

## **MECHANISM OF COPPER CORROSION IN AQUEOUS ENVIRONMENTS**

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### **INTRODUCTION**

Szakalos and Hultquist have proposed that the corrosion of copper in water leads to the production of hydrogen and a previously unreported  $H_xCuO_y$  phase [1-8]. It is claimed that the mechanism of this reaction involves the dissociation of water to produce this phase and H atoms. Subsequently, this surface species may dehydrate to yield the known phase  $Cu_2O$  and the H atoms either combine to evolve  $H_2$  or absorb into the copper. Even in the presence of dissolved  $O_2$  it is claimed that corrosion occurs via this mechanism and that the  $O_2$  present is consumed, not by a direct reaction to corrode copper, but by reaction with the H atoms produced by water decomposition, thereby leading to further corrosion of the copper by water decomposition and reaction with H atoms.

This mechanism represents a radical new view of the process of copper corrosion which contravenes our present understanding of the thermodynamics of copper corrosion as well as proposing a new reaction pathway at odds with a wealth of published information. These results are then used to estimate rates of corrosion of copper nuclear waste containers which are orders of magnitude greater than those calculated by SKB and other national nuclear waste disposal programs.

### **THE WORKSHOP PRESENTATIONS**

At this meeting Hultquist, Szakalos, and SKB had the opportunity to present their research results and/or their approach to investigating the copper corrosion process as it pertained to buried nuclear waste containers. SKB (Lilja) chose to present its wide ranging and extensive program on copper corrosion and also the results of first principles calculations of the thermodynamic properties of Cu-O-H, the phase claimed as a corrosion product by Hultquist ET AL. Hultquist presented the results of his research conducted over the last 23 years, which was already well documented in the available published papers provided before the workshop.

The presentation by Szakalos, however, merits more detailed comment, since it started with the claim that the instability of copper in pure  $O_2$ -free water was undisputed among thermodynamic experts, which rather pre-empted the purpose of the meeting. A case was made that many of the rates measured in the Swedish (SKB) and other national programs (Canada, Finland, Japan) were in the range measured by Hultquist ET AL., implying, without explicitly stating, that even the SKB measurements justified their claims.

In the subsequent discussion period a number, but not all, of these assertions were challenged. For instance, Fraser King (a consultant to SKB) pointed out the inconsistency

in comparing predicted corrosion rates in the Swedish/Finnish programs (0.33 mm in  $10^6$  years) to the results of conservative estimates based on mass balance calculations in the Japanese program (18 – 26 mm in  $10^3$  years) (Quoted from SKB report TR-01-23). Other references quoted in this presentation also do not stand up to scrutiny. For example, it is implied that the observation of intergranular corrosion on copper in *aerated* sulphide-containing salt water by Al.Kharafi et al. [9] indicates this process will occur under anoxic repository conditions, but does not acknowledge the positive electrochemical potentials used in the experiments described in the paper. Such redox conditions are only achievable under fully aerated conditions in the presence of sulphide. The authors [9] claim that “The present results are immediately relevant to the discussion of the proposed use of copper containers for the disposal of Swedish, Finnish and Canadian high-level waste deep in granite environments” is incorrect, but accepted by Szakalos.

The claim that the corrosion of copper cooling systems is an example of copper corrosion in  $O_2$ -free water is a further example of what can only be described as an incomplete analysis of the available literature. The corrosion processes occurring in these systems are well characterized and known to be due to the in-leakage of oxygen [10]. To quote from Park et al.[10], “These problems have been understood from the relationship between the corrosion rate of copper and a DO (dissolved oxygen) concentration. The experimental results showed a bell-shaped relationship (3 references given). The corrosion rate in LOWC (low-oxygen water chemistry) is satisfactorily low owing to its (Cu) thermodynamic stability, and is reduced significantly in HOWC (high-oxygen water chemistry) owing to passive oxide formation. However, intermediate oxygen water chemistry (IOWC) ( $50 \text{ ppb} < \text{DO} < 2 \text{ ppm}$ ) results in much higher corrosion rates. The IOWC may occur when air leaks into the system.”

In fact, contrary to supporting the claim that the extensive corrosion and finely divided corrosion product observed in the 15 year test [7] is due to Cu corrosion by  $H_2O$  to produce  $H_2$ , these observations suggest the copious corrosion observed was due to the maintenance of IOWC conditions or a cycling between LOWC and HOWC conditions. As in the Cu cooling systems the maintenance of totally anoxic conditions would have been very unlikely. King [11] makes a similar point in his review of the experiments of Hultquist et al.

## **REVIEW OF THE CORROSION MECHANISM OF COPPER UNDER ANOXIC CONDITIONS**

The two key processes involved if the corrosion mechanism proposed by Hultquist et al. is to occur are the production of  $H_2$  and the formation of a stable corrosion product at potentials well below those presently accepted in thermodynamic calculations.

### **Hydrogen Production**

The key feature of the corrosion process proposed by Hultquist et al. is the production of  $H_2$ . In their initial publication [1],  $H_2$  was detected using a solid-electrolyte  $H_2$  probe, pre-

calibrated over a range of H<sub>2</sub>/N<sub>2</sub> mixtures. In other experiments (with the much more readily corrodible Zn [2]) the response of this probe was validated against manometric measurements. They also used an ion pump to measure pressure build-up, assumed to be due to H<sub>2</sub> formation, and eventually thermal out-gassing coupled to mass spectrometry to determine hydrogen present in corrosion products and the Cu itself. Except in this last case, there are no grounds to unequivocally dispute that H<sub>2</sub> was formed, despite the number of experimental uncertainties noted by King [11].

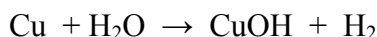
Except for the initial study the authors claim that the development of a H<sub>2</sub> pressure within a sealed vessel will suppress corrosion as thermodynamic equilibration is approached. This argument is used to explain apparent decreases in H<sub>2</sub> generation rates with time, and to account for the major differences in the extents of corrosion observed on specimens corroded over a 15 year period in vessels sealed with Pd (through which, they claim, H<sub>2</sub> can escape and extensive corrosion is possible) and with Pt (through which, they claim, H<sub>2</sub> cannot escape and corrosion should be suppressed). It is also assumed, to account for apparent imbalances in the extent of corrosion and the amount of H<sub>2</sub> detected that considerable amounts of H are absorbed into the Cu. This last conclusion must be treated with suspicion, since the solubility of H in Cu is known to be small (as pointed out by King [11]) and the only analytical evidence provided by Hultquist et al. comes from out-gassing experiments on specimens covered in corrosion products whose degree of hydration is unknown. A similar reservation applies to the SIMS analyses of Hultquist et al., and the claim that the heavily corroded specimen from the 15 year experiment is H embrittled since it cracked on bending is speculative at best. The reference offered in support [12] is not relevant since it involved hydrogen charging of Cu at currents greater than 10 mA.cm<sup>-2</sup>, which is many orders of magnitude greater than could possibly be sustained by corrosion.

### **The Corrosion Product**

For a corrosion process to be sustained by H<sub>2</sub>O reduction, the formation of an anodic corrosion product must occur. This introduces a dilemma since, with the exception of copper sulphides (Cu<sub>x</sub>S with x ~ 2), there are no known stable corrosion products, according to accepted thermodynamic reasoning, if the corrosion potential is maintained in the range where water reduction is thermodynamically possible. The corrosion product formed in their experiments [5] was analyzed by X-Ray Diffraction (XRD) and Secondary Ion mass Spectrometry (SIMS). XRD indicated the presence of CuO and Cu<sub>2</sub>O and the SIMS showed a range of products with varying O and H contents. Consistent with earlier observations [3], the H content of the products was higher in tests performed in the absence of O<sub>2</sub>. Despite the XRD results, the authors claimed the formation of a new phase, H<sub>x</sub>CuO<sub>y</sub>. Unfortunately, both techniques are ex-situ and the phases observed may not be those formed by corrosion, but a combination of the oxides present at the start of the experiment, the corrosion products, and their conversion products when exposed to air prior to analysis. Consequently, these analyses neither confirm nor disprove the formation of H<sub>x</sub>CuO<sub>y</sub>. In response to comments that oxides (particularly Cu<sub>2</sub>O) initially present on Cu specimens at the start of their experiments were ignored, Szakalos et al.[8] claimed that they would have been reduced by the H<sub>2</sub>

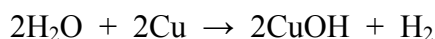
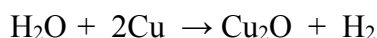
formed in their experiment. This argument is unconvincing since there is considerable evidence to show that air-formed films on Cu are notoriously difficult to fully reduce, even electrochemically [13,14].

To justify their claim that the phase,  $H_xCuO_y$ , was energetically possible, Hultquist et al.[8] used molecular dynamics simulations to obtain a free energy of formation for the reaction



of -311 kJ/mol. Such a value indicates this reaction is energetically favourable. As noted by King [11], this not consistent with the value of + 9kJ/mol calculated by Protopopoff and Marcus [15]. Even if the formation of such a *surface adsorbed* species were energetically possible (Protopopoff and Marcus give a value of -228 kJ/mol for the free energy of formation of  $Cu(OH)_{ads}$  based on a considerable experimental database), it does not demonstrate that the formation of a three dimensional  $H_xCuO_y$  is, therefore, energetically feasible.

In fact, the first principles calculations of Korzhavji (presented in the meeting) showed  $HCuO$  to be an unstable phase with respect to  $Cu_2O$ . His calculations also showed that the corrosion of Cu by  $H_2O$ , taking into account the three dimensional nature of the corrosion product (as opposed to the two dimensional nature of a surface reaction) via the reactions



were both energetically unfavourable. The values of  $\Delta H$  and  $\Delta G$  for these reactions were calculated to be large and positive, leaving little leeway to dispute the validity of the calculations.

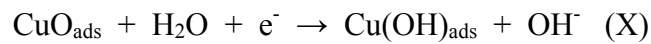
### **Potential-pH Diagrams**

Szakalos et al. [5] then proposed a modified potential – pH diagram to include the  $H_xCuO_y$  phase, assumed to be stable over a potential range from the stability line for  $Cu_2O$  formation to below the stability line for  $H_2O$ . There is a well documented literature based on electrochemical measurements coupled to sensitive in-situ surface analytical techniques such as surface enhanced Raman spectroscopy (SERS) [16], atomic force microscopy (AFM) [17], glancing incidence X-ray diffractometry (XRD) [18] and ellipsometry [19] demonstrating the formation of monolayer to sub-monolayer levels of a  $Cu(OH)_{ads}$  species within the thermodynamically forbidden region of the potential-pH diagram. Two sets of authors [15,17] have proposed modification of the standard potential-pH diagram to include these *surface* states.

The calculations performed by Protopopoff and Marcus [15] are particularly thorough and based on an extensive experimental database. They note that Cu shows an

intermediate behavior between the transition metals (e.g., Fe and Ni), which strongly adsorb OH and H, and the noble metals (e.g., Au and Ag) which do not. According to their calculations there is a narrow underpotential deposition region where adsorbed H and OH could coexist, making it feasible that, on the monolayer scale, the decomposition of H<sub>2</sub>O to produce H<sub>ads</sub> and OH<sub>ads</sub>, leading to the production of H<sub>2</sub> and Cu(OH)<sub>ads</sub> could occur. This would be minor in extent, since it would be limited by the ability to form only a monolayer of what would be the corrosion product, Cu(OH)<sub>ads</sub>. Since their thorough review of literature could find no experimental evidence for the formation of H<sub>ads</sub>, they assumed it would have a comparable bond energy to that for H<sub>ads</sub> at the metal/gas interface.

Only one study [20], performed in alkaline solutions using SERS, has shown evidence for the formation of Cu(OH)<sub>ads</sub> via H<sub>2</sub>O reduction,



the key reaction according to Hultquist et al. It is clear from their Raman results that a pre-oxidized surface state (CuO<sub>ads</sub>) is required for this reaction to progress. Maurice et al. [21] could find no evidence for this reaction using electrochemical techniques coupled to in-situ AFM. The latter authors noted that the key difference between these two studies was the state of the surface; electropolished and smooth in their case, but slightly roughened by an electrochemical oxidation-reduction cycle (necessary to activate the SERS signal) in the experiments of Hartinger et al. [20]. Activation of a SERS signal requires the formation of nanosized surface Cu particles, and the Raman results of Hartinger et al [21] could be explained by the presence of CuO<sub>ads</sub> surface species present due to the incomplete reduction of the oxide formed during the oxidation-reduction cycle. It was speculated that they could be subsurface, i.e., on the underside of the Cu nanoparticles.

The essential feature of this discussion is the formation of nanoparticulate material during the oxidation (to bulk oxide) – reduction cycle on Cu, as well as the possibility that mixed Cu oxidation states (Cu/Cu<sup>I</sup>Cu<sup>II</sup>) coexist on the surface. Such states are known to be catalytic for H<sub>2</sub>O, but especially O<sub>2</sub>, reduction [22]. This raises the real possibility that, in an experiment started with an oxide-covered surface and a solution containing dissolved O<sub>2</sub>, the consumption of O<sub>2</sub> could lead to first the exhaustion of O<sub>2</sub> and then the reduction of the oxide. If, as in the case of the Cu cooling systems discussed above [10], this lead to the formation of partially reduced Cu surface species (i.e., CuO<sub>ads</sub>) then reaction X could be activated leading to the production of H<sub>2</sub>. Of course, such a reaction is only sustainable on nano-particulate material until available surface O states are consumed. An on-going process is only sustainable with a continuing supply of O<sub>2</sub>, as indicated in the heat exchanger studies. Such a mechanism could explain the apparent limited production of H<sub>2</sub> in some of the experiments of H and S. *(I am indebted to Roger Newman, University of Toronto, for the suggestion that the “violation of thermodynamics” would require the surface energy generated by the involvement of nanoparticles in the 2 to 3 nm size range).*

## The Corrosion Mechanism

Despite the fact that dissolved  $O_2$  will be unavoidably present, at least initially, in their experiments, the possibility that dissolved  $O_2$  was involved in the corrosion of Cu was not considered by Hultquist et al. Instead,  $O_2$  was assumed to be consumed by reaction with H atoms produced by the reduction of  $H_2O$ . While this mechanism may apply if the metal was exposed only to the aqueous vapour phase with no condensed liquid phase present, it is at odds with the very extensive literature on the reduction of  $O_2$  dissolved in aqueous solutions. This literature encompasses not only studies in corrosion science and engineering but also energy systems such as batteries and, in particular, fuel cells. This apparent dismissal of a very large body of published experimental evidence suggests a fundamental misunderstanding of the aqueous corrosion process. As discussed above, and in detail for Cu by King [11], the  $O_2$  reduction reaction is strongly catalyzed on oxide/metal interfaces with mixed oxidation states (in this case  $Cu/Cu^I/Cu^{II}$ ) at potentials where surface  $Cu(OH)_{ads}$  species exist, but at potentials too positive for  $H_2O$  reduction. The adoption of a reaction mechanism that applies in the vapour phase ignores this well proven electrochemical mechanism involving the utilization of solution connected anodes and cathodes. It would appear that this conceptual misunderstanding is a key premise in their insistence that  $H_2O$  rather than  $O_2$  reduction dominates the corrosion process.

## Anoxic Corrosion in the Presence of Other Anions

There is a wealth of available literature to show that many other anions besides  $OH^-$ , chemisorb on Cu surfaces. Particularly strongly adsorbed are the halides ( $I^-$ ,  $Br^-$ ,  $Cl^-$ ) [23-26] and especially  $SH^-$ . Of particular interest in the present context are  $Cl^-$  and  $SH^-$  both of which are anticipated in the Swedish groundwaters to which waste containers would eventually be exposed. These adsorption processes occur in the potential region close to the water reduction region. Commonly  $Cl^-$  is more strongly adsorbed than  $OH^-$  and has been observed electrochemically to catalyze  $H_2O$  reduction to  $H_2$  [25]. However, there is no evidence to show that stable chloride-containing oxide/hydroxide phases can be formed by  $H_2O$  reduction. On the contrary,  $Cl^-$  has been shown, by in-situ STM investigations, to be absorbed and desorbed reversibly without interfering with the surface structure of Cu [24]. Phase formation only occurs at considerably more positive potentials where  $H_2O$  reduction to  $H_2$  is thermodynamically impossible.

Despite these published studies, Szakalos (in correspondence after the workshop) has claimed that the Cu hydroxyl chloride, paratacamite ( $Cu_2(OH)_3Cl$ ), containing  $Cu^{II}$  can form by water reduction under anoxic conditions. Offered in support of this claim is a statement from the UK Environment Agency Report [27] claiming this is the case. This statement is not referenced in the report. Also offered in support of this claim is evidence from a study of historical artefacts from which it is concluded that paratacamite is more stable than  $Cu_2O$  [28]. This claim is unjustified (and not made by the authors of the paper). Secondly, the conclusions drawn by Szakalos (that the evidence in this paper justifies his claim that paratacamite, and hence all the corrosion products in the 5-year LOT exposure test [29] were formed under anoxic conditions) are the opposite of those drawn by the authors. It is worth quoting the conclusions from the paper of Domenech-

Carbo et al. [28]; “Thus “green’ samples of C1-13 and C1-14 in which a significant amount of CuCl accompanies copper trioxychloride forms can tentatively be attributed to a corrosion process under wet aerobic conditions, while samples C1-9 containing copper trioxyhydroxychloride (*a category which includes paratacamite*) plus malachite, probably corresponds to a region of the buried helmet in contact with wet oxygenated soil, then exposed to relatively high carbonate concentrations. Finally “reddish” deposits in sample C1-11 is formed by cuprite. Copper trihydroxychlorides accompany cuprite in sample C1-12 while CuCl is absent. These features suggest that the corrosion process in this portion of the helmet occurred in a relatively dry and aerobic environment.” One can only conclude that the observations and conclusions in this paper strongly support the claims made in the 5-year LOT report [28] that the oxide/hydroxide/hydroxychloride phases observed are the products of Cu corrosion involving O<sub>2</sub> reduction.

The only anion for which there is thermodynamic and experimental evidence to show it can lead to the formation of bulk corrosion products by H<sub>2</sub>O reduction is SH/S<sup>2-</sup>. The available information has been comprehensively calculated, reviewed and discussed in SKB reports [30-32]. More recent studies have shown that the corrosion product is exclusively Cu<sub>x</sub>S (with x between 1.8 and 2), with no evidence for the simultaneous formation of oxide/hydroxide/hydroxychloride corrosion products under anoxic conditions [33-36]. Even in solutions containing 5 mol/L chloride there was no evidence for any product other than Cu<sub>x</sub>S [37].

## SUMMARY AND CONCLUSIONS

- A review of the literature provided for this workshop, the presentations made at the workshop, and a personal search of additional literature shows there is no evidence that significant corrosion of Cu can be sustained by water reduction.
- The claims that H<sub>x</sub>CuO<sub>y</sub> and/or Cu<sub>2</sub>(OH)<sub>3</sub>Cl are formed as stable corrosion products by the anoxic corrosion of copper cannot be justified. In the case of H<sub>x</sub>CuO<sub>y</sub> no experimental characterization is available and theoretical calculations show the phase to be unstable. In the case of Cu<sub>2</sub>(OH)<sub>3</sub>Cl the published literature shows it is a product of the aerobic, not the anoxic, corrosion of copper. Its observation in long term tests in which the exclusion of oxygen cannot be guaranteed is to be expected.
- It may be possible that the reduction of oxides/hydroxides present at the start of experiments could lead to nanoparticulate copper able to temporarily support water reduction and the production of hydrogen. However, for such a process to lead to the accumulation of meaningful corrosion damage would require the presence of dissolved oxygen at least intermittently.
- There is evidence to show that the maintenance of low levels of dissolved oxygen (50 ppb to 2 ppm) could lead to much more extensive corrosion than lower or higher oxygen levels. This offers a potential explanation for the extensive corrosion observed by Hultquist et al in one of their 15 year experiments.
- The only anionic species for which there is thermodynamic and experimental evidence to show it can sustain the anoxic corrosion of copper is sulphide. In this

case the stability of the corrosion product ( $\text{Cu}_x\text{S}$ ;  $1.8 < x \leq 2$ ) is well characterized.

- It can be concluded that the anoxic corrosion of Cu can only be sustained in the presence of sulphide.

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