

A note on the rate of corrosion of copper canisters in a KBS-3 type repository

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Summary

Szakálos et al. (2007) and Hultquist et al. (2009) report experiments where they find that copper corrodes in deionised water, producing hydrogen gas. They also show that reaction stops when the hydrogen pressure has reached 0.001 atm. In this short communication I estimate at what rate the hydrogen can escape in a KBS-3 type repository for spent nuclear fuel. The rate of escape of hydrogen determines the rate of corrosion. It is found that the escape rate and therefore the corrosion rate under normal repository conditions will be very low and corrosion will not exceed 1 kg copper in one million years. Accounting also for an assumed rapid microbial catalysis of hydrogen oxidation by sulphate at the buffer/backfill interface, less than 5 kg copper could corrode in one million years. In the extreme situation where all buffer is lost and groundwater is allowed to flow freely in the deposition hole a few hundred kg copper could corrode in one million years. Similarly, if microorganisms can be active and catalyze the hydrogen oxidation at the entire buffer/rock interface a few hundred kg copper could corrode in one million years.

Background and introduction

Szakálos et al. (2007) and Hultquist et al. (2009) report a series of measurements of copper corrosion in oxygen free water. They find that copper corrodes “rapidly” (on a geologic time scale) and that hydrogen evolves during the reaction between copper and water. Based on these observations and the observed corrosion of a more than 300 years old copper coin that has been immersed in oxygen free water in sediments in the Baltic they predict that the 5 cm thick copper canister that is proposed as a container for high level spent nuclear fuel will corrode in about 10 000 years. They base this on the observed rates under the conditions studied where the evolved hydrogen is allowed to escape.

Szakálos et al. (2007) and Hultquist et al. (2009) also found that if the hydrogen is not allowed to escape the hydrogen evolution stops after having reached an equilibrium pressure of about 10^{-3} atmosphere partial pressure. Hultquist et al. (2008) found that in a vessel where the hydrogen was not allowed to escape copper did not corrode.

They do not discuss or consider the conditions that will prevail in the repository at about 500 m depth in the granitic bedrock where the copper canister is embedded in highly compacted water saturated bentonite and where the rate of seeping water in the fractures in the rock is low.

In this short communication I assume that their measurements are correct and that the rate of hydrogen evolution is a measure of the copper corrosion rate under conditions where the hydrogen is allowed to escape freely.

I explore the consequences of this reaction using of well known chemical reaction engineering principles and account for transport limitations of hydrogen dissipating from the canister surface.

Basic principles for reactions in a chemical reactor

For a reaction to be sustained new reactants must be supplied and reaction products must be carried away. If one or more reaction products build up to the equilibrium pressure, or concentration, the reaction stops. It will only resume if the reactions products are carried away. When the chemical reaction rate could be fast, transport limitations will limit the overall rate of reaction. This is a well know fact and is based on fundamental laws of nature.

For the reaction at hand, copper is present in the canister deposition hole and water is abundantly available. The activity of the copper as well as of the water can be set to unity irrespective of the amounts (concentrations) of these substances. The reaction products consist of a copper corrosion product and hydrogen. The activity of the copper corrosion product is taken to be unity and is independent of its amount. For the hydrogen that evolves the activity is well approximated to be proportional to its concentration in the water in the reactor. This is proportional to its partial pressure. If the partial pressure of the hydrogen builds up and reaches the equilibrium pressure the reaction stops, no more hydrogen is produced and no more copper corrodes.

This was demonstrated by experiments where in the closed vessel that did not allow hydrogen to escape, the copper maintained its copper colour after 15 years in water and no corrosion was reported, Hultquist et al. (2008). This shows that if the hydrogen is not allowed to escape corrosion will not occur.

Should an amount of hydrogen be released, more can be produced until the equilibrium pressure is re-established.

If the chemical reaction rate is “rapid”, as found by Hultquist et al. (2009) the rate of escape of hydrogen determines the rate of copper corrosion. The corrosion rate is proportional to the rate of loss of hydrogen.

Estimation of rate of hydrogen release and thus the rate of copper corrosion from a copper canister in a repository

In this section an estimate is made of the rate hydrogen escape from a deposition hole in a KBS-3 type repository. The setting is as follows. The copper canister is embedded in compacted bentonite clay in a deposition hole at about 500 m depth in crystalline rock. The rock is fractured and water seeps in fractures. We can see the deposition hole with canister and the swollen fully water saturated bentonite as a reactor from which the hydrogen migrates out to and into the water in the porous rock and/or into the seeping water in the fracture(s) and is carried away. The question is how fast the hydrogen can escape if the hydrogen pressure at the surface of the corroding copper canister has reached the equilibrium pressure, 0.001 atm, as estimated by Hultquist et al. (2009).

In the following calculations it is assumed that for every mol of hydrogen dissipated two mol copper will have been corroded. Hydrogen that may be contained in the copper corrosion products is neglected.

Various escape or scavenging mechanisms for the hydrogen are explored. Namely:

1. Hydrogen escapes by diffusion in the porous water saturated rock matrix.
2. Hydrogen is consumed by an unspecified but very rapid microbially catalysed reaction at the buffer/backfill interface. (Microbes cannot live in the compacted buffer but could possibly be active in the less compact backfill.)
3. Hydrogen is carried away by the seeping water in the fractures intersecting the deposition hole.
4. Hydrogen is carried away by water flushing the deposition hole should all buffer be lost. This is an extreme case used just for illustration.

Case 1. Hydrogen escapes by diffusion in the porous water saturated rock matrix.

The canister is modeled a sphere with 1.2 m radius (this has same surface as the canister) embedded in an infinitely large medium (the water saturated porous rock matrix) in which the hydrogen dissolved in water can diffuse with spherical symmetry. The concentration profile of hydrogen as it builds up and finally stabilizes can be determined by solving the instationary diffusion equation, Fick's second law. The analytical solution is (Crank 1975).

$$C(r,t) = \frac{r_o c_o}{r} \operatorname{erfc}\left(\frac{r-r_o}{2\sqrt{D_p t}}\right) \quad (1)$$

c_o is the hydrogen concentration in water at the surface of the sphere, r_o is the radius of the sphere, r the distance from the centre of the sphere, t is time and D_p is the pore diffusion coefficient in the porewater in the rock matrix.

This equation is used to determine the concentration gradient at the surface of the sphere, which then directly gives the rate of transport of the hydrogen N .

$$N = A_{sphere} D_p \varepsilon c_o \left(\frac{1}{r_o} + \frac{1}{\sqrt{\pi D_p t}}\right) \quad (2)$$

ε is the porosity of the rock matrix. The equilibrium concentration in the water c_o at a hydrogen pressure of 0.001 atm. is obtained from literature data (Perry 1997). See the data section below.

The hydrogen escape over time is shown in Figure 1.

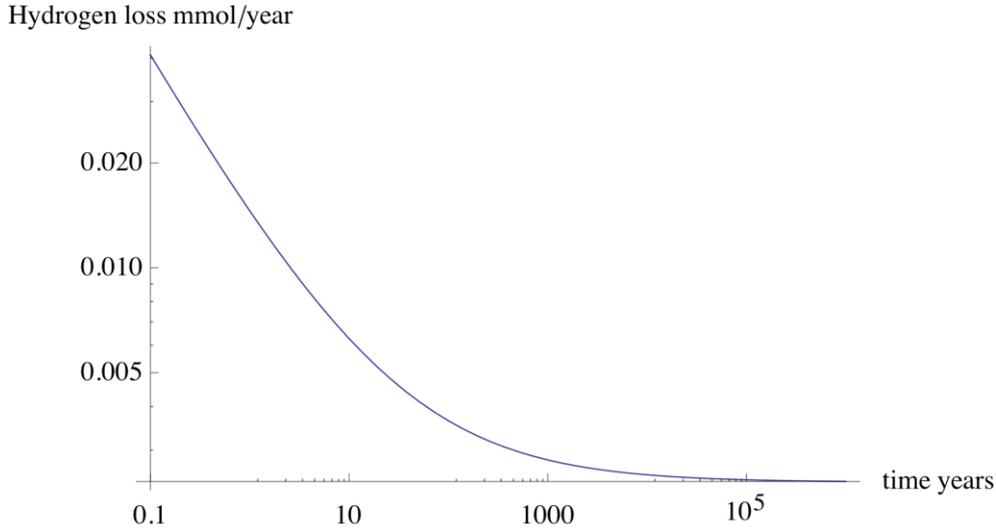


Figure 1. Hydrogen escape over time for spherical diffusion from a sphere with 1.2 m radius.

The rate of copper corrosion is directly obtained from the stoichiometry of the proposed copper corrosion mechanisms that 1 mol of hydrogen results from the corrosion of two mol of copper.

The corrosion in the first million years is obtained to be 0.31 kg.

Case 2. Hydrogen is consumed by an unspecified but rapid microbially catalyzed reaction at the buffer/backfill interface.

In this case it is assumed that the hydrogen produced by corrosion at the canister surface diffuses through the bentonite buffer up to the interface between buffer and backfill where a colony of microorganisms catalyze the reaction between hydrogen and sulphate. The reaction is assumed to be so rapid that all hydrogen that arrives there is immediately consumed. The hydrogen concentration at this interface is zero. From Fick's first law the rate of escape is

$$N = \frac{A_{buffer} D_{buffer} c_o}{d_{buffer}} \quad (3)$$

A_{buffer} is the cross section area of the deposition hole, approximately 2.7 m² for a KBS-3 deposition hole. D_{buffer} is about ten times less than the diffusion coefficient in water. The distance between the top of the canister and the buffer/backfill interface d_{buffer} is taken to be 1 m. This is very conservative because the hydrogen has to diffuse also from the lower parts of the canister and through a smaller cross section area.

The rate of copper corrosion due to hydrogen escape is about 5 kg in one million years in this case.

In the above example it is assumed that that the microorganisms cannot be active in the compact buffer or at the rock/buffer interface because of the high swelling pressure and

because of the small pores in the compacted bentonite buffer. It is also assumed that any microorganisms, if present at rock/buffer interface, are not active for the same reason. Should microorganisms be active at the entire rock/buffer interface the cross section area A_{buffer} is about 50 m^2 and the buffer thickness D_{buffer} is 0.35 m. Then about 300 kg of copper could corrode in one million years.

Case 3. Hydrogen is carried away by the seeping water in the fractures intersecting the deposition hole.,.

The transport capacity of the water seeping in the fractures can be assessed and illustrated by the Q_{eq} concept. This concept is based on a conceptually simple model, Neretnieks (1979), Neretnieks et al. (2010). The solute diffuses from the buffer into the seeping water in the fracture. During the time the water is in contact with the buffer the solute has had time to diffuse a certain distance into the water, which then sweeps it downstream. The flowrate of water that has taken up the solute to a concentration equal to that at the buffer surface is called the equivalent flowrate and is denoted by Q_{eq} .

The rate of release of hydrogen, N , is then obtained as the product of Q_{eq} and the concentration c_o . This is shown in Equation (4)

$$N = Q_{eq}c_o \tag{4}$$

As long as the buffer surrounding the canister is intact the equivalent flowrate is on the order of litres per year and less. (From basic data in SR-Can 2006. Similar results are found from recent data for the Forsmark site).

For Q_{eq} =1 litre/year the loss of hydrogen will be $8.7 \cdot 10^{-7}$ mol/year. In one million years 1.74 mol copper or about 0.11 kg would corrode.

Case 4. Hydrogen is carried away by water flushing the deposition hole should all buffer be lost. This is an extreme case used just for illustration.

In this extreme example it is assumed that the buffer has eroded away so that the deposition hole is empty and offers no resistance to water flow.

An extreme value for the equivalent flowrate Q_{eq} in a KBS-3 type repository for the case when the buffer has eroded away and does not protect the canister is less than $2 \text{ m}^3/\text{year}$ (SR-Can 2006, Table 10-11). The deposition hole acts as a flow through reactor and the flowrate is determined by how much water the fractures in rock allow to flow through the deposition hole.

For Q_{eq} =2 000 litres/year the loss of hydrogen is $1.74 \cdot 10^{-3}$ mol per year. This is equivalent to a copper corrosion rate of 0.22 g/year. In one million years 220 kg of copper could corrode. This is still a small fraction of the total mass of copper in one canister.

Exploration of the corrosion of the copper coin

Copper coins were found in the sediments surrounding the battleship Wasa that capsized in 1628. The corrosion of one such coin was investigated by Hultquist et al. (2009). From the pictures in this paper it seems that a coin may have lost about half its original mass.

One can estimate the loss by diffusion of hydrogen from the coin embedded deep (more than 100 coin diameters) in a very large volume of loose sediment by Equation (2).

Assuming that the diameter is 30 mm and the thickness is 2 mm (estimated from the picture in Hultquist et al. 2009) the mass of the coin is 12.6 grams.

Over the 333 years that the coin resided in the sediments 0.0076 mol of hydrogen would have dissipated. This would have come from 0.97 g of copper. This is about 7.6 % of the original mass of the coin.

If the coin has not sunk to very large depth in the sediment the rate of corrosion can be much greater because the hydrogen can escape more readily. In this simple little example the only mechanisms considered was corrosion by water. Bottom sediments are known to contain sulphide, which also causes corrosion. The sulphide concentration in the pore water sediments can be much larger than that of hydrogen and may well have contributed considerably to the observed corrosion.

Conclusions

Mass transfer resistances to hydrogen transport limit the rate of corrosion to values much smaller than what the proposed reaction rate could be if the hydrogen could escape freely. Under expected repository conditions less than one kg copper could corrode by this mechanism in one million years. This is considerably less than what is expected by e.g. sulphide corrosion.

Even under extreme conditions a few hundred kg of copper could corrode in one million years.

Data from Perry 1997

Solubility of hydrogen in water

Henry's law

$$p = H x$$

x is mole fraction hydrogen in water, H is Henry's constant in atm/(mol H₂/mol H₂O), p is pressure in atm.

Henry's constant, H at 10°C, $H = 6.36 \cdot 10^4$

Henry's constant, H at 80°C, $H = 7.55 \cdot 10^4$

At *one atmosphere* hydrogen pressure the equilibrium concentration of hydrogen in water c mol/kg is

$c = 8.73 \cdot 10^{-4}$ mol/kg at 10 °C or approximately $8.7 \cdot 10^{-4}$ mol/litre

$c = 7.36 \cdot 10^{-4}$ mol/kg at 80 °C or approximately $7.3 \cdot 10^{-4}$ mol/litre

At *0.001 atmosphere* hydrogen pressure the equilibrium concentration of hydrogen in water c mol/kg is

$c = 8.73 \cdot 10^{-7}$ mol/kg at 10 °C or approximately $8.7 \cdot 10^{-7}$ mol/litre

$c = 7.36 \cdot 10^{-7}$ mol/kg at 80 °C or approximately $7.3 \cdot 10^{-7}$ mol/litre

Diffusivity of hydrogen in water, compacted buffer and rock matrix

Diffusivity of hydrogen in unconfined water at 25 °C, $D_w = 5.85 \cdot 10^{-9}$ m²/s.

The effective diffusivity in the compacted buffer D_{buffer} is taken to be $D_w/10$ to account for tortuosity, constrictivity and porosity.

The pore diffusivity D_p in the rock matrix is taken to be ten times less than in unconfined water due to tortuosity and constrictivity effects. The rock matrix porosity ε is taken to be 1%. These data are in the range of observed values in granite and are chosen to be on the high side in the range.

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