Copper corrosion processes in the Cu-O-H system, and their role in long-term safety assessments

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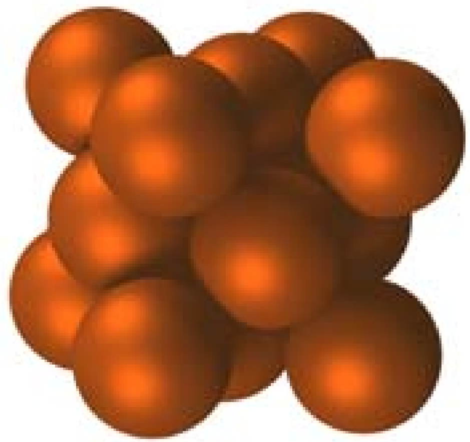
Outline

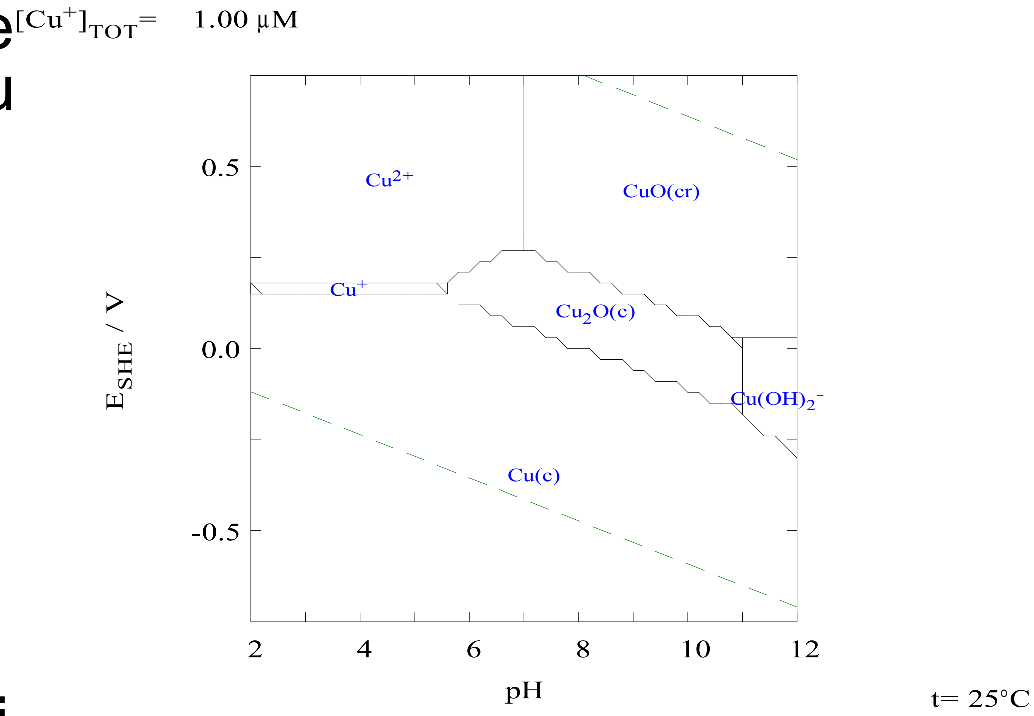
- **Scientific knowledge base**
  - thermodynamics
  - the use of experimental results
  - planned and on-going SKB studies
- **Corrosion in safety assessment**
  - system approach
  - strategy for corrosion calculations
  - calculation results



-  **In other words**

Scientific knowledge base - thermodynamics

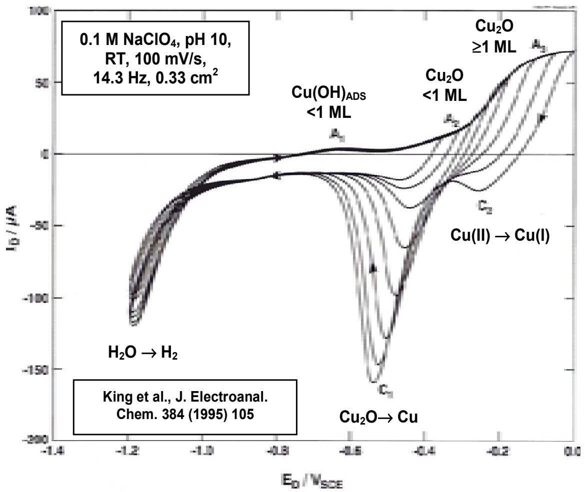
- Cu_2O and CuO are the stable species that can form from Cu and O
- Intermediate phases are known, e.g. $CuOH_{ads}$
  - submonolayer, precursor to Cu_2O
- A study of the possible existence of another Cu(I)-O-H phase will be presented by Pavel Korzhavyi



Pourbaix diagram

Scientific knowledge base - electrochemistry

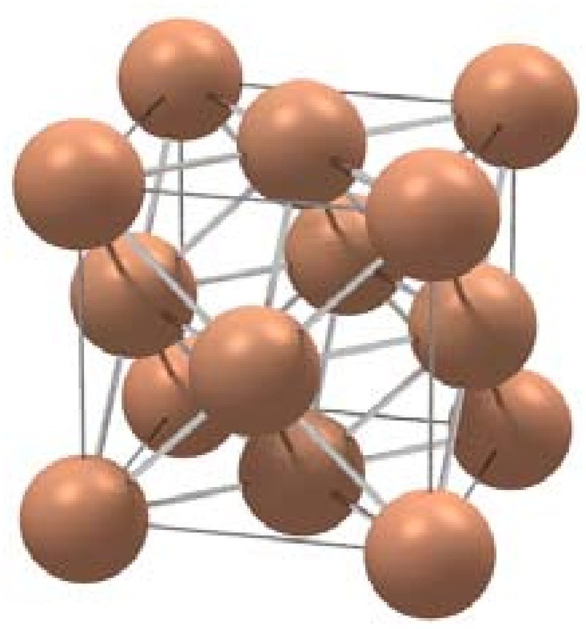
- Voltammetry:
  - shows reactions that include electron transfer
  - Tafael diagrams (potential-current diagrams) can be used to identify different reaction steps



- Impedance spectra give information on for example:
  - rate limiting steps
- Electrical resistance probes – direct measurement of change in amount of metal, hence a direct measurement of corrosion

In other words

- There is a large knowledge base and a wide range of methods to investigate corrosion
- Two types of copper oxides are well-known
- SKB has done several reviews and compilations of the state-of-art on the knowledge of copper



Experiments

- Need the full range of different types of experiments, all with pros and cons:

	Initial state	Control of environment	Representa-tiveness	Timescale
Lab ex. (i.e. electrochem.)	Well known	Very good	Less (simplified system)	Short
In situ exp.	Quite well known	Could be measured	Rather good	Short – medium
Analogues	Not much known	Some could be measured	Poor – good (the entire range)	Long

SKB

Scientific knowledge base - experiments

- Type of results:
  - Electrochemistry/lab – corrosion rate decreases with time (as expected)
  - In-situ experiments – have experienced periods of oxidizing conditions – also Cu(II) corrosion products
  - Analogues – both natural and human artefacts show that copper in native form can be preserved stably for very long times

- Weaknesses
  - Weight loss-measurements not able to distinguish between initial and subsequent evolution of corrosion
  - Measured corrosion depths and corrosion rates could often be composed of different reaction mechanisms – difficult to use for extrapolation in safety assessment

In other words

- Different types of experiments are needed and can be used for understanding different aspects of corrosion
- There is no perfect experiment that can explain everything

Planned and on-going SKB studies of the Cu-O-H system

- **Purpose:**
  - to understand the copper behaviour in water in further detail
- **Literature reviews**
  - update of state-of-the-art on corrosion in copper (King et al, in prep)
  - corrosion of copper by water (King, in prep.)
  - properties of Cu_2O (Korzhavyi et al, in prep.)
- **Experiments**
  - gas measurements as well as more simple closed glass container experiments
  - electrochemistry – short term (Bojinov et al, in prep.) as well as long term
- **Theoretical calculations**
  - stability of phases (Korzhavyi et al, in prep.)
  - equlibrium reactions in water

Summary of critical review of studies of Hultquist and co-workers

- Measured corrosion potential of Cu during supposed evolution of H_2 is 155 mV more-positive than H_2O/H_2 equilibrium potential for 1 atm H_2 /Seo et al. 1987/
- Reported H_2 generation rates vary by factor of 3000 under nominally identical conditions, with no apparent effect of T
  - 17 ng cm^{-2} h^{-1} at room temp /Seo et al. 1987/
  - 0.01 ng cm^{-2} h^{-1} at 45^{o}C /Hultquist et al. 2009/
- Observations have not been reproduced by other researchers
  - H_2 evolution /Simpson and Schenk 1987, Eriksen et al. 1989/
  - Differences between Pd- and Pt-sealed vessels /Möller 1995/
  - Corrosion in anoxic Cl^- /Bojinov and Mäkelä 2003/

Summary of critical review of studies of Hultquist and co-workers (II)

- $CuOH_{ads}$ species known to form at potentials below E_{eq} for Cu_2O/H_2O, but cannot account for H_2 observed
- Contrary to proposed mechanism, there is no evidence in aqueous systems that O_2 is consumed by reaction with H atoms produced by the reduction of H_2O
  - casts doubt on use of evidence from gas-phase studies to infer mechanism in aqueous phase

In other words

- New research results
  - are taken seriously by SKB
  - are analysed in the context of earlier results
- SKB
  - performs further theoretical and experimental studies to learn more of the details of corrosion processes

Conclusion on knowledge base for mechanism

- Cu_2O and CuO are the stable copper oxide phases that can form
- intermediate species, e.g. $CuOH_{ads}$, are possible, but are not sustainable driving forces for corrosion
- there are experiments and measurements from lab scale to analogues supporting the stability of copper in water
- the presented results for the proposed mechanism are non-conclusive and partly contradictory

=> there is no convincing evidence that water oxidizes copper

Safety assessment methodology

- SKB methodology in 10 steps
  - used in safety assessment SR-Can and the coming SR-Site
- Hierarchical structure for documentation
  - FEPs = all features, events and processes
  - Process report - description of each process
  - the handling of each process
- Multidisciplinary description of the evolution of the repository, e.g.
  - geology
  - hydrogeology
  - chemistry
  - climate evolution
  - bentonite
  - copper canister
  - radionuclides
  - ...

Calculation strategy in safety assessment

Generally:

- Use an appropriate mix of:
  - pessimistic assumptions and more realistic descriptions
  - simplified models (e.g. mass balance) and complicated models
- Absolutely necessary to integrate the disciplines!
- Being pessimistic means for example to:
  - only look at amount of material and disregard that it needs to be transported to be able to react
  - only count the rate of one process and disregard that other processes could be rate-limiting
  - set driving forces at high values

Application of this calculation strategy for the corrosion calculations

- **Mass balance**, i.e. how much is available to react (used for pyrite in the bentonite, initially entrapped oxygen etc.)
- **Mass transport** (used for sulphide from groundwater)
  - advection with groundwater to the buffer
  - diffusion over the groundwater/buffer interface
  - diffusion through the buffer
- **Kinetics**; rate of the reaction itself (disregarded for copper reactions – the reactions are assumed to occur instantly)

Development of calculation tools (computer-based models)

- For mass balance – can be done with simple equations
- For diffusive transport - can often be done with simple equations
- For more complex mass transport
  - we use the concept of equivalent flow
  - developed primarily for radionuclide transport and sulphide corrosion, but applicable to other corrodants or corrosion products – adjustment of concentration gradients and diffusivities
  - transport properties (for 6000 canisters) derived from hydrogeology modelling
  - for specific climate evolutions
  - geochemistry gives data for the chemical environment

In other words

- **Corrosion in safety assessement**
  - many disciplines needed
  - often assume the worst – even if we don’t believe it will happen

Treatment of corrosion of copper by oxygen in the safety assessment

- Initial atmospheric corrosion – limited time, amount derived from experiments
- Initially entrapped oxygen in the bentonite – treated with a mass balance
- Possible penetration of glacial meltwater (after a glaciation) – mass transport limited

This should be added to:

- the corrosion by sulphide (mass transport limited)

The further role of corrosion in the safety assessment

- **Calculations**
  - the results of the corrosion calculations are fed into radionuclide transport calculations, resulting in a measure of the risk
  - the risk is compared to limits set by the authorities
- **Formulation of reference evolution and scenarios:**
  - the use of what-if calculations is possible:
    - not included in the reference evolution
    - but analysed to evaluate the effect
  - we use the proposed equilibrium pressure of 1 mbar

Results from what-if calculations

- **First stage: the initial, unsaturated phase**
  - pessimistic upper bound of corrosion: filling all unsaturated void volumes with H_2 to 1 mbar and let it diffuse outwards
  - a corrosion depth < 1 mm in 1,000 years is estimated
- **Subsequent stage: the water saturated repository**
  - disregarding the content of hydrogen gas in groundwater (would stop the reaction when reaching the equilibirum pressure)
  - the transport rate of H_2 is determining the corrosion rate
  - rate of corrosion will be less than the calculated rate for sulphide corrosion (H_2 has higher diffusivity than S^{2-} but the driving force, i.e. concentration gradient is smaller)
  - even without a buffer, flow conditions at Forsmark imply that all canisters are intact after 10 million years

In other words

- The corrosion from sulphide is small, and any corrosion from the proposed mechanism would be even smaller.

Conclusions in SKB's safety assessment

- The scientific basis for a reaction mechanism driven by a proposed new H_xCuO_y phase that is more stable than the known copper oxides is not convincing
- Within the framework of the safety assessment methodology the process is handled as any other process
- What-if calculations of the effect of such a corrosion mechanism can (and will) be included in the assessment
- Corrosion according to the proposed mechanism will not limit the lifetime of the canisters in the final repository