

**Subject: Re: SV: SKB-rapport om kopparkorrosion****Date:** onsdag 24 oktober 2007 15.44**From:** Johan Swahn <johan.swahn@mkg.se>**To:** Olle Olsson <olle.olsson@skb.se>**Cc:** Fred Karlsson <fred.karlsson@skb.se>, Anni Bölenius <anni.bolenius@skb.se>, <bo.stromberg@ski.se>, <Bjorn.dverstorp@ssi.se>, Anders Wiebert <anders.wiebert@ssi.se>, <kaj.nilsson@oskarshamn.se>, "Virpi Lindfors (E-mail)" <Virpi.Lindfors@osthammar.se>, <torsten.carlsson@environment.ministry.se>, <bjorn.hedberg@environment.ministry.se>, Elisabeth André Turlind <elisabeth.andre.turlind@ski.se>, Ansi Gerhardsson <ansi.gerhardsson@environment.ministry.se>, Lisa Hedin <lisa.hedin@mkg.se>, "Mats Lindman (E-mail)" <mali@c.lst.se>, <sven.andersson@h.lst.se>, Fred Karlsson <fred.karlsson@skb.se>, Lars Werme <lars.werme@skb.se>, Tommy Hedman <tommy.hedman@skb.se>, Saida Engström <saida.engstrom@skb.se>, Carl Sommerholt <Carl.Sommerholt@skb.se>**Conversation:** SV: SKB-rapport om kopparkorrosion

Hej Olle!

Tack för ditt meddelande som finns nedan tillsammans med min förfrågan om publiceringen av resultaten av kärnkraftsindustrins kärnavfallsbolag Svensk Kärnbränslehantering AB:s, SKB:s, tidiga arbete om korrosion av koppar i rent syrefritt vatten.

Eftersom rapporten SKB TR 88-17 inte finns på er hemsida (gäller alla TR innan 1993) undrar jag om du kan se till att jag får tre exemplar av den.

Jag har snabbt ögnat igenom de två artiklarna du skickade och konstaterar att arbetena i bägge fallen finansierades av kärnavfallsbolag (NAGRA respektive SKB). Jag uppmärksammar även den "Editors note" som finns i det senare av artiklarna (T.E Eriksen et al., Corrosion Science, Vol. 29, No. 10, pp. 1241-1250, 1989) och som avslutas med:

"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."

Tidskriftsredaktören menar tydligen att termodynamiken inte kan förutsäga alla resultat utan att det kan finnas korrosionsprocesser som inte stämmer överens med termodynamiska teorier. I kontakter som MKG haft med korrosionsforskaren professor Digby D Macdonald vid Pennsylvania State University verkar han tvärtom mena att termodynamiskt kan korrosion av koppar i helt syrefritt kan förutsägas äga rum under vissa villkor (se MKG:s hemsida).

Tydligen finns det en hel del att utröna vad gäller teori och verklighet i fråga om korrosion av koppar i syrefritt vatten. När frågan nu på nytt är aktualiserad med nya forskningsrön menar jag att det är viktigt att frågeställningen undersöks grundligt och av industrin oberoende, även internationellt oberoende, aktörer. Angelägenhetsgraden ökar enligt min mening när Peter Szakálos och Gunnar Hultquist i bilagan till sitt brev till SKI (dnr 2007/1789, finns på MKG:s hemsida) kritiserar tolkningen av resultaten i SKI rapport 95-72 "Kopparkorrosion i rent syrefritt vatten" av Kenneth Möller.

Det förvånar mig inte att "industrins bedömning är att även om teorin skulle stämma skulle inte det leda till en korrosionsprocess som skulle äventyra säkerheten i

förvaret". Det som oroar mig är att resultaten stämmer. detta skulle innebära att industrin och dess konsulter, med den världsledande ställning inom området kopparkorrosion som de tillsammans ska ha, inte har sett frågeställningen som viktig i sitt forskningsprogram och sin säkerhetsanalys.

Bästa hälsningar,

Johan

cc Ursprunglig kopielist

--

Johan Swahn

Kanslichef  
Miljöorganisationernas kärnavfallsgranskning (MKG)  
Box 7005, 402 31 Göteborg

Telefon: 031-711 00 92 Fax: 031-711 00 93

Mobil: 070-467 37 31

E-post: johan.swahn@mkg.se

Skype: jswahn

Hemsida: <http://www.mkg.se>

Besöksadress: Norra Allégatan 5

On 07-10-24 12.34, "Olle Olsson" <olle.olsson@skb.se> wrote:

> Hej Johan!

>

> Först av allt vill jag betona att självfallet är alla forskningsresultat  
> tillgängliga. Detta för att både de granskande myndigheterna och andra aktörer  
> ska kunna bedöma våra slutsatser kring forskningen.

>

> Hultqvists teorier har utretts av både SKB och SKI utan att resultaten kunnat  
> upprepats. De vetenskapliga referenser som Ni även efterfrågar i ert brev till  
> SKI daterat 2007-10-23 är

>

> SKB TR 88-17

> On the corrosion of copper in pure water

> Eriksen, T E 1); Ndalamba, P 1); Grenthe, I 2)

> 1988

>

> Dessutom bifogas två referenser publicerade i vetenskapliga tidskrifter. SKI  
> 95:72 behandlar också detta.

> Vår bedömning är att även om teorin skulle stämma skulle inte det leda till en  
> korrosionsprocess som skulle äventyra säkerheten i förvaret.

>

> Hoppas att denna information är det ni efterfrågar.

>

>

> Med vänlig hälsning

>

> Olle Olsson

> Avdelningschef Platsundersökningar

> Svensk Kärnbränslehantering AB (SKB)

> Box 5864

> 102 40 Stockholm

> tel: 08-45 98 405

> mobil: 070-565 22 64

> fax: 08-45 98 465

> olle.olsson@skb.se

>

>

>

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> -----Ursprungligt meddelande-----

> Från: Johan Swahn [mailto:johan.swahn@mkg.se]  
> Skickat: den 17 oktober 2007 11:31  
> Till: Olle Olsson  
> Kopia: Lisa Hedin; Johan Swahn  
> Ämne: SKB-rapport om kopparkorrosion  
>  
>  
>  
> [Ursäkta att det kom flera meddelanden. Använder just nu web-mejl och är lite  
> ovan. Nu fick jag med en titel på meddelandet. J]  
>  
> Hej Olle!  
>  
> På er hemsida har ni gjort en kommentar till KTH-forskarnas resultat vad  
> gäller kopparkorrosion i syrefritt vatten. Där står det bland annat att:  
>  
> "Teorin är inte ny utan lanserades redan för cirka tjugo år sedan. SKB gjorde  
> tidigt försök att återupprepa experimentet, utan att lyckas."  
>  
> Kan du skicka mig rapporten från det försöket?  
>  
> Bästa hälsningar,  
>  
> Johan

## SHORT COMMUNICATION

### HYDROGEN EVOLUTION FROM CORROSION OF PURE COPPER.

J.P. Simpson, R. Schenk.

Sulzer Brothers Ltd., CH-8401 Winterthur, Switzerland.

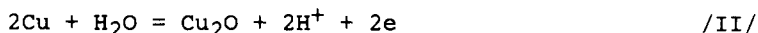
**Abstract.** Using a sensitive direct gas analysis technique, an attempt was made to detect hydrogen evolution from copper corroding in neutral oxygen free chloride solutions. No hydrogen was detected at evolution rates 3 orders of magnitude lower than those reported for copper in pure water.

In a recent paper, Hultquist <sup>1</sup> reported that hydrogen was evolved from copper corroding in pure water at 25°C at a rate of  $15 \cdot 10^{-6} \text{ g(H}_2\text{)} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$ , equivalent to a corrosion rate of 0.96  $\mu\text{m/a}$  if copper is oxidised to the cuprous state by water via the reaction:



The amount of hydrogen reported to be in the corrosion cell after ca. 1100 h exposure was 0.8 mg in a volume of 0.02 dm<sup>3</sup> equivalent to a hydrogen partial pressure ( $p_{\text{H}_2}$ ) of about 0.45 bar.

The partial reactions involved are <sup>2</sup>:



$$\text{where } E(\text{V nhe}) = 0.471 - 0.0591\text{pH} \quad \text{at } 25^\circ\text{C} \quad /III/$$



$$\text{where } E(\text{V nhe}) = -0.0591\text{pH} - 0.0295 \log(p_{\text{H}_2}) \quad \text{at } 25^\circ\text{C} \quad /V/$$

From equations III and V <sup>2</sup>, the equilibrium partial pressure for hydrogen over copper/cuprous oxide in water at 25°C is ca.  $10^{-16}$  bar. Hultquist suggests that reaction I is irreversible and that the hydrogen evolved can thus accumulate and reach any partial pressure given time.

Corrosion rates of the magnitude reported by Hultquist and the amounts of hydrogen evolved are not to be expected for copper immersed in pure water.

In the course of an experimental programme on candidate materials for high level nuclear waste containers, corrosion rates on copper in oxygen free granitic groundwaters were measured using hydrogen evolution rate as the measuring technique. The method had previously been used to measure hydrogen evolution rates from

plain carbon steel<sup>3</sup>. The purpose of this paper is to compare the results of these tests on copper with those reported by Hultquist.

### Experimental

#### Measuring technique.

The apparatus layout is shown in figure 1. The principle of the technique is as follows:

The specimens are placed in three glass flasks along with the test medium, the flasks are immersed in a water bath for temperature regulation.

A nitrogen gas stream is first water saturated by bubbling it through a wash bottle in the water bath and then passed over the test medium in the flasks. (The gas stream is not bubbled through the test solution.) As the carrier gas passes over the cells it will pick up any gas evolved by corrosion reactions.

The gas stream is then partially dried by passing it through a water cooled water trap before being sampled for analysis in a gas chromatograph.

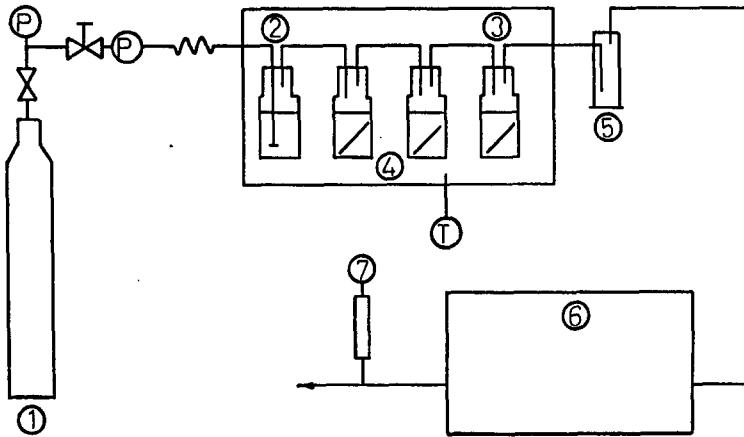


Figure 1 Experimental apparatus (schematic)

- |                           |                                      |
|---------------------------|--------------------------------------|
| [1] Nitrogen gas flask.   | [5] Cold trap to remove excess water |
| [2] Water to moisten gas. | [6] Gas chromatograph                |
| [3] Specimen flasks (3).  | [7] Gas flow rate meter              |
| [4] Water bath            |                                      |

The test solution is nitrogen saturated before the specimens are inserted, immediately closed and the air space above the test solution immediately flushed with a high flow rate of nitrogen.

The nitrogen gas flow rate is then reduced to the desired level.

The corrosion reaction of interest is reaction I, the gas chromatograph was thus calibrated for hydrogen. The instrument was calibrated for a gas concentration of 10-100 ppm by volume hydrogen accurate to  $\pm 1$  vol.ppm in this range. The detection limit was less than 1 vol.ppm hydrogen, i.e. the analysis is semi-quantitative down to 1 vol.ppm hydrogen.

The hydrogen evolution rate,  $N \text{ g(H}_2\text{).h}^{-1}\text{.m}^{-2}$ , at steady state is given by:

$$N = 0.088.10^{-6}.G.T/F \quad /VI/$$

where G is the concentration of hydrogen in the gas stream in vol.ppm and T is the gas flow rate in  $\text{l.h}^{-1}$  and F is the total surface area of copper in  $\text{m}^2$ .

### Materials

The copper was 0.1 mm thick foil of > 99.7% purity. (Sb <0.005, As <0.002, Pb <0.05, Fe <0.005, Mn <0.005, Ag <0.002, Sn <0.005 % by weight.)

The carrier gas was 5 nines nitrogen with  $\text{O}_2$  <2 vol.ppm,  $\text{H}_2$  <1 vol.ppm, and  $\text{H}_2\text{O}$  <2 vol.ppm.

Two different test solutions were used:

A: a synthetic granitic groundwater;

B: a sodium chloride solution.

The compositions of the two solutions are given in table 1.

Test medium	mg/l	$\text{Cl}^-$	$\text{SO}_4^{=}$	$\text{F}^-$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{++}$	$\text{Mg}^{++}$
A		8100	1820	4	4800	54	1100	3
B		8000	-	-	5408	-	-	-

Table 1. Composition of the test solutions.

The copper sheet was washed, degreased, dried and weighed before the experiments. Fresh sheet was used for each experiment. The sheet was washed, dried and weighed after the experiment.

The sample flasks each hold about 100 ml of test solution, the top ends of the copper coil are about 10 mm below the water surface. The total gas volume is ca. 100 ml.

The conditions for each experiment are given in table 2.

Test	Medium	Temp. °C	Test Period h	Area of copper m <sup>2</sup>	Gas flow rate l.h <sup>-1</sup>	H <sub>2</sub> detection limit g(H <sub>2</sub> ).h <sup>-1</sup> .m <sup>-2</sup>
1	A	50	1008	0.24	0.1	0.037.10 <sup>-6</sup>
2	B	50	1008	0.24	0.1	0.037.10 <sup>-6</sup>
3	A	80	672	0.12	0.1	0.073.10 <sup>-6</sup>
4	B	80	672	0.12	0.1	0.073.10 <sup>-6</sup>

Table 2. Details of the experiments performed.

Hydrogen evolution would be detected by the gas chromatograph if the hydrogen evolution rate from copper exceeds the value given in the last column of the table. The detection limit was calculated using equation VI assuming the detection limit for the gas chromatograph to be 1 vol. ppm H<sub>2</sub>.

## Results

Hydrogen evolution was not detected under any of the conditions investigated.

After 1008 h the gas flow in experiments 1 and 2 was interrupted. The copper was left to corrode for another 50 h. The gas above the copper specimens was then collected by displacing with 400 ml nitrogen. The displaced gas was collected in a balloon and analyzed in the gas chromatograph. This is equivalent to a gas flow rate of 500 ml in 50 h, compared to the standard condition of 5000 ml in 50 h, i.e the sensitivity was increased by a factor of about 10 by this means. No hydrogen was detected.

Weight gains of about 1 mg at 50°C and 0.5 mg at 80°C ( $\pm 0.5$ ) were found in medium A and a weight loss of about 0.4 mg ( $\pm 0.5$ ) in medium B at 50°C.

## Discussion

The measurements show that the rate of hydrogen production on copper in neutral chloride solutions containing about 8000 mg/l chloride ion at 50°C is less than  $0.0037.10^{-6} \text{ g(H}_2\text{).h}^{-1}\text{.m}^{-2}$  (balloon experiment). This is 4000 times lower than that reported by Hultquist for copper in pure water at 25°C. The corrosion rate of copper is therefore  $< 0.0003 \text{ } \mu\text{m/a}$  in these oxygen free chloride solutions.

It is difficult to explain the the differences between the results described in this paper to those of Hultquist <sup>1</sup>.

Hultquist used a solid electrolyte hydrogen concentration cell. Initially there was air in the gas space over the specimen. He detected hydrogen after ca. 130 h as indicated by the first rise in potential of the hydrogen cell, well before the oxygen in the cell was consumed. He estimated the oxygen to be consumed after

about 650 hours, which would suggest that copper oxidation by water was detectable with a considerable amount of oxygen (partial pressure ca 0.1 bar) still present in the airspace above the cell. It is also clear that the oxygen in the carrier gas (oxygen partial pressure  $2 \cdot 10^{-6}$  bar) would not according to Hultquist's results prevent the oxidation of copper by water.

According to Bjordahl and Nobe <sup>4</sup> the corrosion of copper in chloride solutions is controlled by the reaction:



$$E(\text{V nhe}) = -0.277 + 0.059 \log[\text{CuCl}_2^-]/[\text{Cl}^-]^2 \quad \text{/VIII/}$$

The cathodic partial reaction is the same as that in the absence of chloride ions, i.e.:



Reaction VII is thus also oxidation by water producing hydrogen. Assuming that the solubility of copper as  $\text{CuCl}_2^-$  is  $10^{-5}$  mol/l <sup>5,6</sup>, the hydrogen partial pressure in equilibrium with copper would be of the order of  $10^{-13}$  bar using equations V and VIII. This is higher than the partial pressure in the absence of chloride but is still well below detectable levels. The formation of copper chloride complexes only becomes significant in concentrated chloride solutions.

The weight changes are near the resolution of the technique used. Assuming that the weight gain in solution A at 50°C is due to  $\text{Cu}_2\text{O}$  formation via reaction I, 0.125 mg of hydrogen would be produced. If produced continuously this corresponds to a production rate of  $0.5 \cdot 10^{-6}$  g( $\text{H}_2$ ).h<sup>-1</sup>.m<sup>-2</sup>. This would be detected by the gas chromatograph. The weight gain is probably due to reaction of copper with residual oxygen initially present in the cells. The corresponding steady state hydrogen production rate for solution B at 50°C assuming loss of copper is  $0.05 \cdot 10^{-6}$  g( $\text{H}_2$ ).h<sup>-1</sup>.m<sup>-2</sup>. Copper chloride complex solubility would account for a 0.64 mg weight loss. The weight change determinations cannot be used as a control for the hydrogen evolution as they are not precise enough and both weight losses and weight gains are possible.

The results presented here do not support the observations of Hultquist. No hydrogen evolution could be detected from the corrosion of copper in dilute chloride solutions, supporting the thermodynamic evidence that water cannot be an oxidant for copper in pure water or dilute chloride media.

#### Acknowledgement

The authors would like to thank the Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (NAGRA), Baden, Switzerland, for funding this work.



**References**

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2. M. Pourbaix. Atlas d'Equilibres Electrochimique à 25°C; Gauthier-Villars, Paris, 1963
- 3 J.P. Simpson, R.Schenk, B. Knecht. In "Scientific Basis of Nuclear Waste Management", Mat. Res. Symp. Proc. Vol. 50, 1985, Materials Research Society.
4. W.D. Bjorndahl, K. Nobe. Corrosion **40**, 82, (1984).
- 5 The Swedish Corrosion Institute and its Reference Group: Copper as a Canister Material for Unprocessed Nuclear Waste - Evaluation with respect to Corrosion. Technical Report 90, Stockholm, KBS, 1978.
- 6 Experiments on Container Materials for Swiss High Level Waste Disposal Projects, Part II. Technical Report NTB 84-01, Baden, NAGRA, 1984.

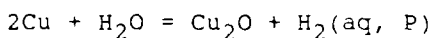
## SHORT COMMUNICATION

### ON THE CORROSION OF COPPER IN PURE WATER.

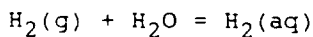
T.E. Eriksen<sup>1</sup>, P. Ndalamba<sup>1</sup> and I. Grenthe<sup>2</sup>  
Departments of nuclear<sup>1</sup> and inorganic<sup>2</sup> chemistry  
The Royal Institute of Technology  
S-100 44 Stockholm

**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.  $\text{Cu}_2\text{O}$  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<sup>1,2</sup>. The work has also been summarized by Mattsson<sup>3</sup>. However, the corrosion of copper in pure oxygen free water has been disputed by Hultqvist in a recent publication<sup>4</sup>. In his study the corrosion of copper in initially aerated distilled water was followed by monitoring the hydrogen ( $\text{H}_2$ ) concentration in the reaction vessel with a solid electrolyte probe described by Lyon and Fray<sup>5</sup>, working on the basis of a concentration cell. From the voltage versus time of exposure plot the  $\text{H}_2$  production by a 99.7 wt% copper foil with surface area  $1460 \text{ cm}^2$  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  $\text{Cu}_2\text{O}$  and  $\text{H}_2\text{O}$  and the equilibrium constant  $K = 0.85 \cdot 10^{-3} \text{ M/atm}$  for the reaction



Manuscript received 10 June 1989.

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 cm<sup>2</sup> surface area) and Alfa 99.9995 wt% (0.025 mm thick, 600 cm<sup>2</sup> 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 cm<sup>3</sup> 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 cm<sup>3</sup> respectively. Assuming the solubility of  $O_2$  and  $H_2$  to be 1.4 and 0.85 mmol·dm<sup>-3</sup> respectively at 25°C<sup>7</sup> 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  $H_2$ .

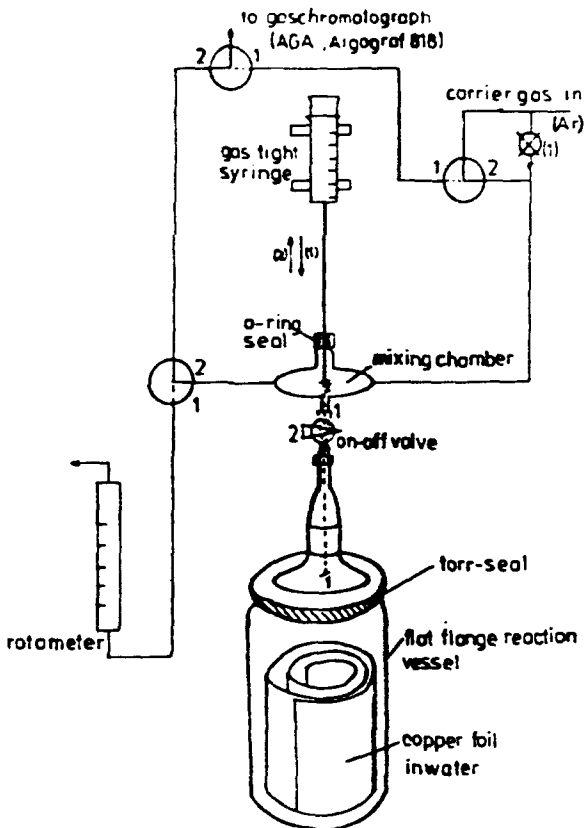


Fig 1: Schematic of reaction vessel and gas sampling system.

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 ( $50 \text{ cm}^2$  surface area) were immersed for 120 minutes in  $50 \text{ cm}^3$  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 reduction<sup>9</sup>. 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 HClO<sub>4</sub>.  
(50 cm<sup>2</sup> surface area, 50 cm<sup>3</sup> solution)

Copper quality	Dissolved Cu mg·dm <sup>-2</sup>	Average corrosion layer thickness (Å)	Comments
Merck > 99.7%	2		as received
	21.5		discoloured surface
	19.6	235	
	21.5		
	11.4		slightly discoloured surface
	15.0	132	
	9.0		
Alfa 99.9995%	30		discoloured surface
	40	354	
	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 cm<sup>2</sup> samples of the discoloured parts and the results obtained from dissolving the corrosion products in 1M HClO<sub>4</sub> 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 H<sub>2</sub> 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 Schenk<sup>10</sup> 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 H<sub>2</sub> 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 <sub>2</sub> (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 <sub>2</sub> consumed mg	Req initial O <sub>2</sub> 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  $\text{Cu}_2\text{O}$  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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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  $\text{Cu}_2\text{O}$  on the copper surface. Then we would have to take into account the hydrogen electrode reaction on  $\text{Cu}_2\text{O}$ , 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."