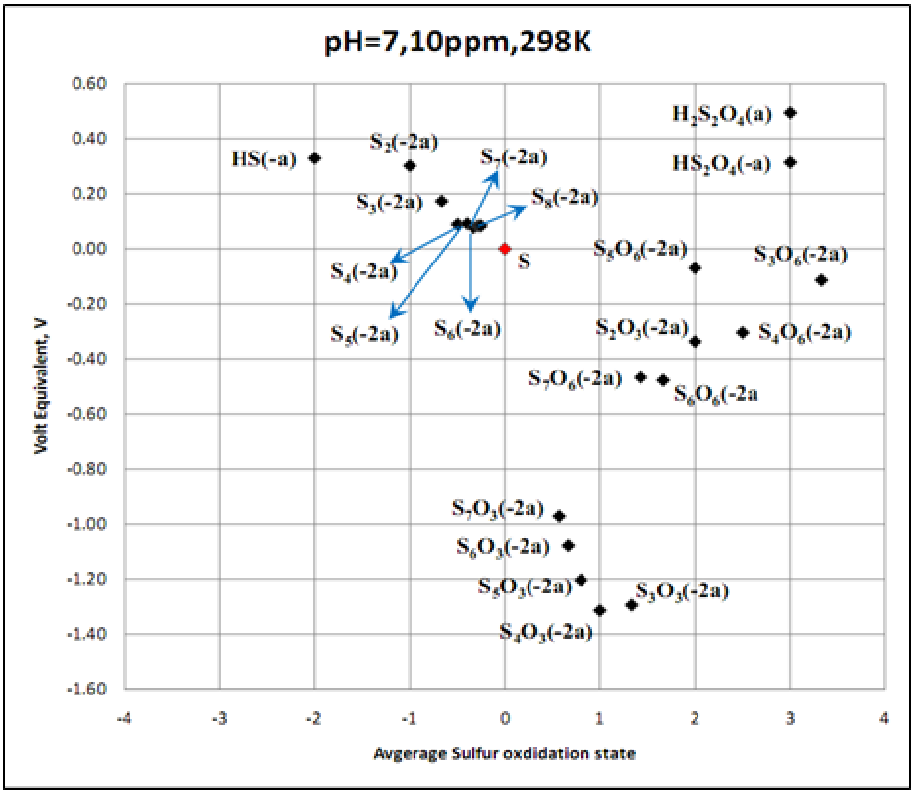

Figure 7: Volt-Equivalent Diagram for sulfur in Forsmark ground water, pH = 7, [S] = 10 ppm, 25°C. The red point represents elemental sulfur.

The vehicle chosen in this work to explore these issues is the Volt-Equivalent Diagram (VED). Volt equivalent for a species is the equilibrium potential for the reduction reaction of the species (e.g., $S_xO_y^{2-}$) with respect to elemental sulfur

$$S_xO_y^{2-} + 2yH^+ + 2(y-1)e^- == (x/8)S_8+yH_2O \tag{13}$$

multiplied by the average oxidation state of sulfur [$z = 2(y-1)/x$]. The volt equivalent diagram is then formed by plotting the volt-equivalents for the various species versus the average oxidation state. In doing so, we first calculate the standard potential vs the standard hydrogen electrode by using

$$E^o = -\Delta_f G^0/2(y-1)F \tag{14}$$

where ΔfG0 is the change in standard Gibbs energy for the cell reaction

$$S_xO_y^{2-} + 2H^+ + (y-1)H_2 == (x/8)S_8+yH_2O \tag{15}$$

The equilibrium potential is then given as

$$E^e = E^o - 2.303RT/(2(y-1)]log[1/a_s.(a_{H+})^{2y}] \tag{16}$$

where a_s is the activity of the sulfur species and aH+ is the corresponding quantity for H^+. The volt-equivalent (VE) for $S_xO_y^{2-}$ is then simply zE^e.

A typical VED for the sulfur-water system under simulated repository groundwater conditions at 25 °C is presented in Figure 7. The concentrations of dissolved species were set arbitrarily at 10 ppm, but later work will employ actual concentrations as determined by Gibbs energy minimization speciation calculations. The interpretation of the diagrams follows from the following rules:

- Any two species connected by a straight line will tend to react to produce all of the species that lie below that line. Thus, for the reaction of HS^- and H_2SO_4 is predicted to generate essentially all other species plotted on the diagram.
- If a species lies above the straight line joining two other species, it will tend to disproportionate to produce the latter. Thus S_2^{2-} lies above the line joining S^{2-} and S_3^{2-}, so that the disproportionation reaction, $2S_2^{2-} \rightarrow S^{2-} + S_3^{2-}$, is predicted to occur.
- If several species lie on or close to a straight line joining two terminal species, the solution will contain all species in equilibrium at finite concentrations.
- The reactivity of any given species toward a metal in which a metal sulfide is formed is measured by the value of the VE. The more reactive species are characterized by high (more positive) VE values. Indeed the most reactive species tend to be located in the upper left quadrant, implying high reactivity and high electron density being simultaneously present, followed by species in the upper right quadrant. Species in the lower quadrants tend to be the least reactive toward a metal.

With respect to the activation of copper, which is of specific interest in this work, the activating species all have VE values more positive than -0.60 V_{she}, while the non-activating polythiosulfate species, $S_xO_3^{2-}$, $x \geq 3$, all have VE values more negative than -0.80 V_{she}. The one species in this homologous series that is activating, thiosulfate, $S_2O_3^{2-}$, has a VE value of -0.35 V_{she}, in keeping with this classification. Thus, we conclude that the thermodynamics plays at least a part in determining whether a species is activating and hence is capable of destroying thermodynamic immunity of copper in repository environments. However, we have been unable to identify a thermodynamic “on/off” switch that would account for the activating effects of the various sulfur species, so that some other factor must be involved. On the basis of our present state of knowledge of the chemistry of these systems, we propose that the orientation of the adsorbed species on the Cu surface, as discussed above, is the deciding factor.

A VED for the sulfur-H_2O system at a higher temperature but much lower species concentration (activity) is displayed in Figure 8. The reader will note that Figure 8 is qualitatively similar to Figure 7 with the following notables:

- The data for the polysulfides have moved little in terms of VE values, despite the changes in temperature, concentration, and pH.
- The data for the polythiosulfates, and especially, for the polythionates have shifted sharply in the negative direction, largely eliminating the previously-noted differences between the two homologous series of thiooxyanions. Thus, the VE values for the two series overlap, but still the CDDs predict that the polythionates activate copper, while the polythiosulfates do not. This is a further argument for factors other than thermodynamics being important is the activation of copper.

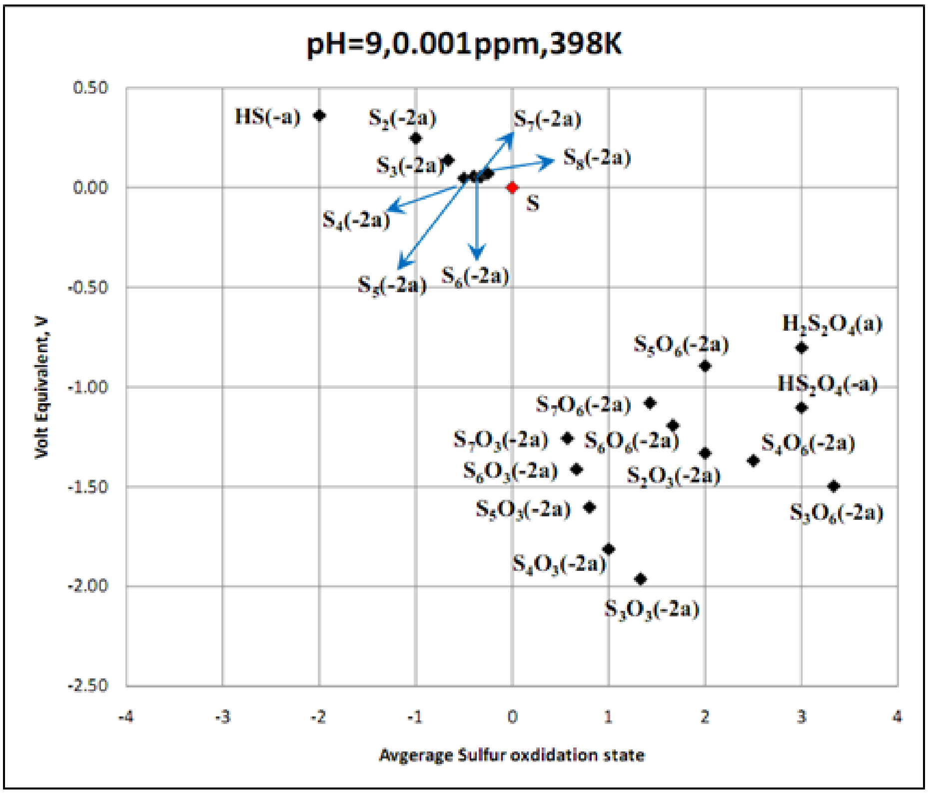

Figure 8: VED for the sulfur-water system at 125°C, pH = 9, [S] = 0.001 ppm.

More than 100 VEDs have been derived to date and probably an additional 100 or so will need to be derived in this first phase. When completed, the diagrams will permit a systematic analysis of the impact of each of the independent variables on the activation of copper under repository conditions.

Future Work in Phase I

The work that is scheduled for completion in this initial phase is summarized below. Work proposed for the following phase will be submitted to SSM in the form of a new Statement of Work upon completion of Phase I:

- Big holes still exist in the data bases for certain species; e.g., $CuOH$, H_2S_x, HS_x^-, $H_2S_xO_y$, and $HS_xO_y^-$. Data for Δ_fG^o, S^o, and C_p^o, in particular, need to found or estimated theoretically.
- Continue deriving CDDs, particularly for complexing reactions, e.g. $Cu + 2Cl^- + H^+ = CuCl_2^- + ½ H_2$.
- Speciation must be performed to ascertain what species are likely to be present. This task is underway using Gibbs Energy Minimization.
- Derivation of CDDs and VEDs along the corrosion evolutionary path of the repository. This task will provide a picture of how the repository is expected to evolve thermodynamically as the waste decays and the temperature decreases.
- Submission of report no later than December 1, 2010.

Summary and Conclusions

The work reported here has resulted in a number of important conclusions that have a bearing on the behavior of copper in a Forsmark type repository. These conclusions are as follows:

Corrosion Domain Diagrams

- The thermodynamic conditions for the corrosion of copper in water have been defined. For all practical purposes copper is not a noble metal, except possibly in very pure water, which will not exist in a repository.
- The current controversy with respect to the nobility of copper can probably be attributed to variability in the initial conditions of the experiments.
- The results are expressed in corrosion domain diagrams as P^e versus pH, where P^e is the partial quotient of the reaction at equilibrium. For any other value of the reaction quotient, P, where $P \neq P^e$, the system is not at equilibrium and the composition (as described by P) will change such that $P \rightarrow P^e$.
- Corrosion is spontaneous for $P < P^e$. Cu is immune for $P > P^e$.
- Certain species commonly found in ground water, e.g. HS^-, polysulfides, and certain polythionates are deleterious by (thermodynamically) activating copper and hence denying the metal thermodynamic immunity.
- Some polythionates, notably, $S_xO_3^{2-}$, x = 3 – 7, are found not to activate copper, for reasons that are not yet completely understood. These species tend to possess very negative volt equivalencies and to have low, positive average sulfur oxidation states.
- All polysulfides are predicted to activate copper.
- The halides, F^-, Cl^-, Br^-, and I^-, except bromide and iodide, are weakly activating and hence do not pose a threat to immunity. Bromide and iodide appear to activate copper only at low pH.
- Complex formation, e.g. $CuCl_2^-$, induces activation in chloride-containing media.
- The possibility of doping the bentonite with a *Cu(I)* salt, such as Cu_2SO_3, should be explored to determine whether immunity might be maintained over expended periods. Thus, the “back-of-the-envelope” calculations reported above suggest that immunity might be maintained over periods of several hundreds of thousands of years. Given that the performance horizon of the repository is 10,000 years, it may well be possible to impose immunity on the system over the entire, planned storage period. Practically, this issue could be explored by inserting source terms in the model outlined in 2 above for Cu^+ and SO_3^{2-} from the bentonite overpack.
- *Volt-Equivalent Diagrams*
- Volt Equivalent Diagrams (VEDs) are enormously useful in interpreting and predicting the chemistry of complex systems, such as S-H_2O.
- VEDs derived for the expected repository conditions predict that for any given homologous series; e.g., S_x^{2-}, $S_xO_y^{2-}$, and their acid forms, equilibrium mixtures of all members of the series will form.
- The activating effect appears to be attributable to the ability of the species to donate atomic sulfur or sulfide to the metal surface. However, resolution of the activating effect will probably require density functional theoretical estimates of the charge densities on the sulfur atoms in the molecule.
- Only the thermodynamic conditions have been examined. The kinetics must also be examined, because, even though copper is active, the rate of corrosion may be sufficiently low to meet the engineering requirements.

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11. Sulphide induced SCC of copper

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Copper canister is a central technical barrier for radioactive release from high level nuclear waste in the so-called KBS-3 concept planned to be used in Finland and Sweden for disposal of spent nuclear fuel. Canisters will be placed in the granitic bedrock at about 400-500 m depth and surrounded by a layer of bentonite clay acting planned to protect the canister from any chemical and mechanical damage, and especially acting as a diffusion barrier.

In 2007 a Japanese research group claimed [1] that sulphide (HS^-/S_2^-) can cause stress corrosion cracking (SCC) in pure copper under anoxic high chloride water conditions. These experiments were performed with the Slow Strain Rate Technique (SSRT), and crack indications were found on the specimen surface in ex situ examination at sulphide concentrations of 320 mg/l and 160 mg/l, but not at 32 mg/l. The present investigation, results of which have been communicated in a symposium [2], was aimed at revealing the susceptibility to SCC of phosphorus micro-alloyed copper, Cu OFP, when exposed to groundwater with sulphides at room temperature.

Cu OFP samples of 25 mm CT (Compact Tension) design were extracted from a block of copper canister sheet (Posiva Co). The CT geometry simulates the stress/strain state of canister wall (plane strain). Test pieces were pre-cracked in air to simulate defects. Constant load test mode was used with a load level of about 4 kN producing a stress intensity of roughly $K_I = 9$ $MPam^{1/2}$. The potential drop (PD) technique was used for on-line crack length monitoring. The base electrolyte used was the Finnish Saline Reference groundwater [3] corresponding to Olkiluoto groundwater. The sulphide (100 and 200 mg/l) was added as Na_2S.

The digital image of the fracture surface of the test specimen after exposure to groundwater with 200 mg/l sulphide for about six weeks is shown in Fig. 1. In the figure it can be noticed that there are some dark spots ahead of the crack tip, having become visible through the air fatigue crack growth used to open up the specimen after the test in the groundwater environment had been stopped. Dark spots can be observed up to and beyond the available distance of about 10 mm. A compositional analysis of a representative part of the area with SEM/EDX showed 58.7 a% Cu and 22.5 a% S. This indicates that a considerable part of the exposed grain boundaries are covered with a sulphide film. Comparison of normal and backscattered SEM images of a representative area ahead of the crack tip revealed that there are some particles which seem like precipitates, and that also most grain boundaries that are perpendicular to the fracture surface contain of a lighter phase, presumably a Cu-S-precipitate. Spot analysis of a single grain boundary in this area showed basically only Cu and S.

In the case of the test piece shown in Fig. 1, the potential drop (PD) signal increased throughout the exposure time, indicating a decrease of the electrical conductance of the material ahead of the crack tip. As no crack extension was noticed, presumably this was caused by formation of Cu-S-precipitates ahead of the crack tip (copper sulphides are far less electrically conducting than copper metal itself).

Based on the results it is clear that sulphur can diffuse into the Cu OFP material when it is exposed at room temperature to saline groundwater with 100 to 200 mg/l sulphide. Indications were found that the in-diffusion preferentially occurs through grain boundaries. Individual grain boundaries were found to contain above 20 a% sulphur. Based on SEM/EDS studies of the surfaces the extent of diffusion depth of sulphide into Cu OFP was more than one millimetre per week.

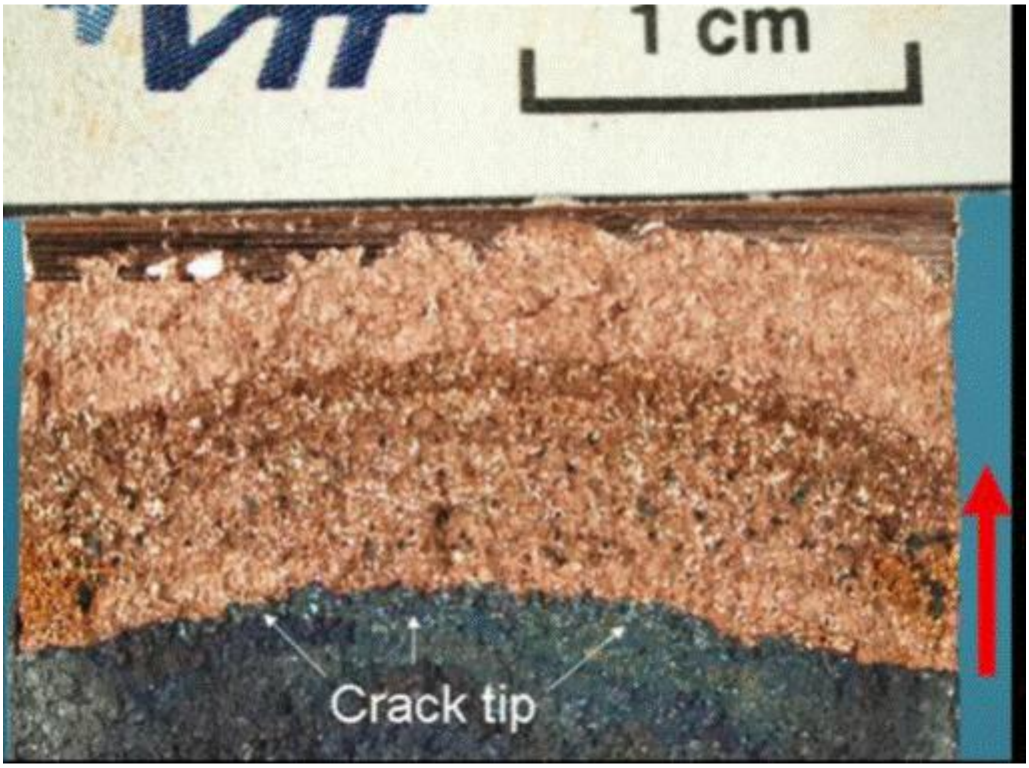

Fig. 1. Surface of Cu OFP specimen after a six week exposure to groundwater with 200 mg/l sulphide. Small dark coloured areas can be seen ahead of the crack tip.

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2. E. Arilahti, T. Lehtikuusi, M. Olin, T. Saario and P. Varis, Sulphide induced stress corrosion cracking of CuOFP in groundwater, 4th International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems, Brugge, Belgium, June 29 – July 2, 2010.
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12. Some general considerations regarding copper corrosion

Peter Szakálos
Royal Institute of Technology (KTH), Surface and Corrosion Science

According to the 2nd law of thermodynamics copper is expected to react with water molecules and continuously corrode in open systems. All systems where hydrogen can escape or be consumed, that comprise most of our engineered systems including a repository, are considered to be open systems, see Appendix 1.

In water with dissolved oxygen following schematic reaction (1) takes place:

1) $Cu + O_2$ (dissolved in water) $\Rightarrow$ Cu-oxides and Cu-hydroxides

When the dissolved oxygen is consumed reaction (2) and (3) is thermodynamically expected:

2) $Cu + H_2O \Leftrightarrow Cu_2O + H_2 \quad \Delta G^o = -147$ kJ/mole ($pH_2 = 10^{-9}$ mbar @ 80°C)

3) $Cu + H_2O \Leftrightarrow CuOH_{surf.} + H_2 \quad \Delta G^o = -228$ [1] to -549 [2] kJ/mole ($pH_2 \geq 1$ mbar)

In fact, bivalent corrosion products such as CuO and $Cu(OH)_2$ can also be stable in “anoxic” water since the borderline between “anoxic” and “oxic” water is found between the water stability lines in a Pourbaix diagram at a height of 2/3, see Appendix 2, page 5. This can be understood by the fact that water contains 2/3 of hydrogen and 1/3 of oxygen. “Anoxic water” means a water solution with more dissolved hydrogen gas than dissolved oxygen gas and vice versa for “oxic water”.

It is possible to compare the Gibbs energy of formation of the products in reaction 2 and 3 directly since they consists of equal amount of oxygen atoms. Thus it is seen that $CuOH_{surf}$ is a very stable product and the highest value of -228 kJ/mole corresponds to an equilibrium hydrogen partial pressure of 1 mbar. If CuOH exists solely as a surface phase the measured hydrogen pressure in a laboratory experiment is dependent on the surface finish and ultimately on the ratio “effective copper surface” on an atomic level divided by the “available gas volume” in the experiment. The situation might be even more complicated since the “effective copper surface” normally gets larger with exposure time due to copper dissolution and precipitation processes.

An important empirical fact is that copper corrosion rates are *always* reported to be in the µm/year range in copper cooling systems with pure anoxic water at elevated temperature, see Appendix 2, page 1-2.

Irrespective of quite low measured equilibrium hydrogen pressure in pure water corrosion, it is important to realize that water is an oxidant for copper which might be an explanation why copper corrodes faster than expected in anoxic saline water and anoxic ground water. In a UK Environment Agency report on technical issues associated with deep repositories for radioactive waste in different geological environments [3] it is stated on page 96:

"Under anoxic conditions, copper corrosion will be accompanied ***by reduction of water to produce hydrogen gas****, the solids produced being Cu-bearing hydroxide phases that will typically contain some chloride within their structures; the concentration of Cl in a solid corrosion product depends upon the concentration of* Cl^- *in the aqueous phase."*

Some additional copper corrosion processes that should be considered in a simulated repository corrosion model

Each one of the following corrosion mechanisms seems to be several orders of magnitude faster than the mass-balance sulfide transport corrosion model predicts.

i) Copper corrosion by dissolution-precipitation in the bentonite. The "barriers" copper and bentonite destroy each other with quite fast kinetics which could be understood by short diffusion distances between sources and sinks. Saline water has a high solubility of copper and the canister surface act as a "source". The "sink" is the negatively charged bentonite particles. It seems that bentonite acts as a sink for copper ions in several ways where one way is by precipitation of new minerals, i.e. copper corrosion products, see Appendix 2, page 2

ii) Evaporation induced salt /sulphide corrosion. It is known that the most aggressive corrosion tests in the laboratory are performed by salt/sulphide water evaporation on heated test samples. Almost all engineering alloys, including copper, corrode fast in such tests. The situation in Forsmark site with a salty and semi-wet/moist environment in combination with radiation heated copper canisters for perhaps thousand years represents a potentially dangerous situation, see Appendix 2, page 3.

iii) Stress Corrosion Cracking (SCC). Resent results from Japanese researchers shows that copper do suffer from sulphide induced SCC, see Appendix 2, page 3.

iv) Copper is one of the most sensitive metals for radiolysis accelerated corrosion, this is shown by researchers at the Los Alamos National Laboratory, see more details in Appendix 2, page 3.

1) Cu (111) surface: E. Protopopoff and P. Marcus, Electrochim. Acta, 51 (2005) 408
2) Cu (100) surface: G. Hultquist et al., Cat. Lett. 132:311-316 (2009)
3) Environment Agency report on technical issues associated with deep repositories for radioactive waste in different geological environments, Science report: SC060054/SR1 (2009) http://publications.environment-agency.gov.uk/pdf/SCHO0809BQVU-e-e.pdf

APPENDIX 1

Copper corrosion in water without dissolved oxygen

Some thoughts by C. Leygraf and S. Seetharaman , Kungl Tekniska Högskolan, Stockholm

The following argumentation does not claim to be complete. It is an effort to answer a question raised by Ms. Eva Simic from the Swedish National Council for Nuclear Waste, and is based on the assumption that copper during the deep repository exposure is situated in an open system. By an open system we mean an exposure condition allowing exchange of matter and heat with the surrounding environment, the most common condition in engineering applications.

Assume the following overall reaction:

$$2Cu(s) + H_2O = Cu_2O + H_2 \qquad (1)$$

At equilibrium, the total Gibbs energy of the products of the reaction will be equal to the total Gibbs energy of the reactants. The equation from 2nd law of thermodynamics will be

$$\Delta G = \Delta^o G + RT \ln K \qquad (2)$$

where K is the equilibrium constant for reaction (1) at temperature T and gas constant R, and

$$\Delta^o G = \sum {}^o G \text{ (products)} - \sum {}^o G \text{ (reactants)} \qquad (3)$$

In the open system that we assume here, at least one of the products (H_2) is continuously removed from the reaction zone. According to Le Cateliers Principle [1], or the law of mass action, the corrosion reaction should then be shifted to the right, meaning that corrosion will be favored. Hence, copper reacts continuously with water molecules in an open system, even without any access to dissolved oxygen, since hydrogen is allowed to escape.

It should be emphasized that reaction (1) is only an overall reaction, which does not consider short-lived or long-lived intermediate reaction steps when going from Cu(s) to Cu_2O. Evidence for such intermediates can be found, for instance, during the atmospheric corrosion of copper [2], a process that results in different reaction products ranging from the most early stages (formed within much less than a second of exposure) to advanced stages (after decades of exposure). During atmospheric corrosion, analyzed by *in situ* analytical techniques, there is direct experimental evidence of oxide-like or hydroxide-like reaction intermediates ranging from monolayer thickness and upwards [2]. In fact, equilibrium potential-pH diagrams for two-dimensional surface species formed on copper have been reported [3]. They show that adsorbed OH-monolayers on Cu(111) are far more stable than Cu_2O in bulk form.

Hence, we can modify the bulk reaction (1) by introducing a corresponding surface reaction (4) according to

$$2Cu(s) + H_2O = CuOH_{surface} + 1/2H_2 \qquad (4)$$

The experimental findings of stable surface species, according to (4), together with the assumption that the corrosion reaction occurs in an open system with continuous removal of H_2, favors the corrosion of copper in water, even without any dissolved oxygen gas. Similar to what is observed in atmospheric corrosion, one may expect that the surface species with time gradually transforms into a more three-dimensional reaction product of type Cu_2O.

It should be noted that this thermodynamic analysis does not give any information on the rate at which the reaction proceeds, e.g. of copper corrosion in water without dissolved oxygen.

Reported values of copper corrosion rates were in the range 1-10 µm per year in copper cooling systems in generators for electric production and in particle accelerators, despite the fact that active measures were taken with respect to water treatments in order to minimize the corrosion [4]. Furthermore, literature reviews show that all published corrosion rates of copper in municipal or distilled water are roughly in the range of 1-25 µm per year and 15-250 µm per year in salt containing neutral waters [5, 6]. Even if these exposure conditions of copper are far from the conditions during the deep repository exposure, they nevertheless show that evidences for reported copper corrosion rates below 1 µm per year seem very difficult to find.

In all, we conclude that the statement that copper corrodes in water without dissolved oxygen does not violate any thermodynamic principles, and we also notice that copper corrosion rates slower than 1 µm per year are hard to find under any exposure condition .

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[3] E. Protopopoff and P. Marcus, Electrochim. Acta, 51 (2005) 408
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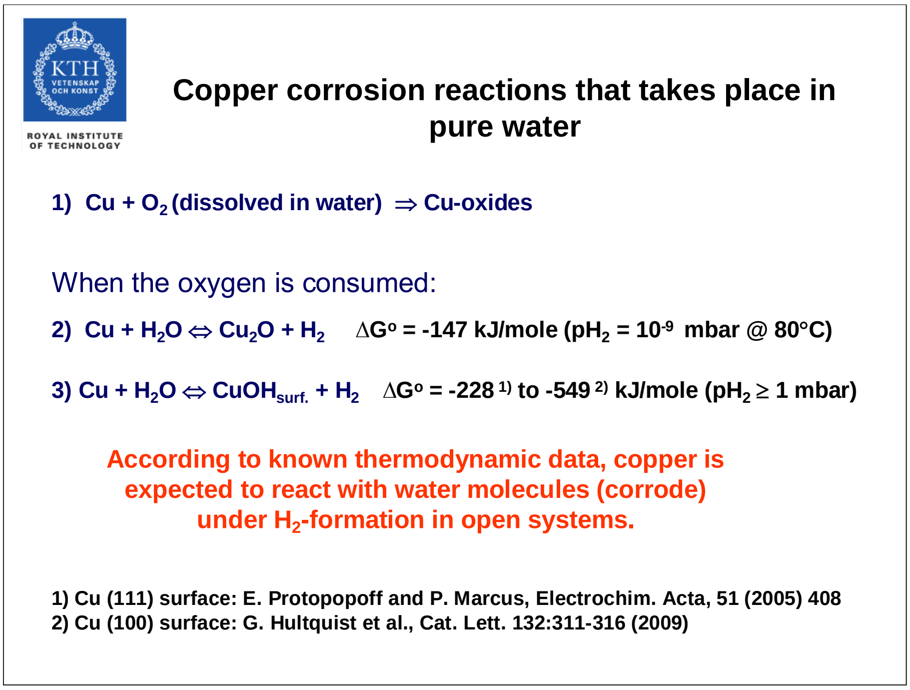
[6] http://www.corrosionist.com/copper_pipe_corrosion.htm

APPENDIX 2



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Copper corrosion reactions that takes place in pure water

1) $Cu + O_2$ (dissolved in water) ⇒ Cu-oxides

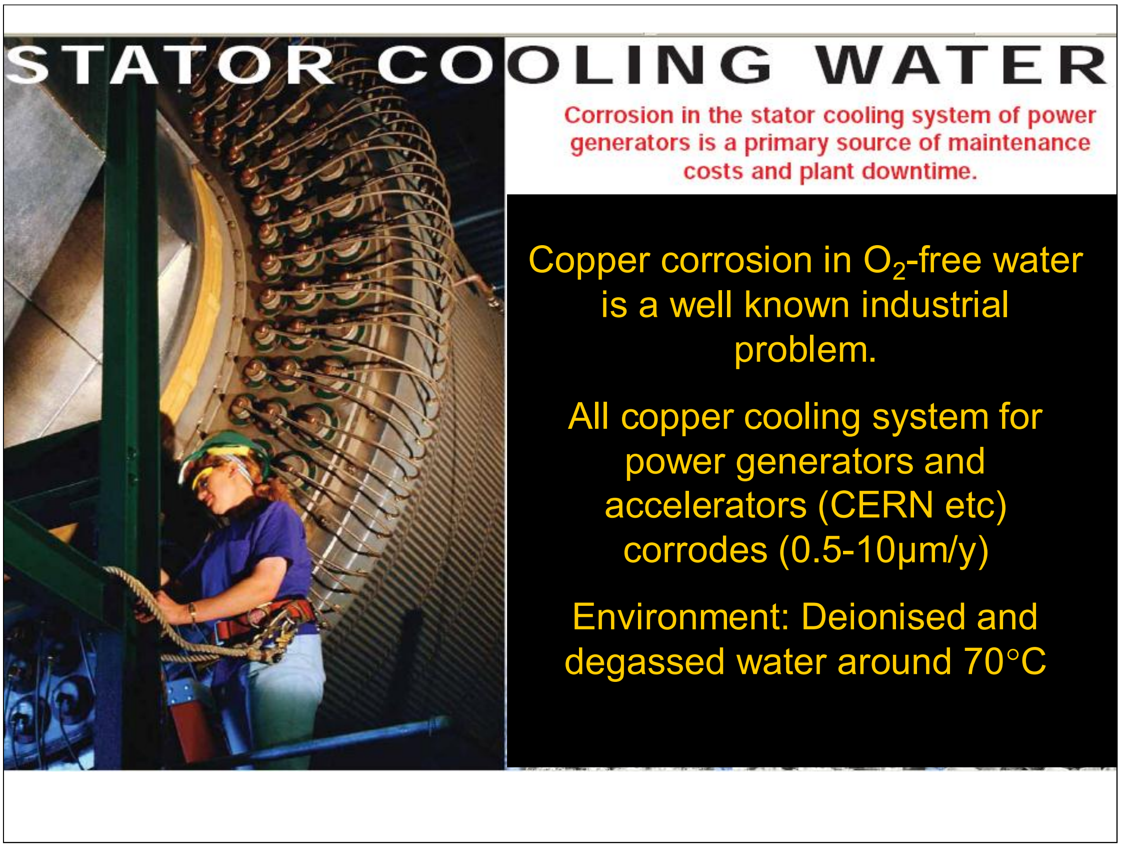
When the oxygen is consumed:

2) $Cu + H_2O \Leftrightarrow Cu_2O + H_2$ $\Delta G^o = -147$ kJ/mole ($pH_2 = 10^{-9}$ mbar @ 80°C)

3) $Cu + H_2O \Leftrightarrow CuOH_{surf.} + H_2$ $\Delta G^o = -228$ [1] to -549 [2] kJ/mole ($pH_2 \geq 1$ mbar)

According to known thermodynamic data, copper is expected to react with water molecules (corrode) under H_2-formation in open systems.

1) Cu (111) surface: E. Protopopoff and P. Marcus, Electrochim. Acta, 51 (2005) 408
2) Cu (100) surface: G. Hultquist et al., Cat. Lett. 132:311-316 (2009)



STATOR COOLING WATER

Corrosion in the stator cooling system of power generators is a primary source of maintenance costs and plant downtime.

Copper corrosion in O_2-free water is a well known industrial problem.

All copper cooling system for power generators and accelerators (CERN etc) corrodes (0.5-10µm/y)

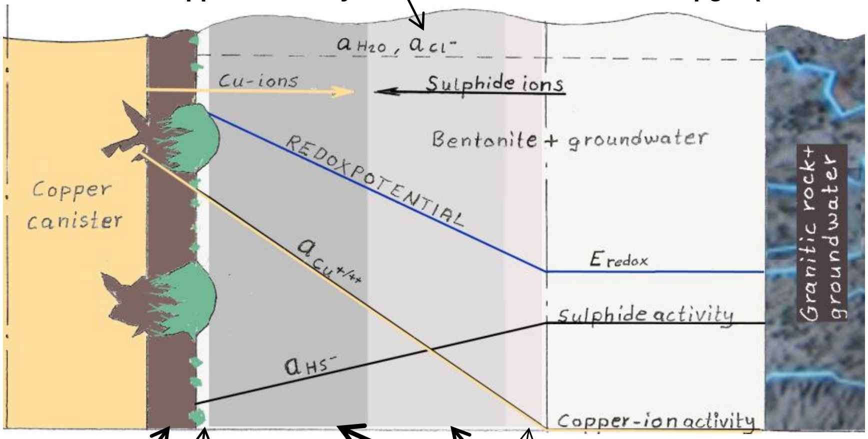
Environment: Deionised and degassed water around 70°C

Study identifies copper corrosion problems with water-cooled generators, EPRI

Figure 1. Partial plugging by copper corrosion products (oxides and hydroxides) prior to cleaning of water-cooled generator at SONGS 2. Photo courtesy of EPRI

Figure 2. Videoscopic inspection after Cuproplex cleaning of SONGS 3 water-cooled generator. Photo courtesy of EPRI

A corrosion model explaining the observations from the LOT-project; copper corrosion by dissolution-precipitation



Copper solubility in saline water at 80°C: 2300µg/L (POSIVA 2003:45)

Cu-oxides, mostly Cu_2O (LOT, Rosborg)

Cu-hydroxides, mostly Cu-hydroxide-chlorides (LOT, Rosborg)

CuS and (Cu,Fe)-sulphides precipitated irreversibly on the bentonite particles (LOT, BGR in Berlin)

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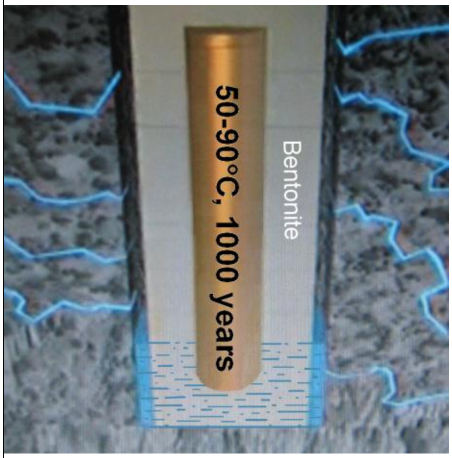
KBS-3 concept and the "Forsmark situation" :

It could take up to 1000 years to fully water saturate the bentonite in Forsmark (According to SKB 2009)



-Atmospheric corrosion: up to 0.3 mm/year at 90°C

-Moist gas phase corrosion with salt: µm/year?

-Evaporation induced salt/sulphide corrosion, Several µm/year - mm/year (IGC, SCC)

-Groundwater and bentonite induced general corrosion, up to 20 µm/year.

-Hydrogen embrittlement.

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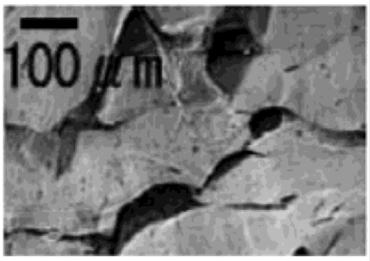
Stress Corrosion Cracking, SCC

European Commission: 5´th EURATOM FRAMEWORK PROGRAMME 1998-2002, COBECOMA, final report (2003). B. Kursten, L. Werme et al. Page 166:

"The candidate container material copper, and especially those containing phosphorus, has been found, in the past, to be highly susceptible to SCC"

N. Taniguchi and M. Kawasaki, Journal of Nuclear Materials 379, p. 154 (2008):

Sulphide, does indeed induce SCC in copper. "The threshold of sulphide concentration for the SCC initiation is likely to be in the range 0.005-0.01 M".



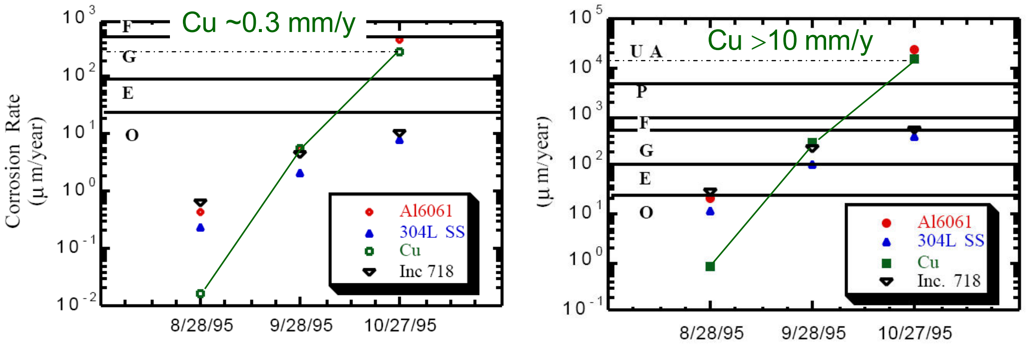
SCC at 80°C on OFHC-Copper with 45ppm P

The "Forsmark situation" with hot copper and groundwater evaporation ⇒ salt/sulphide enrichment:

SCC is likely to occur within the first 1000 years

Corrosion accelerated by radiolysis of water

Los Alamos National Laboratory, Los Alamos, USA



General corrosion

Pitting corrosion

Three months exposure of different metals during radiolysis of water. Copper is found to be very sensitive to radiolysis and display extreme corrosion rates.

R. S. Lillard and D. P. Butt, *Preliminary Spallation Neutron Source Corrosion Experiments*. Los Alamos National Laboratory Report, LAUR 96-1011, 1996.

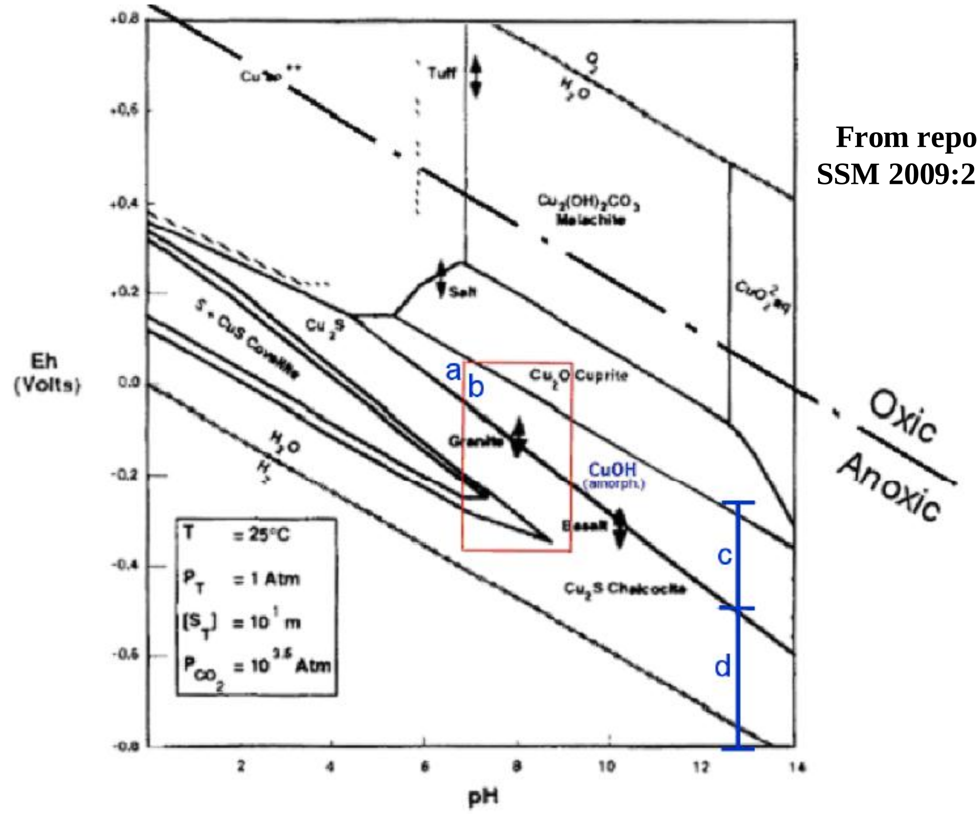
Corrosion accelerated by radiolysis of water

Los Alamos National Laboratory, Los Alamos, USA

In conclusion, the present investigation has demonstrated that the corrosion rates of materials in a spallation neutron cooling can be mitigated by carefully controlling water purity, hydrogen water chemistry, and eliminating copper and copper alloyed components.

R.S. Lillard *, D.L. Pile [1], D.P. Butt [2]

Journal of Nuclear Materials 278 (2000) 277–289



From report SSM 2009:2639

13. Corrosion of copper in oxygen free condition

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Copper canister is a central technical barrier for radioactive release from high level nuclear waste in the so-called KBS-3 concept planned to be used in Finland and Sweden for disposal of spent nuclear fuel. Canisters will be placed in the granitic bedrock at about 400-500 m depth and surrounded by a layer of bentonite clay acting planned to protect the canister from any chemical and mechanical damage, and especially acting as a diffusion barrier.

Recently, a new general corrosion mechanism of copper has been proposed, involving oxidation of copper by water under anoxic conditions. Hultquist et al. and Szakálos et al. [1-3] have proposed that copper reacts with water under anoxic conditions producing a copper hydroxide film, and that a major part of the hydrogen liberated in the process enters copper, possibly making it mechanically brittle. An expert group (BRITE) financed by SSM analyzed one of the publications by Szakálos and Hultquist (the one published in ESS Letters [1]) and came to the conclusion that the publication does not substantiate the occurrence of copper corrosion in pure water [4]. More so, even if the corrosion mechanism would be operable, it would not likely be significant under the expected disposal conditions.

There is an ongoing debate on this issue at the moment and therefore further evidence is needed before any decisive conclusions can be made.

At present, at least three independent research projects are being conducted to investigate the plausibility of the hypothesis and possible consequences thereof. In an already finalized project funded by SKB, no proof of surface film forming was gained under anoxic conditions [5].

In the project funded by Posiva Co. [6] copper coupons are being exposed to ion pure water. Part of the test flasks have been sealed with a Pt-foil, and part with a Pd-foil. Part of the flasks were loaded and sealed within a glovebox under strictly oxygen free conditions, while in the other part of flasks the dissolved oxygen and small volume of remaining air were left in. Up to now (about six months of exposure time) the copper foils in those flasks which were loaded and sealed in the glovebox show no colouring, irrespective of the sealing material. However, copper foils in the flasks sealed without removing the initial dissolved oxygen and remaining air volume do show some colouring.

In a project executed and funded as part of the Finnish Research Program on Nuclear Waste Management (KYT 2010), copper coupons will be exposed in both ion pure water and groundwater, with an arrangement for measurement of possible hydrogen development. Possible hydrogen will be transported through a Pd-foil into a separate chamber which has been evacuated down to about 10^{-9} bar vacuum. The separate chamber is equipped with a pressure gauge having a range of 1.1 mbar and resolution of about 10^{-8} bar. First results from these tests are expected by the end of January 2011.

SSM is currently financing further research work conducted by Szakálos and Hultquist.

1. P. Szakálos, G. Hultquist and G. Wikmark, (2007). Corrosion of Copper by Water. Electrochemical and Solid-State Letters, 10 (11) C63-C67.
2. G. Hultquist, P. Szakálos, M. Graham, G. Sproule and G. Wikmark (2008). Detection of hydrogen in corrosion of copper in pure water. Proc. 17th ICC, 2008, paper 3884.
3. G. Hultquist, P. Szakálos, M. Graham, A. Belonoshko, G. Sproule, L. Grasjo, P. Dorogokupets, B. Danilov, T. Astrup, G. Wikmark, G.-K. Chuah, J-C. Eriksson and A. Rosengren, Water Corrodes Copper. Catalysis Letters (2009) 132, pp.311–316.
4. M. Apted, D. Bennett and T. Saario, A review of evidence for corrosion of copper by water. SSM Report 2009:30.
5. M. Bojinov, I. Betova and C. Lilja, A mechanism of interaction of copper with a deoxygenated neutral aqueous solution. Corrosion Science Volume 52, Issue 9, September 2010, Pages 2917-2927.
6. M. Vähänen, Presentation at the Finnish Research Program on Nuclear Waste Management Seminar, Helsinki Technical University, 29.4.2010.

2011:08

The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 270 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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