

SHORT COMMUNICATION

HYDROGEN EVOLUTION FROM CORROSION OF PURE COPPER.

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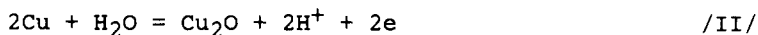
Abstract. Using a sensitive direct gas analysis technique, an attempt was made to detect hydrogen evolution from copper corroding in neutral oxygen free chloride solutions. No hydrogen was detected at evolution rates 3 orders of magnitude lower than those reported for copper in pure water.

In a recent paper, Hultquist ¹ 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 dm³ equivalent to a hydrogen partial pressure (p_{H_2}) of about 0.45 bar.

The partial reactions involved are ²:



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



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

From equations III and V ², 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 steel³. 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.

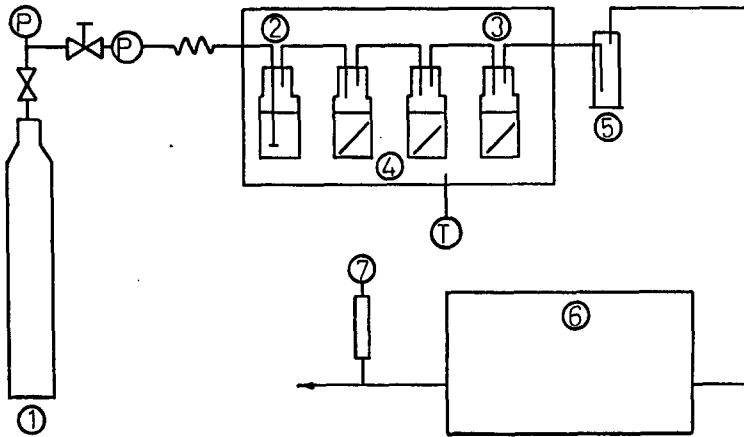


Figure 1 Experimental apparatus (schematic)

- | | |
|---------------------------|--------------------------------------|
| [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 ± 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 l.h^{-1} and F is the total surface area of copper in 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 O_2 <2 vol.ppm, H_2 <1 vol.ppm, and H_2O <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	Cl^-	$\text{SO}_4^{=}$	F^-	Na^+	K^+	Ca^{++}	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 ²	Gas flow rate l.h ⁻¹	H ₂ detection limit g(H ₂).h ⁻¹ .m ⁻²
1	A	50	1008	0.24	0.1	0.037.10 ⁻⁶
2	B	50	1008	0.24	0.1	0.037.10 ⁻⁶
3	A	80	672	0.12	0.1	0.073.10 ⁻⁶
4	B	80	672	0.12	0.1	0.073.10 ⁻⁶

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 H₂.

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 (± 0.5) were found in medium A and a weight loss of about 0.4 mg (± 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 ¹.

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 ⁴ 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 CuCl_2^- is 10^{-5} mol/l ^{5,6}, 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 Cu_2O 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(H_2).h⁻¹.m⁻². 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(H_2).h⁻¹.m⁻². 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

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