

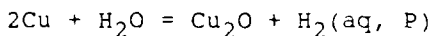
SHORT COMMUNICATION

ON THE CORROSION OF COPPER IN PURE WATER.

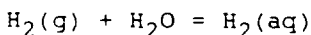
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Abstract. Due to a recent publication questioning well known thermodynamic data the corrosion of copper in distilled water has been studied. No hydrogen evolution was observed during an exposure period of 61 days using a gaschromatographic technique. Cu_2O was the only corrosion product detected by means of ESCA and cathodic reduction. The corrosion rates obtained for two different copper qualities are much lower than the corrosion rate reported by Hultqvist and are ascribed to the reaction between the copper foils and residual oxygen initially present in the water. In conclusion the present investigation confirmed well established thermodynamics, which means that oxidation of copper by pure deoxygenated water under the formation of hydrogen as proposed by Hultqvist is not thermodynamically feasible.

Copper has been proposed as a reasonably inert material for the production of canisters for radioactive waste. The main advantage of copper is its stability in ground water (Cu is a noble metal). A thorough discussion of the stability of copper and possible corrosion reactions has been given in technical reports published by the Swedish Nuclear Fuel and Waste Management Co^{1,2}. The work has also been summarized by Mattsson³. However, the corrosion of copper in pure oxygen free water has been disputed by Hultqvist in a recent publication⁴. In his study the corrosion of copper in initially aerated distilled water was followed by monitoring the hydrogen (H_2) concentration in the reaction vessel with a solid electrolyte probe described by Lyon and Fray⁵, working on the basis of a concentration cell. From the voltage versus time of exposure plot the H_2 production by a 99.7 wt% copper foil with surface area 1460 cm^2 was found to be $2.2 \cdot 10^{-6} \text{ g} \cdot \text{h}^{-1}$, corresponding to a corrosion rate of $0.1 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$ if copper is oxidized by water according to the reaction.



Using standard free energies of formation of Cu_2O and H_2O and the equilibrium constant $K = 0.85 \cdot 10^{-3} \text{ M/atm}$ for the reaction



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we obtain the equilibrium partial pressure (H_2) = $3 \cdot 10^{-18}$ bar. The highest partial pressure in the corrosion cell was reported by Hultquist to be close to 0.45 bar.

In view of this inconsistency, Hultquist suggests a non reversible cathodic reaction, ultimately leading to the formation of H_2 , "for which we cannot predict an upper hydrogen pressure (in an oxygen free corroding system)". This statement is clearly contradictory to the second law of thermodynamics.

Due to the important application of copper canisters for final storage of nuclear waste we have made a reinvestigation of the copper corrosion by pure deoxygenated water using direct gas analysis.

EXPERIMENTAL

The copper foil qualities used in this investigation are Merck >99.7 wt% (0.1 mm thick, 1600 cm² surface area) and Alfa 99.9995 wt% (0.025 mm thick, 600 cm² surface area).

The water used was deionized, double distilled in a quartz apparatus and deaerated by purging with Ar (AGA SR-quality) containing less than 1 ppm oxygen. The foils were rinsed with methanol followed by ethanol and quickly dried in a stream of Ar before use. The foils were thereafter placed in glass vessels (1365 cm³ volume) in such a way that all parts of the surface areas were accessible for contact with water and the vessels flushed with Ar (AGA SR-quality). Water was thereafter transferred to the copper containing vessels by applying an overpressure of Ar to the water reservoir. The water and gas volumes of each vessel were 900 and 465 cm³ respectively. Assuming the solubility of O_2 and H_2 to be 1.4 and 0.85 mmol·dm⁻³ respectively at 25°C⁷ more than 98% of these gases should be in the gas phase of the reaction vessels. To monitor the H_2 the vessels were connected to the sampling loop of an Argograf (AGA) allowing small volumes of the gas phase to be transferred to the carrier-gas stream (Fig. 1). The

gaschromatograph was calibrated by applying the same sampling procedure to a corresponding vessel containing Ar and known concentrations of H_2 .

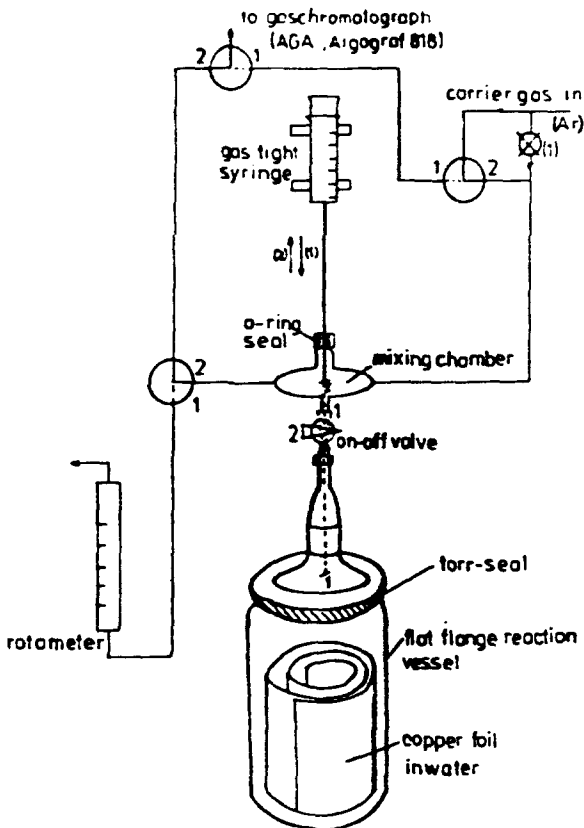


Fig 1: Schematic of reaction vessel and gas sampling system.

At the end of the experiment the exposed copper foils were quickly dried in a stream of Ar and small areas of the surfaces analyzed by ESCA and cathodic reduction. Larger samples (50 cm^2 surface area) were immersed for 120 minutes in 50 cm^3 of a thoroughly deaerated $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$ solution. The solutions were thereafter analyzed for copper by atomic absorption spectrophotometry. Unexposed copper foils were used to obtain reference solutions.

RESULTS

The exposure lasted for 61 days and no H_2 was detected during the time of the experiment. The detection limit was approximately 10 ppm. To ensure that the absence of H_2 was not due to any leakage small volumes of H_2 , yielding a concentration of 100 ppm in the gas phase of the reaction vessels were added and the H_2 concentration monitored for 12 days. No change in concentration i.e. no leakage was observed.

The two species present on the surface of the exposed copper foils were, according to the ESCA data Cu and Cu_2O . The result of the ESCA measurements was corroborated by the potential of the cathodic reduction, showing that Cu_2O was the only corrosion product. The thickness of the corrosion product layer on small areas of the most corroded parts of the copper foils was calculated from the integrated current during the time of reduction⁹. The results are given in table 1.

Table 1

Thickness of corrosion product layer by cathodic reduction.

Sample		Thickness (Å)
Merck	(1)	1347
>99.7	(4)	484
Alfa	(2)	4613
99.9995%	(3)	3229

The amount of Cu_2O going into solution in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$ from exposed samples are summarized in table 2.

Table 2

Corrosion products dissolved in 1M HClO₄.
(50 cm² surface area, 50 cm³ solution)

Copper quality	Dissolved Cu mg·dm ⁻²	Average corrosion layer thickness (Å)	Comments
Merck > 99.7%	2		as received
	21.5		discoloured
	19.6	235	surface
	21.5		
	11.4		slightly
	15.0	132	discoloured
	9.0		surface
Alfa 99.9995%	30		discoloured
	40	354	surface
	25		

DISCUSSION

The surface of the exposed copper foils were unevenly corroded, large areas were seemingly unaffected whereas smaller areas were clearly discoloured. The cathodic reduction was carried out on 0.5 cm² samples of the discoloured parts and the results obtained from dissolving the corrosion products in 1M HClO₄ probably better characterize the average thickness of the corrosion product layer. The ratio between the corrosion depths measured by the two methods is approximately 10.

Based on the detection limit of 10 ppm H₂ and the reaction $H_2O + 2Cu = Cu_2O + H_2$ the upper limits for the copper corrosion were calculated and are given in table 3 together with the average corrosion rates calculated from the dissolution data in table 2.

It is quite clear, based on the upper limit for hydrogen production, that the amount of copper corrosion caused by oxidation of water is at most $4 \cdot 10^{-5}$ $\mu\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$. By using an

alternative method Simpson and Schenk¹⁰ have decreased the detection limit of hydrogen to $3.7 \cdot 10^{-8} \mu\text{g} \cdot \text{h}^{-1} \cdot \text{m}^2$ as compared to $0.1 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$ reported by Hultquist.

Table 3

Average Cu corrosion rate calculated from dissolution of corrosion products and H₂ evolution at the detection limit 10 ppm.

Copper quality	Corrosion rate ($\mu\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$)	
	corrosion prod	H ₂ (detection limit)
Merck > 99.7%	0.014	$1.1 \cdot 10^{-5}$
	0.0082	
Alfa 99.9995%	0.021	$3.6 \cdot 10^{-5}$

Corrosion may be caused by oxygen present in the reaction vessels i.e. according to the thermodynamically feasible reaction $2\text{Cu} + 1/2 \text{O}_2 \rightarrow \text{Cu}_2\text{O}$, the total amount of oxygen required by the mass balance of the corrosion products are given in table 4.

Table 4

Oxygen consumption from average corrosion rates.

Cu-quality	O ₂ consumed mg	Req initial O ₂ conc in gasphase %	Purging efficiency %
Merck > 99.7%	4.3	0.65	96.4
	2.4	0.36	98.0
Alfa 99.9995%	1.9	0.30	98.3

As can be seen if the deoxygenation by Ar-purging was less efficient than approximately 97%, which is quite probable as no extreme measures were taken, the oxygen content of the reaction vessels would be sufficient to explain the corrosion. The higher rate of corrosion of the Alfa 99.9995% copper foil with the smaller surface area also gives support to the assumption of oxygen corrosion. The corrosion rates calculated from dissolution of the corrosion product Cu_2O from the exposed copper surfaces in our study are at least 5 times smaller than the corrosion rate given by Hultquist. It should be noted that more oxygen was initially available per unit surface area in the work of Hultquist and this probably accounts for the higher rate of corrosion observed in his experiments.

The results presented in this paper do not support the observation of Hultquist. Taking into account also the paper published by Simpson and Schenk, some doubts must be put on Hultquist's method of measuring hydrogen. It is to be noted that the long time stability of the electrolyte probe under localized humid conditions has not been satisfactorily demonstrated as the longest time of exposure in the work of Lyon and Fray is 28 hours. A likely explanation of the time dependence observed by Hultquist is that his emf system gradually deteriorated.

CONCLUSIONS

No hydrogen evolution by corrosion of pure copper in deoxygenated distilled water was observed during an exposure period of 61 days. The experimental data do not support the claims by Hultquist that

- hydrogen is evolved during corrosion of copper in water i.e. pure copper is oxidized by water
- the escape rate of hydrogen from the corroding system is of decisive importance for the corrosion kinetics.

ACKNOWLEDGEMENTS

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REFERENCES

1. The Swedish Corrosion Institute and its reference group
Copper as canister material for unprocessed nuclear
waste, evaluation with respect to corrosion.
KBS TR-90 (1978).
2. Corrosion resistance of a copper canister for spent
nuclear fuel.
KBS TR 83-24 (1983).
3. E. Mattsson in
Scientific Basis for Nuclear Waste Management.
Ed: G.J. McCarthy
Vol 1, 271 (1978).
4. G. Hultquist
Corrosion Science 26, 173 (1986).
5. S.B. Lyon and D.J. Fray
Br. Corros. J. 19, 23 (1984).
6. Handbook of Chemistry and Physics
46th Edition
The Chemical Rubber Co 1965
7. S. Zakipour
Korrosionsinstitutet 1987-04-02 (in Swedish).
8. J.P. Simpson and R. Schenk
Corrosion Science 27, 1365 (1987).

Editor's Note: There has been much discussion on the results of Dr Hultquist with the three authors of this paper. The situation has been examined by at least five reviewers one of whom writes:

" In the three papers by Hultquist, Simpson et al. and Eriksen et al. it seems to me that there are essentially two problems. One is the experimental observation on the hydrogen evolution in the copper/water systems and the other is the thermodynamic interpretation of the experimental observations. From the standpoint of scientific appraisal, it seems to me that the former would be more important than the latter. Hultquist detected an increase of hydrogen concentration in his copper/water system using a hydrogen probe, while Simpson et al. and Eriksen et al. detected no hydrogen evolution by use of direct gas analysis techniques different from that used by Hultquist in their copper/water systems. Obviously we need further experiments, since the experimental conditions as well as hydrogen detectors are not the same in the three papers.

As to the thermodynamic arguments, it can be thermodynamically predicted that a pure copper/water system would produce no hydrogen and that no oxidation of copper by water would occur, as pointed out by Eriksen et al. in their submitted manuscript. The real experimental system, however, is not always an ideal system consisting of a pure copper sample and a liquid of pure water. For instance, the copper/water system Hultquist employed was not an ideal system for the thermodynamic discussion on the copper/water reactions, but contained in the later stage of observation some amount of copper oxide probably as Cu_2O on the copper surface. Then we would have to take into account the hydrogen electrode reaction on Cu_2O , which is a p-type semiconductor and which may photocatalyze the cathodic hydrogen evolution at potentials more noble than the hydrogen evolution potential of metallic copper. I am not intending to say that this kind of argument should have been made in the three papers. I

would rather like to say that thermodynamic arguments, which in most cases are valid only for simplified systems, may not be enough to provide conclusive evidence for denying the experimental facts reported by workers of complicated phenomena such as metallic corrosion. I know that thermodynamics is of fundamental importance in understanding and predicting corrosion phenomena. Nevertheless, I would not refuse to believe that there might be complicated phenomena which appear to contradict the thermodynamic prediction."