

Additional material to the Expert Panel 2009-12-08

As already discussed in “References and comments, KTH 2009 10 02” submitted to the expert panel, copper is thermodynamically expected to be corroded with formation of both monovalent and bivalent corrosion products in pure degassed water, see the Pourbaix diagram in Figure 1. An aqueous solution with more dissolved H₂ than O₂ is here used as the definition of an “anoxic” environment.

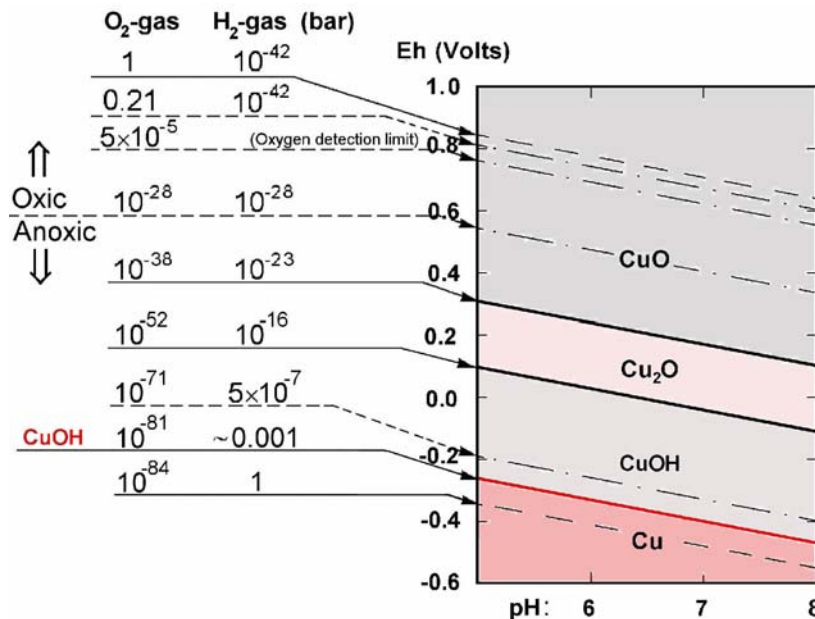


Figure 1. Pourbaix diagram for the system Cu-H-O with gas pressures from equilibrium with water, calculated by Nernst equation. The proposed phase CuOH is added in the diagram. Both bivalent products such as CuO and Cu(OH)₂ and monovalent products such as Cu₂O and CuOH are expected in oxidation by water.

This means that the experimental set-up originally designed by Gunnar Hultquist with glass containers with Pd or Pt membranes is fundamentally important with an observed *and* thermodynamically expected copper corrosion in case of a hydrogen permeable Pd-membrane. One similar test with Pd/Pt-containers was performed by SP in 1995 and a visible difference was also noticed by K. Möller (SKI 95-72). These containers were UHV-tested at Chalmers technical university to exclude any gas leakage.

Pd metal is used as a membrane to separate hydrogen from other gases and is also as an effective catalyst for H₂-dissociation and H₂O-formation also in liquid water¹. This means that the H-activity is low in a container with a Pd-membrane in contact with air on the outside, thermodynamically corresponding to 10⁻⁴² bar H₂. Thus copper corrosion with formation of both monovalent and bivalent corrosion products are expected as shown Figure 1.

The academic questions that should be answered are:

- What is the effect/role of CuOH in anoxic copper corrosion and what is the equilibrium hydrogen pressure?
- Is it a bulk phase or a monolayer precursor to oxide formation?
- Might CuOH, in presence of chloride ions, be a precursor to formation of more stable copper hydroxide chlorides?

Since copper is not thermodynamically immune in pure degassed water, the issue with CuOH is at least an important academic question. A more crucial question for the KBS-3 model should be:

- What is the thermodynamics and kinetics of copper corrosion in anoxic saline water?

This is partly discussed in a new UK Environment Agency report on technical issues associated with deep repositories for radioactive waste in different geological environments² and 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.”

On the same page it is also stated that²:

“If sulphide occurs in the water, corrosion of copper to Cu₂S and CuS is also possible. Thus, if there are high SO₄ - concentrations and conditions are reducing, producing reduced sulphur, there may be a detrimental impact on the longevity of copper.”

The KBS-3 corrosion model which only considers sulphide-ion diffusion through 35 cm bentonite clay/pore water is probably not sufficient. This is further indicated by published results from the LOT-project^{3,4}. A summary of the LOT-results and a proposed corrosion model are shown in Figure 2 which was presented by Szakálos at the seminar/workshop the 16 Nov. 2009.

A corrosion model explaining the observations from the LOT-project; copper exposed in ground water saturated bentonite

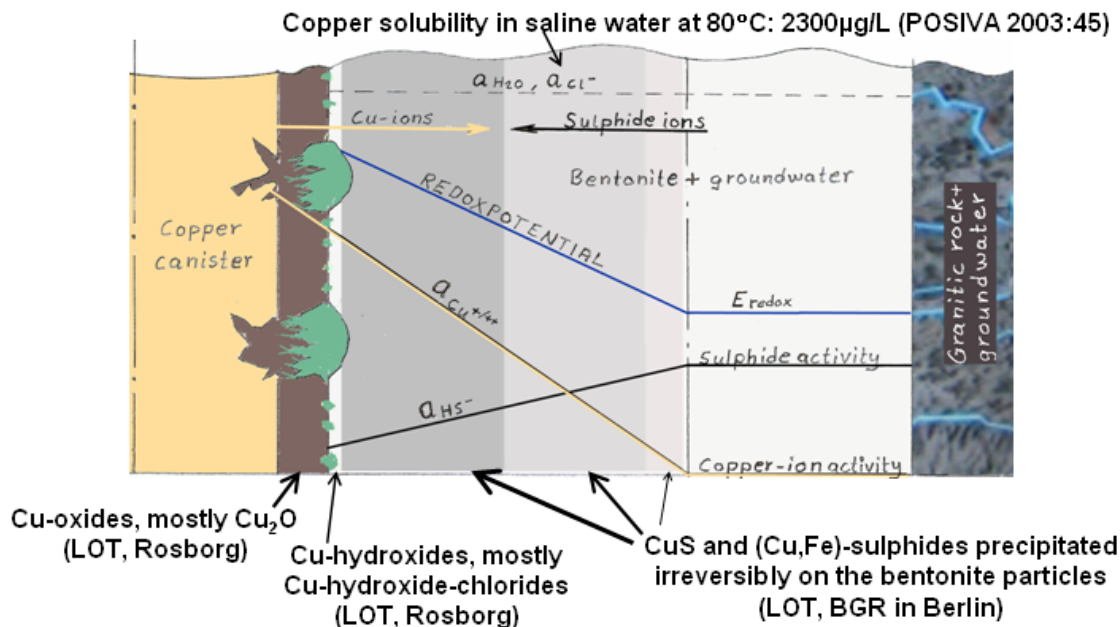


Figure 2. By considering the corrosion results from the LOT-project, a corrosion model with multi corrosion processes is proposed. The model includes copper dissolution and precipitation on the bentonite as sulphides and reduction of water molecules together with chlorides under formation of hydroxide-chlorides and copper oxide.

The Cu-hydroxide-chloride is identified as paratacamite, $Cu_2(OH)_3Cl$ in the LOT-project⁴ and in the “Canister Retrieval Test”⁴. The thermodynamic data regarding this phase are scarce and it is not indicated in any Pourbaix diagram for systems with copper/various ground waters⁵ or in Europe’s most comprehensive thermodynamic database, SGTE⁶. The equilibrium hydrogen pressure for paratacamite formation/reduction is most likely unknown. However, paratacamite is found to be more stable than Cu_2O by electrochemical measurements⁷, i.e. stable at lower redox potentials than Cu_2O , see Table 1.

Both the atacamite phase, ortorombic $Cu_2(OH)_3Cl$, and paratacamite (rhombohedral) are detected in various oxic and anoxic environments. Atacamite seems to be the dominating Cu-hydroxychloride at ambient atmospheric conditions⁸ and paratacamite in aqueous corrosion of copper⁹.

Table 1, E_p are the peak potential (from Ref. 7).

Table 1. Electrochemical characterization of reference materials involved in copper/bronze corrosion. From SQWVs performed at PIGE-modified electrodes immersed into 0.50 M phosphate buffer (pH 7.0). Potential scan initiated at +650 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz

Modifier	E_{onset} (mV)	E_p (mV)	Tafel <i>SL</i>	Tafel <i>OO</i>	$W_{1/2}$ (mV)
CuCO ₃	+80	-100	0.024	0.90	175
Azurite	+60	-85	0.025	0.86	180
Malachite	+70	-95	0.025	0.96	170
Cu ₂ O	+50	-110	0.028	2.02	90
Atacamite	+35	-125	0.017	1.56	160
<u>Paratacamite</u>	+15	<u>-135</u>	0.018	1.61	150
Anarakite	+25	-130	0.019	1.52	160
Botallackite	+20	-120	0.022	1.17	160
CuCl	-115	-335	0.021	4.60	255
CuCl ₂ · 2H ₂ O	+10	-115/-185	0.016	2.32	140

This means that all identified corrosion products in the 5-year LOT exposure; CuS, (Cu,Fe)S, Cu₂(OH)₃Cl and Cu₂O are all thermodynamically expected in an anoxic environment. By all means it is not necessary to explain the LOT-results by assuming a partially oxic environment.

More corrosion research is obviously needed in at least three areas before the use of KBS-3:

- 1) Fundamental theoretical and experimental research regarding the system Cu-H-O.
 - Analysis of anoxic corrosion products.
 - First Principle calculations, is CuOH an amorphous bulk phase or only a surface product?
- 2) Copper corrosion studies in saline anoxic water.
 - What corrosion products are expected?
 - Assess thermodynamic data (incl. Pourbaix diagram) for Cu-hydroxide chlorides.
 - What is the corrosion kinetics?
- 3) Long term exposures during prevailing conditions in Forsmark.
 - Atmospheric corrosion in presence of different salts in an O₂-depleted moist atmosphere.
 - Evaporation induced corrosion.
 - Strictly anoxic corrosion in groundwater with and without bentonite.

Stockholm 2009-12-08

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