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INTERACTION.
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Abstract

The chemical corrosion of three potential canister materials, Fe, Cu, and Pb is reviewed in terms of their thermodynamic and kinetic behavior in a repository. Thermodynamic predictions which are compatible with sedimentological observations indicate that for all three metals, chemical corrosion is expected at any time in a repository. From the kinetic information obtained by experimental and archeological data, long-term corrosion rates are assessed. In the case of Fe, the selected data allow extrapolation to repository conditions with a tolerable degree of uncertainty except for the possible effect of local corrosion in the initial oxic phase. For the other two metals, the scarcity of consistent experimental and archeological data limits the feasibility of this approach. In view of this shortcoming, a kinetic, single-box model, based on the STEADYQL code, is presented for quantitative prediction of long-term canister-bentonite interaction. The model is applied to the corrosion of Cu under anoxic conditions and upper and lower limits of corrosion rates are derived. The possibilities of extending this single-box model to a multi-box, diffusion-extended version are discussed. Finally, further potentials of STEADYQL for future applications of near field modelling are highlighted.

Abstract (Swedish)

Den kemiska korrosionen granskas för tre möjliga kapselmaterial, Fe, Cu och Pb
utifrån deras termodynamiska och kinetiska beteende i ett slutförvar. Termodynamiska
förutsägelser, som är i överenstämmelse med sedimentologiska observationer, pekar på
att kemisk korrosion av alla tre metallerna kan förväntas vid vilken tidpunkt som helst
i förvaret. Från den kinetiska informationen som erhållits ur experimentella och
arkeologiska data uppskattas korrosionshastigheter efter långa tider. För Fe tillåter de
data som valts en extrapolering till förvarsförhållanden med en tolerabel grad av
osäkerhet med undantag för möjlig inverkan av lokal korrosion under den inledande
oxiderande fasen. För de andra två metallerna begränsar knappheten på experimentella
och arkeologiska data möjligheterna att tillämpa den använda metoden. Med hänsyn till
denna begränsning presenteras en kinetisk "single-box" modell, baserad på koden
STEADYQL, för kvantitativ förutsägelse av kapsel-bentonit växelverkan under långa
tider. Modellen tillämpas på Cu-korrosionen under anoxiska förhållanden och övre och
undre gränser för korrosionshastigheterna härleds. Möjligheterna att utvidga denna
"single-box" modell till en "multi-box" version som inkluderar diffusion diskuteras.
Slutligen belyses ytterligare möjligheter att i framtiden tillämpa STEADYQL på
närområdesmodellering.

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1   Introduction

Understanding corrosion of canister material is crucial for quantitative prediction of radionuclide release in a HLW repository. The favored canister materials in common repository designs are, for a variety of reasons, steel or copper, where the latter is envisioned to contain an inner lead layer [1, 2]. Thus, prediction of the chemical behavior of metallic Fe, Cu, and Pb is of primary importance. This is not a trivial task because of large uncertainties in quantitative predictions concerning the physical and chemical behavior of the near field. However, although important chemical variables remain uncertain (redox conditions, alteration of clay), our understanding of chemical behavior of the near field has improved by recent work, e.g., by prediction of chemical composition of major components (CO_3, SO_4, Cl, pH, Ca, Na) [3]. Thus, appropriate information is available for defining chemical boundary conditions which help to quantify the extent of corrosion.

This work is an extension of the SKB corrosion program which has focused mainly on the thermodynamic boundary conditions of copper in bentonite medium [1, 4, 5]. We extend this thermodynamic approach also to the other important material candidates Fe and Pb and review kinetic data for all three metals. On the basis of this thermodynamic and kinetic information we develop a kinetic model using the quasi steady-state concept. This model is applied to the copper-bentonite system under anoxic conditions. Furthermore, the usefulness of the model for predicting various important chemical changes in the near field (e.g., redox evolution) is pointed out.

2   Thermodynamic boundary conditions

In this section we review the thermodynamic boundary conditions of Fe, Cu, and Pb in a repository. On the basis of the newest available thermodynamic data we construct predominance diagrams for each element under chemical conditions expected in the near field. Thus, the main chemical variables (pH, Eh, carbonate, sulfate, sulfide) are included in this calculation.

a.

Fe$_2$O$_3$(s)

FeS$_2$(s)

Fe^{2+}

Fe$_3$O$_4$(s)

Fe(s)

pe

pH

b.

Cu^{2+}

Cu$_2$O(s)

Cu$_2$(OH)$_2$CO$_3$(s)

Cu(s)

Cu$_2$S(s)

Cu(s)

pe

pH

c.

Pb^{2+}

Pb$_3$(CO$_3$)$_2$(OH)$_2$(s)
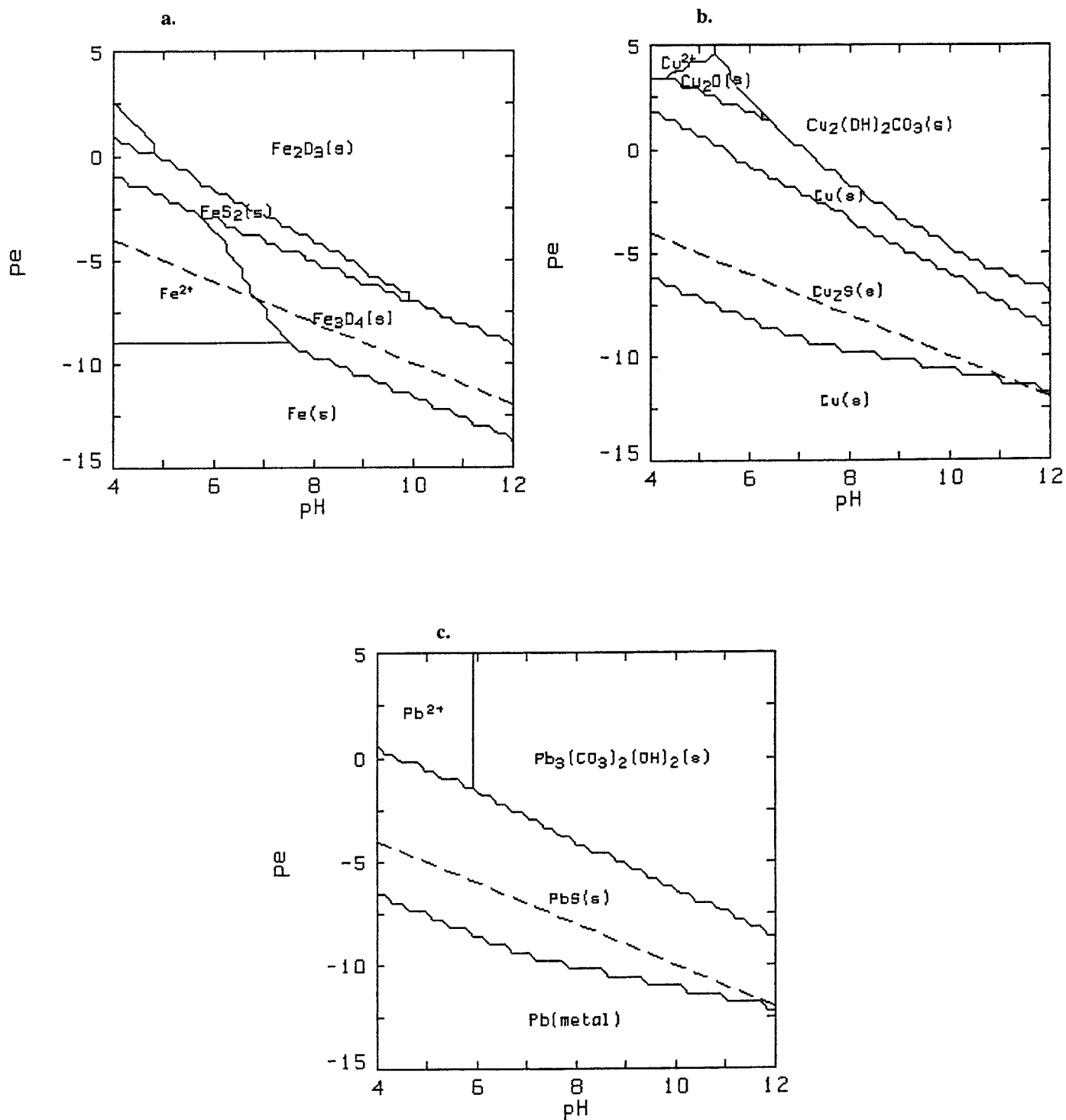
PbS(s)

Pb(metal)

pe

pH

Fig. 1. pe - pH diagrams constructed for relevant chemical conditions in a bentonite system with $[CO_3]_t = 10^{-3}$ M, $[S]_t = 10^{-6}$ M, $[M]_t = 10^{-4}$ M.
a: predominant Fe species, b: predominant Cu species, c: predominant Pb species.

2

2.1 Iron

A pe - pH diagram reveals the stability fields of the dominant iron species (Fig. 1a). This indicates that under oxic conditions Fe metal is expected to corrode to hematite. From sedimentological observations [6], which indicate that more soluble oxyhydroxide phases prevail over long time periods, a kinetically more favored Fe(III) oxide (e.g., ferrihydrite) is expected to form in a repository. Under anoxic conditions magnetite and to a lesser extent pyrite are expected to form (Fig.1a). The stability field of sulfur-bound iron species is dependent on the nature of the forming mineral phase. Sedimentological observations indicate the persistence of FeS over FeS_2 over long time scales [6, 7]. This suggests that, under the expected pH-conditions (8-10) of a repository, the formation of magnetite is favored over pyrite which agrees with corrosion studies in bentonite media [8]. Furthermore, observations made in sedimentary rocks which have been formed under more alkaline conditions also indicate the presence authigenic magnetite [9].

2.2 Copper

Figure 1b illustrates that metallic copper is limited to a relatively narrow window in the intermediate range of redox potential. This diagram has been constructed on the basis of realistic assumptions concerning the concentrations of components: $[HS]_t = 10^{-6}$ M which is compatible with FeS equilibrium as is observed in anoxic sediments, and $[CO_3]_t = 10^{-3}$ M which is expected from bentonite porewater in equilibrium with calcite [3]. The stable copper solid under the expected range of redox conditions is chalcocite (Cu_2S) which reveals an extremely low solubility. Copper sulfide phases which occur in recent sediments [10] show compositions between end members of Cu_2S and CuS. Chalcocite is the dominant copper mineral in low to intermediate temperature Cu-rich formations (e.g., supergene zones) [11]. On the other hand native Cu is extremely scarce in these type of deposits [12]. Under oxidizing conditions copper is much more soluble and malachite and cuprous oxide are thermodynamically stable. This is in agreement with experimental, archaeological and geological observations [13]. Low temperature Cu deposits under more oxidizing conditions commonly show Cu carbonate precipitates. Under these conditions there appears to be noticeably higher proportions of native copper as shown from copper ores, e.g., c.f. Michigan County, Arizona [12]. This is compatible with thermodynamic relationships (Fig. 1b) which indicate that native copper is stable under slightly oxidizing conditions.

2.3 Lead

Pb shows similar stability relationships as Cu (Fig. 1c). It shows high affinity for the sulfide ligand and therefore is expected to form galena in a repository under anoxic conditions. Due to its less noble character compared to Cu it shows no stability field under intermediate redox conditions. In oxic soil environments carbonate and hydroxy carbonate phases are observed [14]. Under near field conditions hydroxycarbonates are expected to form.

In summary, thermodynamic calculations indicate that - for three metals - corrosion is expected in a repository both under oxic and anoxic conditions.

3 Kinetic information

In order to assess the kinetics of the corrosion process we review the available information from experimental and archaeological data.

3.1 Iron

3.1.1 Experimental data

There is a vast amount of information available from the corrosion literature. Also, a number of corrosion experiments have focused on systems relevant to radioactive waste disposal. Thus, a number of experiments were performed in alkaline media [15] and some in a bentonite matrix [8, 16]. From statistical analysis and estimated activation energies empirical relationships have been postulated. Thus, for anoxic corrosion Grauer [13] suggests following kinetic rate expression:

$$P = 276 * t^{0.76} \exp(-2850 / T)$$

where P is the corrosion rate in mm/y, t is in years, and T is in K.

This agrees with corrosion data in a bentonite matrix where a corrosion rate of <0.01 mm/y is derived. High temperature experiments and observations from soil systems are compatible with this finding [13].

Contrary to anoxic media, a large spread of corrosion data depending on electrolyte concentration (chloride, sulfate) is noted under oxic conditions. Moreover, a number of authors, e.g., [17, 18] emphasize the formation local corrosion. Therefore, extrapolation of corrosion rates to repository conditions are characterized by a large degree of uncertainty. A

selected range of corrosion rates for oxic and anoxic conditions derived from experimental data is given in Table 1.

3.1.2 Archaeological data

Various findings of ancient iron from soils usually indicate low corrosion rates (<0.02 mm/y) (cf. [13]). This is generally not true for object lying in the sea which show high corrosion (up to 1mm/y). Under conditions where the iron objects remained in a homogeneous anoxic medium (e.g., marine sediments) corrosion rates are low and agree with experimental data (<0.01 mm/y) (see Table 1).

3.2 Copper

Contrary to Fe, there is relatively little experimental data available. A revue of corrosion data of copper and its alloys is given by [19]. These data mainly include corrosion of pipe-lines and thus reflect almost exclusively oxidizing conditions. The surface erosion is usually very small (<0.01 mm/y). However, at high CO_2 content, higher values were derived (up to 0.4 mm/y) [19]. Moreover, in many cases damage of the pipes by local corrosion (crevice corrosion and stress corrosion cracking) was observed. The possible influence of different hydraulic regimes makes interpretation of these data difficult. Under anoxic conditions no useful data was found.

Some insight into long-term corrosion behavior of copper can be gained from archaeological observations. Antic copper and bronze objects show relatively high variations in corrosion behavior [13] yielding up to 5 mm erosion in 1000 years. [20] deduced from a bronze cannon lying in a marine sediment a corrosion rate of about 0.01 mm/y. A Swedish study of bronzes derives pitting factors in the range of 3 [21]; [5] suggests a realistic pitting factor of 2 and an upper limit of 5. The vast majority of archaeological observations reflect oxidizing conditions and therefore can be extrapolated to repository conditions only for the initial oxic phase. A summary of corrosion data is given in Table 1.

3.3 Lead

In the case of Pb even less corrosion data than for Cu are available. From a study of [22] the estimated rates are generally below 0.005 mm/y. However, the differences measured were high (ranging up to 1mm/y), which would imply a high pitting factor. This effect is confirmed by archaeological observations. [23] estimated from five Pb findings a rate of 0.3 to 8 mm in 1000 years. According to [13] corrosion depends to a great extent on particle size, where

coarsely grained material shows rapid corrosion. Unfortunately, no quantitative data of this effect are available. The available corrosion data is summarized in Table 1.

Table 1 Range of corrosion rates selected from literature. Rates given in mm/y.

	Experiments		Archaeology	
	oxic	anoxic	oxic	anoxic
Fe	0.01 - 1	10^{-4} - 10^{-3}	0.01 - 10	< 0.01
Cu	0.01 - 0.4	??	10^{-5} - 10^{-3}	??
Pb	10^{-3} -1	??	0.3 - 8	??

3.4   Extrapolation of kinetic data to repository conditions

In general, extrapolation of kinetic corrosion data to near field conditions is difficult due to differences in (1) time factor, (2) physical properties of surrounding medium (e.g., electric conductivity), (3) chemical properties (e.g., ligand concentration, reactivity of metal surface). However, there are notable differences in the quality of data depending on the material. Thus, the approach to assessing long-term corrosion also differs.

3.4.1   Fe

As shown in Table 1 there is relatively good agreement between experimental and archaeological data in the case of anoxic conditions. This fact has led to a conservative estimate of a corrosion rate of 0.01 mm/y for a HLW repository [24]. Further justification for this assumption lies in the homogeneity of the surrounding bentonite medium which significantly limits the impact of local corrosion under anoxic corrosion. However, the possibility of significant local corrosion which has been emphasized by e.g., [17, 18] cannot be ruled out under oxic conditions and therefore upper limits of corrosion rates are still uncertain. In view of this, we suggest that the temporal evolution of redox conditions in the near field should be re-evaluated.

3.4.2   Cu

In the case of oxic conditions there is some kinetic data available which show a relatively large spread of more than two orders of magnitude. In addition, higher corrosion rates due to local corrosion effect   (e.g., crevice cracking) cannot be excluded. For the anoxic no quantitative data is available. From geologic observations on low temperature copper deposits, the strong preference of sulfides over native copper suggests transformation to Cu_xS which is in agreement with thermodynamic relationships.

3.4.3   Pb

There is a serious lack of reliable data. Nevertheless they suggest that intracrystalline corrosion is an important process and may need further attention when quantitative predictions are assessed.

In summary, the long-term prediction of chemical corrosion of potential canister materials on the basis of kinetic data is still subjected to a number of uncertain factors. This has lead us to develop a robust kinetic model which takes the physical/chemical boundary conditions in a repository into account.

4   Steady-state model

4.1   Presentation of model

We have applied a kinetic model, known as STEADYQL, which is based on steady-state and was originally developed for the study of soil solutions by Furrer and co-workers [25, 26]. The basics of this approach are illustrated in Fig. 2. Consider a box through which water flows in and out at a constant velocity. The interaction of this water (and its dissolved solutes) and the material within the box is represented by fast and slow processes. Fast processes include chemical equilibrium reactions between dissolved, solid, and surface constituents. Slow processes involve kinetically-driven chemical reactions as well as diffusion processes. The STEADYQL algorithm takes into account mass action equations, flux balance, and mole balance. Thus, it calculates the appropriate fluxes of the solutes upon interaction at a steady-state regime. The usefulness of this models lies in its applicability to a large range of different geochemical systems. So far its has been used for the quantitative assessment of acidity of different soils [26], of redox processes in column experiments [27], and redox processes in lake systems [28]. Depending on the system of interest, the steady-state model has been used as "single-box" or as "multi-box" model. A further advantage of STEADYQL is that it allows sensitivity analysis on the basis of normalized sensitivity parameters. Alternatively, the relative importance of input parameters is easily checked by conventional sensitivity analysis.
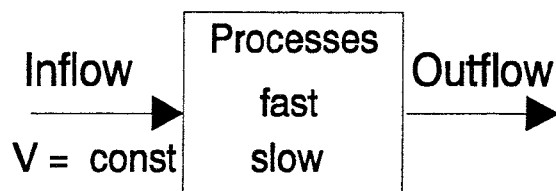
Fig. 2. Basics of steady-state model illustrated with a simple box.

## 4.2 Application of model: Anoxic corrosion of copper

An appropriate description of the system requires the understanding of the important chemical and physical processes. In the following we discuss these processes in the bentonite - copper system and show how they can be approximated within the steady-state model.

4.2.1 Description of the bentonite - copper system at steady-state

Fast processes: These are represented by chemical equilibrium reactions between the components Cu, Fe, H, HS, Ca, and CO_3. Solid equilibrium with respect to calcite and, depending on the case, FeS (as discussed below) are treated as fast processes.

Slow processes: Slow processes considered here include corrosion of Cu, precipitation of CuS, and diffusion of HS⁻.

As derived from thermodynamic relationships the overall corrosion occurs as redox process according to: Cu ----> Cu_xS. In order to be conservative we assume that CuS is the stable phase. Possible oxidants in bentonite are sulfate, Fe(III) and water. According to [29] inorganic reduction of sulfate is extremely slow and thus considered to be an insignificant process. However, reduction of sulfate in the presence of reactive organic matter is fast:

$$2 \, Cu + 2 \, SO_4^{2-} + 3 \, CH_2O + H^+ \longrightarrow 2 \, CuS + 3 \, HCO_3^- + 2 \, H_2O$$
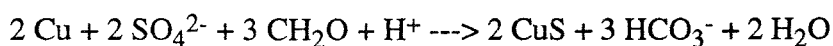
This process is limited by the low availability of reactive organic C in bentonite which displays much lower pore space than the size of reducing microorganisms [9]. This physical protection of organic carbon has preserved organic matter in clays for millions of years as exemplified in Paleozoic mudstones. Another thermodynamically possible redox process involves the direct participation of HS⁻:

$$Cu + HS^- + H^+ \longrightarrow CuS + H_2 \tag{1}$$

$(\Delta G_r^\circ = -35.9 \text{ kJ/mol})$

This reaction (1) is expected to be very slow [4] but its kinetics are unknown. In view of this, it has been postulated that for conservative purposes, copper oxidation reactions involving HS^- are controlled by HS^- diffusion in the bentonite medium [4, 5, 13]. Under steady-state conditions the diffusion process can be separated into a forward and backward process. Thus, from Fick's law, the flux of HS^-, J_{HS^-} can be approximated by:
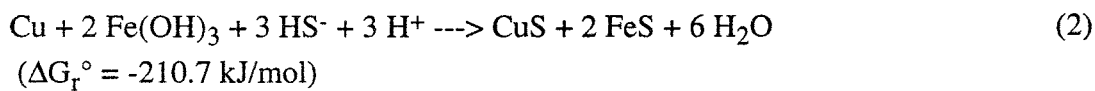
$$R_{(1)} = J_{HS^-} = -D \, (C_b - C_x)/\Delta x$$

where C_b and C_x are the concentrations of HS^- in bentonite and at the copper plate respectively, Δx is the diffusion distance, and D the apparent diffusion coefficient of HS^-. At constant C_b this is equal to:

$$J_{HS^-} = d_f \, C_x - d_r$$
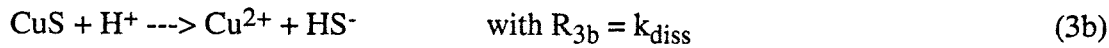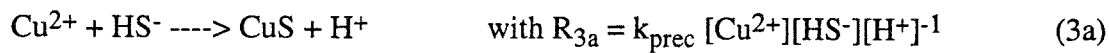
where $d_f = D/\Delta x$ and $d_r = D * C_b/\Delta x$

Assuming $\Delta x = 1$ mm [28], and taking $D = 10^{-11} - 10^{-12}$ m²/s from diffusion experiments [30], and $C_b = 10^{-6}$ M on the basis of FeS equilibria [7]: $d_f = 10^{-7} - 10^{-8}$ dm s^{-1}, $d_r = 10^{-13} - 10^{-14}$ mol dm^{-2} s^{-1}. These reaction constants can be inserted into STEADYQL according to Table 2.

A further redox reaction involving HS^- and Fe(III) is thermodynamically possible:

$$\text{Cu} + 2 \text{ Fe(OH)}_3 + 3 \text{ HS}^- + 3 \text{ H}^+ \text{---> CuS} + 2 \text{ FeS} + 6 \text{ H}_2\text{O} \qquad (2)$$
$$(\Delta G_r^\circ = -210.7 \text{ kJ/mol})$$

Although it is questionable that the oxidation potential of Fe(III)/Fe(II) is sufficient to induce copper oxidation, we feel this possibility should be considered because of (1) thermodynamics as outlined above. Moreover, the reactivity of surface-bound iron for redox reactions has shown to be variable and dependent on the nature of ligand involved [31]. Redox reactions involving Fe(III)/ Fe(II) in anoxic sediments are limited by zero-order kinetics of Fe(III) dissolution [31, 32]. Therefore, one limiting case is to assume that process (2) is controlled by Fe(III) dissolution: $R_{(2)} = k_{Fe(III)}$, where $k_{Fe(III)}$ is in the range of $10^{-12} - 10^{-11}$ mol dm^{-2} s^{-1}.

So far, we have neglected the removal of Cu by precipitation of CuS. One strength of the steady-state approach is that precipitation kinetics can be described by a forward and a back reaction:

$Cu^{2+} + HS^- \longrightarrow CuS + H^+$ with $R_{3a} = k_{prec} [Cu^{2+}][HS^-][H^+]^{-1}$ (3a)

$CuS + H^+ \longrightarrow Cu^{2+} + HS^-$ with $R_{3b} = k_{diss}$ (3b)

where $k_{prec} / k_{diss} = K_{S0} = 10^{-22.0}$ where K_{S0} is the solubility constant.

The slow processes are summarized in Table 2.

Table 2 Slow processes and rate equations.

Process	Rate equation
(1) Oxidation of Cu by water and HS⁻	
Forward diffusion of HS⁻	$R_{(1a)} = d_f [HS^-]$
Backward diffusion of HS⁻	$R_{(1b)} = d_r$
(2) Oxidation of Cu by Fe(III) and HS⁻	
Dissolution of Fe(III) oxides	$R_{(2)} = k_{Fe(III)}$
(3) Formation of CuS	
Precipitation of CuS	$R_{(3a)} = k_{prec}[Cu^{2+}][HS^-]/[H^+]$
Dissolution of CuS	$R_{(3b)} = k_{diss}$

4.2.2 Limiting boundary conditions

In a first approach the limiting boundary conditions are evaluated on the basis of the "single-box model". A constant flow of water is assumed in and out of the box and all slow processes occur in direction of the flow. This is illustrated in Fig. 3 for the copper - bentonite system. Table 3 shows the assumed values for the input parameters. The first limiting case (case 1) is based on the conservative assumption that the flux of Cu out of the box is directly related to the diffusion of HS⁻. Immobilization of Cu by CuS precipitation is neglected (see e.g., [4]). The other limiting case (case 2) assumes that the oxidation of copper is controlled by the precipitation of CuS at constant HS⁻ activity, imposed e.g., by the equilibrium condition with FeS. In other words, there is no concentration gradient between the bulk bentonite water and the copper surface. The results of both limiting cases are illustrated in Fig. 4. For case 1 a flux of Cu out of the box of $J_{Cu} = 3*10^{-4} - 3*10^{-3}$ mol m⁻² yr⁻¹ is calculated whereas for case 2 the calculated flux is much lower, $J_{Cu} = 6*10^{-18} - 6*10^{-17}$ mol m⁻² yr⁻¹.
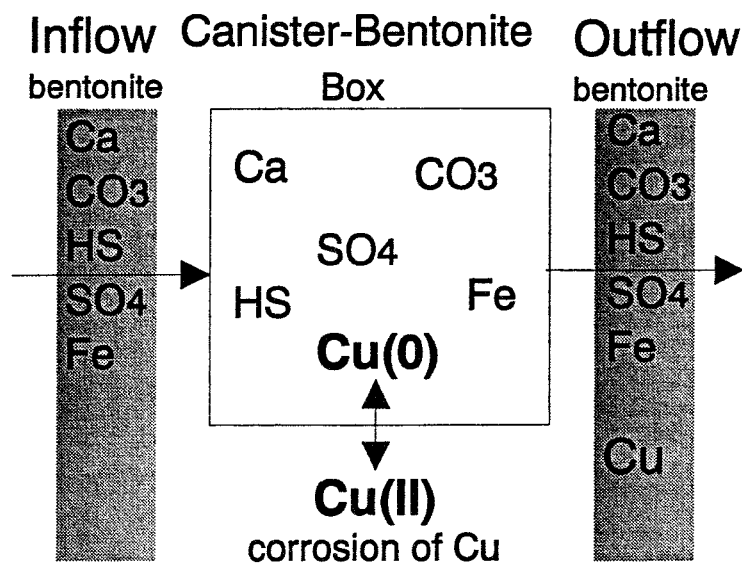
Fig. 3. Single-box model of canister -bentonite interaction. Dotted area depicts fluxes of the inflowing and outflowing bentonite porewater, respectively, before and after reaction with the copper canister.

Under the assumption of homogeneous corrosion, this flux in case 1 corresponds to a corrosion rate of the canister surface of: $2.2 * 10^{-6}$ - $2.2 * 10^{-5}$ mm/y. For case 2 this conversion yields: $4.4 * 10^{-20}$ - $4.4 * 10^{-19}$ mm/y.

The low flux of Cu in case 2 results from the very low solubility of copper sulfide and the imposed high activity of HS$^-$. This case is unrealistic since there is expected to be a concentration gradient of HS$^-$ at the bentonite - copper interface, but this case can be regarded as lowest boundary. Case 1 yields corrosion rates that are similar to those observed from archaeological evidence. However, for anoxic conditions, this case also seems unrealistic because of the strong interaction that is expected between HS$^-$ and Cu. Furthermore, transport by flow in bentonite, as imposed by the single-box model, is insignificant compared to diffusion. Therefore, in the following, we discuss the need of a multi-box model in order to constrain our system in the light of copper corrosion rates.

Table 3 Input parameters for single-box model

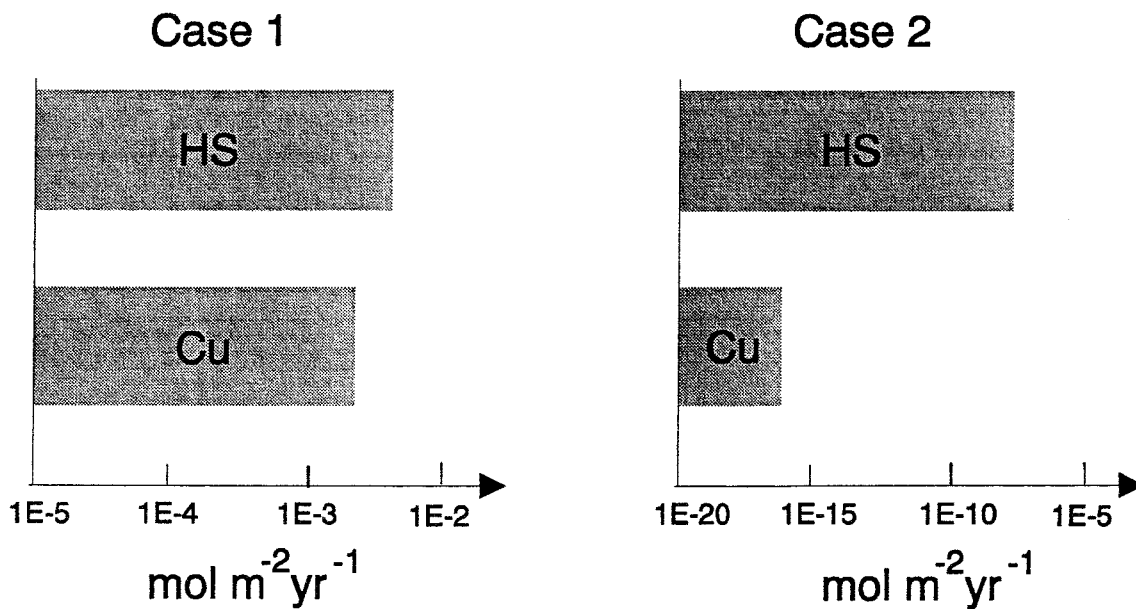| Parameter	Value
Inflow, v_{in}	$3*10^{-9}$ dm s^{-1}
Diff. of HS$^-$, d_f	10^{-8} - 10^{-7} dm s^{-1}
Diff. of HS$^-$, d_r	10^{-14} - 10^{-13} mol dm^{-2} s^{-1}
Diss. of Fe(III), $k_{Fe(III)}$	10^{-13} - 10^{-12} mol dm^{-2} s^{-1}
$^\$$Prec. of CuS, k_{prec}	10^2 dm s^{-1}
$^\$$Diss. of CuS, k_{diss}	10^{-20} mol dm^{-2} s^{-1}

$^\$$ is not considered for case 1

Fig. 4. Calculated fluxes of Cu and HS out of box (see text).

4.2.3 Preliminary presentation of multi-box model

So far the system has been regarded as single-box model exhibiting a constant inflow and outflow. Therefore the fluxes are determined by the flow velocity through the system. The bentonite medium is characterized by very low flow regime and transport is thought to occur principally by diffusion. This situation is taken into account by an extended version of STEADYQL which models the flux of constituents between 2 boxes (in our case bentonite and copper) by inserting an arbitrary number diffusion boxes. Diffusion in and out of the

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diffusion box is considered as a slow process for every solution species which is treated in the same manner as outlined above for HS⁻. The advective flow is set perpendicular to this set of boxes. Thus, following schematic model could be represented in a repository (Fig.5).

At the present time we are in the process of adapting this extended version of STEADYQL to our system. The following steps are assessed. In a first approach one diffusion box with a width of 1 mm is put between the bentonite and the copper box and the copper corrosion process is formulated according to e.g., reaction (3) and (4). Under the assumption that CuS forms a protective layer on the copper surface, a second diffusion box can be inserted in which the diffusion through this protective layer is modelled by an additional slow process. The big advantage of the "diffusion box" approach over the "simple box" is that fluxes can be viewed independently of the advective flow. Moreover, the effect of a change in flow regime can be examined by increasing the inflow and outflow. In our case the local flow of water along the boundary of bentonite and canister can also be envisioned.

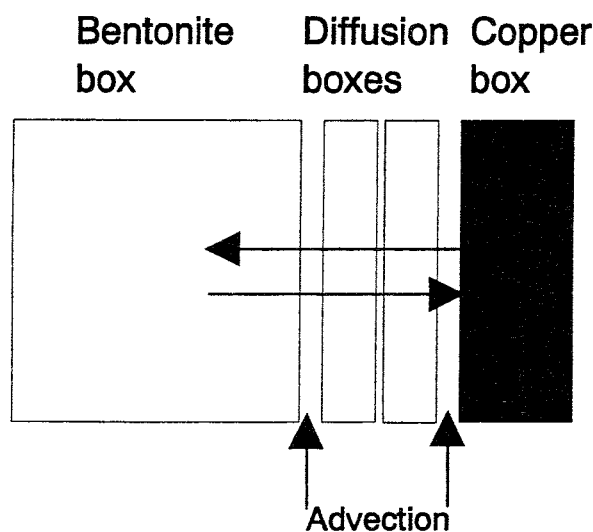**Bentonite box   Diffusion boxes   Copper box**

Advection

Fig. 5. Multi-box model of canister - bentonite interaction. Diffusion occurs between bentonite box and copper box via diffusion boxes in which slow processes take place. Advective flow occurs perpendicular to diffusion along the bentonite/copper boundary.

5   Objectives for further work

As we have outlined above, the STEADYQL model is a powerful tool for evaluating the relative importance of kinetically-driven processes in complex chemical systems. Thus, we showed that it can yield quantitative information of corrosion processes whose kinetics are poorly understood. Furthermore, it offers a range of possibilities of predicting other long-term processes in the near field. These include:

1) Modelling corrosion of Cu and Fe in the multi-box, diffusion-extended STEADYQL model. This includes both anoxic and oxic conditions and allows to constrain the rates of chemical corrosion under repository conditions.

2) Modelling the consumption of O_2 in a repository after emplacement of the canisters. The simple model based on pyrite oxidation of Spahiu and Bruno [5] could be checked and improved by STEADYQL. The relative importance of this process could be compared to the process of H_2 production by corrosion of steel canisters (see 2)).

In order to guarantee adequate interpretation of modelling results, independent experimental information would be very valuable. This mainly involves the corrosion process of copper and the change in redox conditions within the bentonite system. With regard to the copper corrosion process under anoxic conditions, our preliminary results from STEADYQL indicate that corrosion is drastically lowered by the formation of a protective layer of sulfide on the copper surface. However, there is, according to our literature search, no experimental, archaeological, or geological evidence for this process. Therefore, experimental data would be useful to elucidate the process of copper sulfide formation. Thus, the interaction of sulfide with metallic copper in a bentonite system under well-controlled conditions (e.g., pH, E_h) could be studied with special focus on the distribution of precipitated material on the Cu metal and yield information on uniform vs. non-uniform covering. Also, the possible influence of HS^- on stress corrosion cracking can be tested with the adequate set up. In this regard we expect, that the occurrence of a protective layer would decrease this problem. Another important chemical variable related to corrosion is the redox potential. The effect of O_2 on corrosion could be elaborated relatively simply by the study of two parallel experiments under identical conditions other than E_h.

6 Summary and conclusions

This study focuses on the corrosion of three potential canister materials, Fe, Cu, and Pb, under chemical conditions encountered in a bentonite medium. First, we investigate the interaction between these canister materials and the bentonite-water system thermodynamically and compare the obtained stability relationships to geological observations. Chemical corrosion of metallic Fe is dominated by the formation of iron oxides. In the case of Cu and Pb, carbonate precipitates are expected in the presence of O_2, whereas at low redox potential insoluble sulfides are stable. Thus, chemical corrosion of all three metals is expected at any time in a repository.

Second, kinetic information on corrosion of Fe, Cu, and Pb from experimental and archaeological data are reviewed. The data indicate that, in the case of Fe, available corrosion data allow extrapolation to repository conditions with a tolerable degree of uncertainty, except for the possible effect of local corrosion in the presence of O_2. In the case of Cu, the range of available data can be used to get a crude estimate of corrosion rates at oxic conditions. Under anoxic conditions, the lack of data precludes any simple extrapolation. In the case of Pb, the available kinetic data is scarce and displays a large range of corrosion rates which precludes reliable long-term predictions

Third, a kinetic model based on steady-state is developed for quantitative prediction of Cu corrosion in bentonite at anoxic conditions with aid of the STEADYQL code. The processes involved in this model are assigned to as fast (processes at equilibrium), and slow (processes for which the kinetics are specified explicitly). Reactions of dissolved species and $CaCO_3$ are considered to be at equilibrium. The slow processes include (1) oxidation of Cu by interaction with HS^- and the oxidants H_2O, Fe(III) and (2) precipitation of copper sulfide. The limiting cases of copper release are calculated on the basis of a single-box model and converted to corrosion rates of the canister surface. An extension of the single-box to a multi-box model, which gives a realistic implementation of diffusion and allows to constrain the long-term corrosion process, is discussed. Furthermore, we discuss the possibilities of testing the impact of important parameters, such as formation of a protective copper sulfide layer and the effect of advective flow at the canister - bentonite boundary.

Finally, we highlight the potential of the steady-state model for future applications of near field modelling. These include predictions of the temporal evolution of the redox conditions and the modelling of corrosion in the presence of O_2. Furthermore, the required experimental information which would be useful to constrain the steady-state model is presented.

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7   Acknowledgments

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