



# Volt Equivalent diagrams as a means of displaying the electrochemical thermodynamics of the sulfur–water system



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## ABSTRACT

In this paper, we describe the use of Volt-Equivalent Diagrams (VEDs) to display the electrochemical thermodynamics of one of the most complicated chemical systems in nature; the S–H<sub>2</sub>O system, as it relates to the use of copper for the isolation of high level nuclear waste (HLNW) in granitic repositories in Sweden. The complexity stems from this element having oxidation states that vary from –2 to +8 including a multitude of fractional oxidation states. The volt equivalent describes the reactivity of a species and foretells the various chemical transformations that may occur between different sulfur-containing species in the system.

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## 1. Introduction

It is well-known that sulfur-containing species are often powerful thermodynamic activators of copper, nickel, and iron through the formation of solid sulfide phases at more active (negative) electrochemical potentials than those at which the oxides form; in some cases, by as much as several 100 mV. 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 compounds containing multiple sulfur atoms with different oxidation states. This is referred to as “fractional” oxidation state (actually, compounds containing multiple sulfur atoms in different formal 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, oxygen (air) and UV radiation, is also oxidized to sulfuric acid in an abiogenic process [1], 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. Previous work by one of the present workers [DDM] [2],

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has shown that a convenient and effective way of displaying the complex chemistry of the S–H<sub>2</sub>O system as a function of temperature, pH, and specie activity is in the form of the Volt-Equivalent Diagram (VED). The Volt-Equivalent of a species is the equilibrium potential for the reduction reaction of the species with respect to elemental sulfur multiplied by the average sulfur oxidation state (SoS) in the compound. The VED is then formed by plotting the VEs for the various species versus the average SoS for given values of temperature, pH, and specie activity.

In Sweden, SKB (Swedish Nuclear Fuel and Waste Management Co.) has, since 1977, been developing a method for final disposal of high level nuclear waste [3]. The method SKB finally chose for disposal of spent nuclear fuel is called KBS-3. The method relies on three barriers: the canister, the buffer material (bentonite clay), and granitic bedrock (Fig. 1), which alone and together should isolate and retard the spent nuclear fuel from release to the biosphere for periods exceeding 100,000 years. The safety philosophy in the KBS-3 concept relies mainly upon: (1) Placing the repository in a stable geological environment that is assumed to be of no economic interest for future generations; (2) The spent fuel is placed in both engineered and natural passive barriers. A passive barrier in this perspective is a barrier that will effectively retard the dispersal of released waste without the artificial supply of energy or other inputs; (3) The primary safety function of the barriers is to contain the spent nuclear fuel in the canisters. In order to contain the spent nuclear fuel in the canisters for very long periods, SKB has chosen the outer material of the canister to be phosphorous alloyed, oxygen-free copper (Fig. 1). The purpose of the canister 5-cm

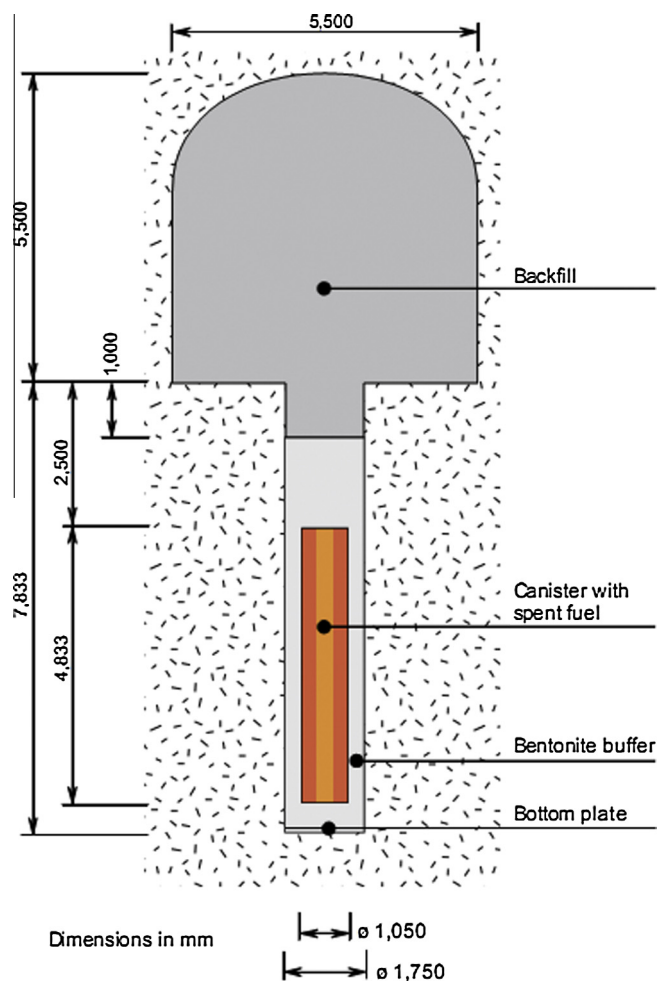


Fig. 1. Schematic of an emplaced canister in the Swedish envisioned granitic rock repository, according to the KBS-3 plan for the isolation of high level nuclear waste [4].

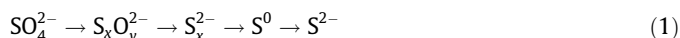
thick copper shell is to provide corrosion protection from atmospheric corrosion before placement into the repository, as well as corrosion protection after placement in the boreholes in the drifts (tunnels) in the repository that eventually will be inundated with groundwater without any dissolved oxygen (anoxic). In the anoxic groundwater environment, other corrosion mechanisms involving sulfides have been identified by SKB to be important in controlling canisters life time. At the repository depth of 500 m, bacterial reduction of sulfate has also been identified as a process that can increase the corrosion rate of copper [3]. The copper shell has no part in the canisters mechanical integrity; this is, instead, accomplished by use of an insert made of ductile iron. The granitic groundwater that is expected to inundate the repository and eventually contact the copper canisters has a typical composition as indicated in Table 1. The temperature is predicted to evolve over 10,000 years as indicated in Fig. 2. Of particular interest, in this analysis, is the temperature at the buffer inner surface, representing the interface between the copper and the environment. The temperature is predicted to increase over the first 10–20 years of storage, corresponding to the placement of more canisters and the loss of convective air cooling as the tunnels are backfilled with a sand/bentonite mixture. At longer times, the temperature decreases as the various radioactive isotopes in the waste decay, such that after 10,000 years the temperature is predicted to be near ambient.

The objectives of the present paper are to:

- Develop a rational basis for classifying the redox 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 as expressed through their Volt-Equivalents; and
- To ascertain whether an explanation of the abilities of the various sulfur species to activate copper lies within the thermodynamics of the S–H<sub>2</sub>O system.

## 2. Sulfur redox chemistry

As our work on Corrosion Domain Diagrams (CDDs) demonstrates [6], various, but not all, sulfur species can activate copper and hence their presence in the groundwater at the Forsmark repository in Sweden raises the specter of their representing a corrosion threat to copper canisters in the repository. In addition to chemical and electrochemical process, biochemical processes may be important. Thus, 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 authors know 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 [5,7], which is a component of bentonite, which is employed in the repository as a “buffer” between the copper canister and the rock (Fig. 1). However, sulfur-containing species are ubiquitous in ground-water systems, such as granitic rock HLW repositories, and their presence at low, but nevertheless significant concentrations must always be assumed when assessing the potential for corrosion. With regard to biological process, the path-independence condition of thermodynamics dictates that the processes that they affect must be thermodynamically viable (negative change in Gibbs energy for the reaction) in the environments of interest and that the bacteria themselves simply act as catalysts. Thus, for SRBs to reduce sulfate to sulfide, the change of Gibbs energy for the reaction  $\text{SO}_4^{2-} + 4\text{H}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$  must be negative, regardless of the presence of the bacteria. 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:



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, and that each of the intermediates may be available to attack the copper canister.

Eq. (1) 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:  $\text{S}_x\text{O}_6^{2-}$ ; sulfur oxidation state ( $z$ ) =  $10/x$  ( $z < 6$ ), ranging from  $z = 5$  ( $\text{S}_2\text{O}_6^{2-}$ , which does not appear to have been synthesized) to 1.67 for  $\text{S}_6\text{O}_6^{2-}$ .
- Polythiosulfates:  $\text{S}_x\text{O}_3^{2-}$ ; sulfur oxidation state ( $z$ ) =  $4/x$  ( $z < 4$ ), ranging from  $z = 2$  ( $\text{S}_2\text{O}_3^{2-}$ , “thiosulfate”) to 0.57 for  $\text{S}_7\text{O}_3^{2-}$ .
- Elemental sulfur,  $\text{S}^0$ ,  $z = 0$ .
- Polysulfides:  $\text{S}_x^{2-}$ ; sulfur oxidation state ( $z$ ) =  $-2/x$  ( $z < 0$ ), ranging from  $-2$  ( $x = 1$ ,  $\text{S}^{2-}$ ) to  $-0.33$  ( $x = 6$ ,  $\text{S}_6^{2-}$ ).

Thermodynamic data for the various species are summarized in Table 2, together with the sources from which the data were taken.

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