

C O N T R A C T W O R K R E P O R T

C O N F I D E N T I A L

Exposure of Copper in Äspö Groundwaters

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Summary

This report describes an exposure that Korrosionsinstitutet performed at SKB's hard rock laboratory at Äspö. Copper coupons were exposed to groundwater at two different depths.

Experimental

Copper coupons were exposed to the natural ground water at two locations at the Äspö hard rock laboratory. The sites are referred to as 1420 and 2880 respectively, where the numbers indicate the distance from ground level along the tunnel.

Copper coupons were exposed in pressure vessels. Ground water was allowed to flow through the pressure vessels at a low flow rate. Bacterial growth or particles caused disturbances in the flow and pressure. The intended flow of about 1 litre per minute could not always be maintained and the pressure varied with the flow. The flow rate was adjusted periodically.

The bore hole 2880 was selected as a groundwater representing a chloride rich ground water, Cl⁻ = 11 400 - 13 500 mg/l. The bore hole 1420 was selected as a groundwater representing a sulphide rich ground water, HS⁻ = 0.1 - 0.4 mg/l. The depths below ground were approximately 300 meters and 150 meters respectively.

Six coupons were mounted on a plastic support structure. The support structure was inserted into a pressure vessel that was mounted on the rock wall and connected to the local ground water at the natural pressure of the bore hole. Three different sites were originally selected although only two were actually used. Figure 1 shows the three parallel sets of test coupons. Figure 2 shows one of the pressure vessels, containing set of copper coupons, mounted on the rock wall. The pressure vessels were equipped with wiring so that the corrosion potential of one of the copper coupons could be measured. Double outlet values from the pressure vessels allowed a reference electrode to be inserted and removed without loss of pressure. A platinum wire was also mounted on the plastic racks and wired so that the free potential of platinum could be measured.

The exposure was intended to last three years. However, because of decreasing flow from the boreholes, the pressure, as read from the manometers, decreased gradually. It was decided to

interrupt the exposure after two and a half years. The outlet tubing was arranged so that the vessels could never run dry and so that siphoning could not occur. Nevertheless, at too low flow of water through the vessels, oxygen diffusing in from the outlet, through the water filled pipe and through the likewise water filled outlet valve, could possible cause corrosion of the copper coupons.

Water Compositions

Tables AI and AII in Appendix 1 show the composition of the groundwater at the two exposure sites.

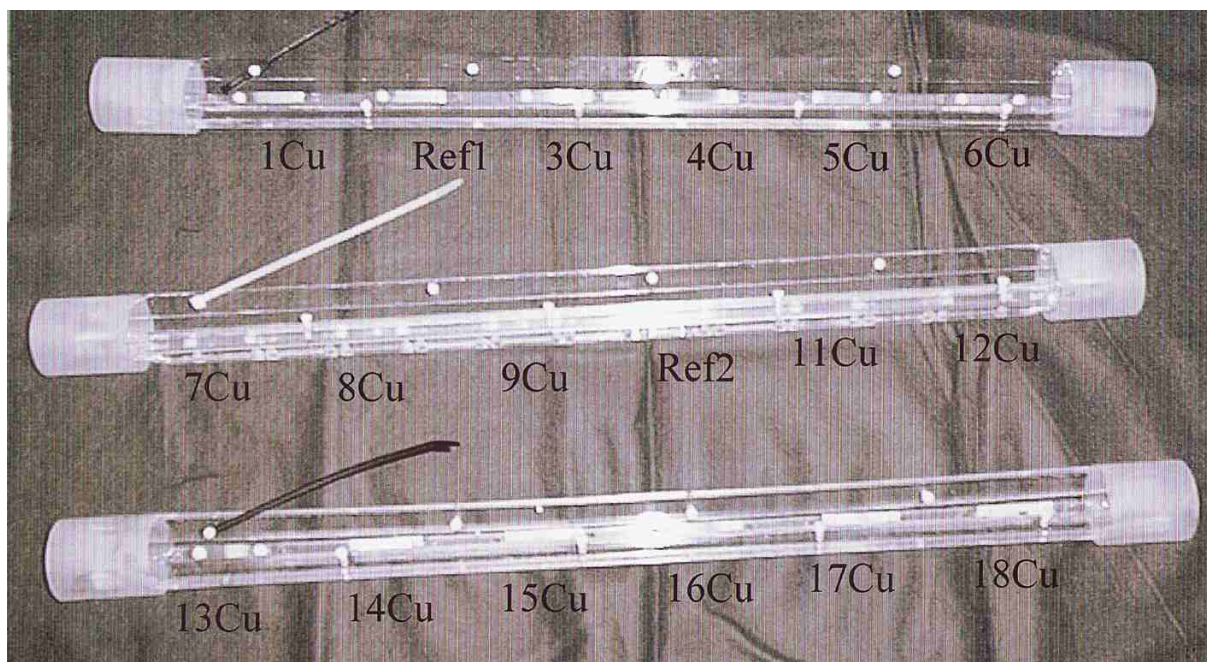


Figure 1. Three parallel sets of six copper coupons mounted on a plastic rack to be inserted into the pressure vessels.

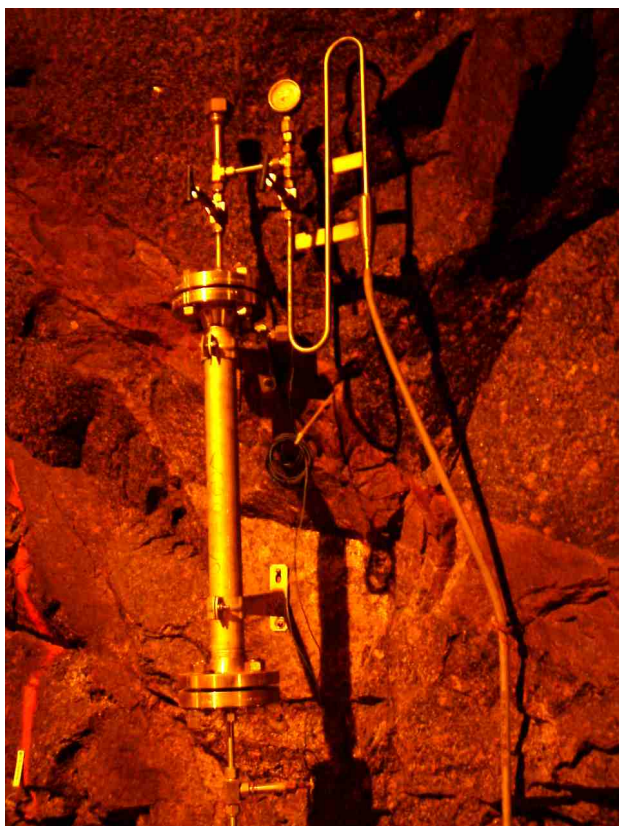


Figure 2. One set of six copper coupons contained in a pressure vessel mounted on the rock wall at Äspö.

Results

Mass loss

Table I shows the weights of the copper coupons before and after the exposure. The estimated mass loss after pickling is also shown. As table I shows, the coupons exposed to the sulphide rich water 1420-3, 1420-4 and 1420-5 have lost almost 10 milligrams during the exposure. The pickling procedure removes a further ~3 milligrams of adherent solids. The coupons exposed to the chloride rich water 2880-2, 2880-3, 2880-4 have gained about 1 milligram during the exposure. Pickling removes the mass gained and a further 6-8 milligrams of adherent solids.

Table I. Mass of the coupons after exposure and after pickling

Coupon ID	Mass (mg)			
	Initial	After Exposure	Mass loss after pickling	Mean mass loss
1420-3	2092.409	2083.274	13.221	
1420-4	2089.523	2079.649	12.380	
1420-5	2052.148	2042.450	12.953	12.852
2880-2	2016.803	2017.527	6.056	
2880-3	2073.587	2074.698	8.414	
2880-4	2067.502	2068.295	6.243	6.905

(N. B. the ID-numbers are not the same as those in figure 1)

The average depth of attack and the average corrosion rate was calculated using the following parameters:

Time of exposure:	2.56 years
Coupon area:	10 cm ²
Density:	8.94 g/cm ³

Table 2 shows the average depth of attack and the average corrosion rate as mean values for each site of exposure.

Table II. Mass loss after pickling converted to corrosion depths and corrosion rates.

Exposure site	Mass loss (mg)		Average Corrosion Depth (µm)		Average Corrosion Rate (µm/year)	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
1420	12.852	0.430	1.438	0.048	0.560	0.019
2880	6.905	1.311	0.772	0.147	0.301	0.057

Visual appearance

Figures 3 and 4 show photographs from the when the equipment was disassembled. The equipment in figure 3 was exposed in the chloride rich water and the equipment in figure 4 in the sulphide rich water. As figure 3 shows the coupons from the chloride rich water are bright and shiny whereas the coupons from the sulphide rich water (figure 4) are covered with a black substance that easily falls off in flakes.

Microscope images

Figures 5 and 6 show microscope images. The coupon exposed in the chloride rich water in figure 5 shows the scratches and grooves left from the grinding of the surface. Similar grooves can be discerned in figure 6, on the coupon exposed in sulphide rich water. Beneath the dark layer that easily flakes off, the original topography is still visible.

Surface profile

The surface profile on one coupon from each exposure sites was measured using AFM. The measurements were made after pickling to remove solid corrosion products. AFM images are shown in figures 7 and 8. The coupon exposed in the sulphide rich water at 1420 meters tunnel length showed a singular attack in the studied area. An approximately 0.5 μm deep cavity with a hemispherical appearance was found. The coupon exposed in the chloride rich water at 2880 meters tunnel length showed a very even surface without significant features.

Potential Measurements

Potentials, corresponding to corrosion potentials and redox potentials, were measured at several occasions during the exposure period. Erratic and non-systematic values were obtained and results from these measurements are not presented.

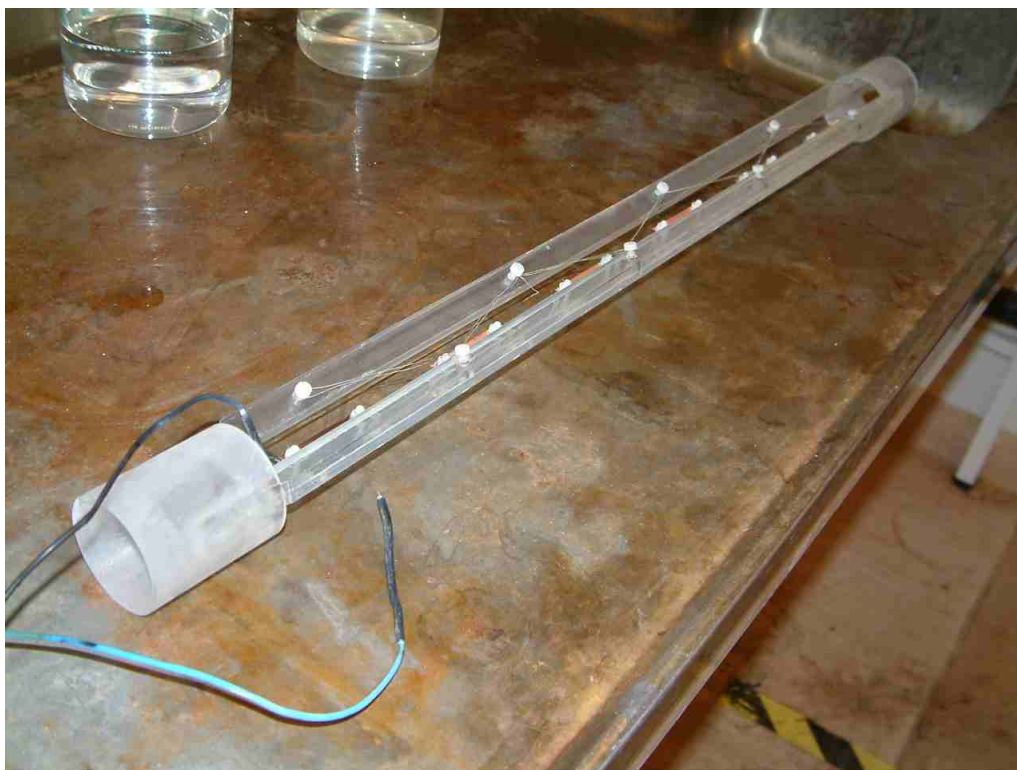


Figure 3. Dismounting the equipment exposed in the chloride rich water at site SA 2880A.



Figure 4. Dismounting the equipment exposed in the sulphide rich water at site SA 1420A.

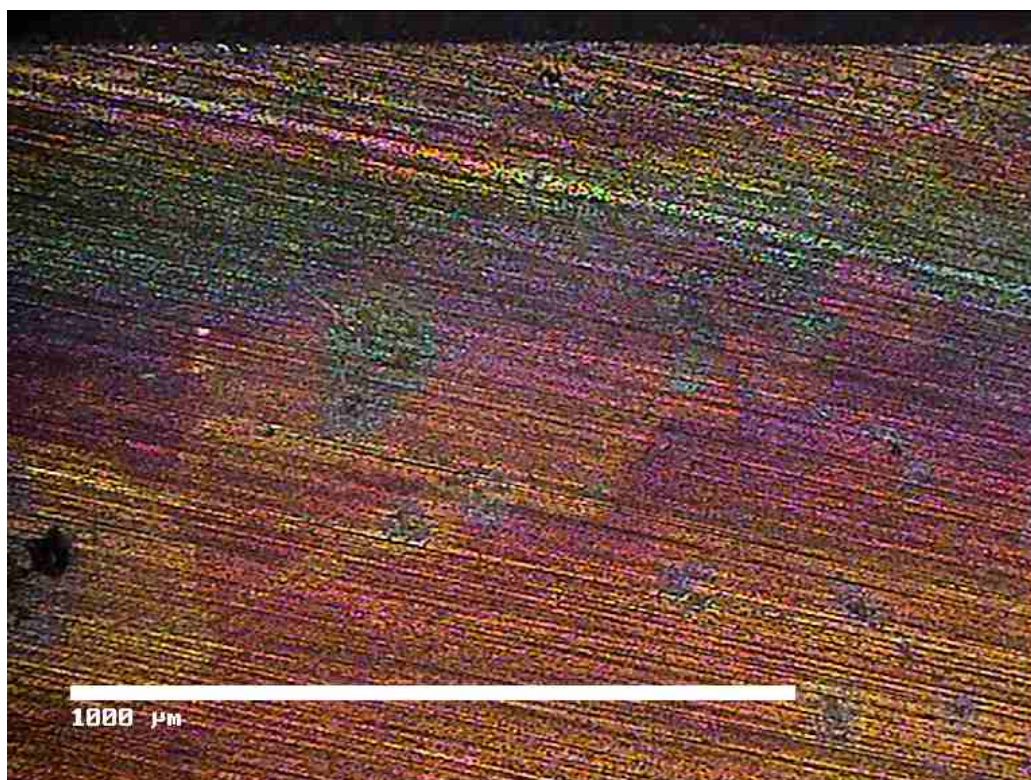


Figure 5 Microscope image of a coupon exposed in the chloride rich water. Before pickling.

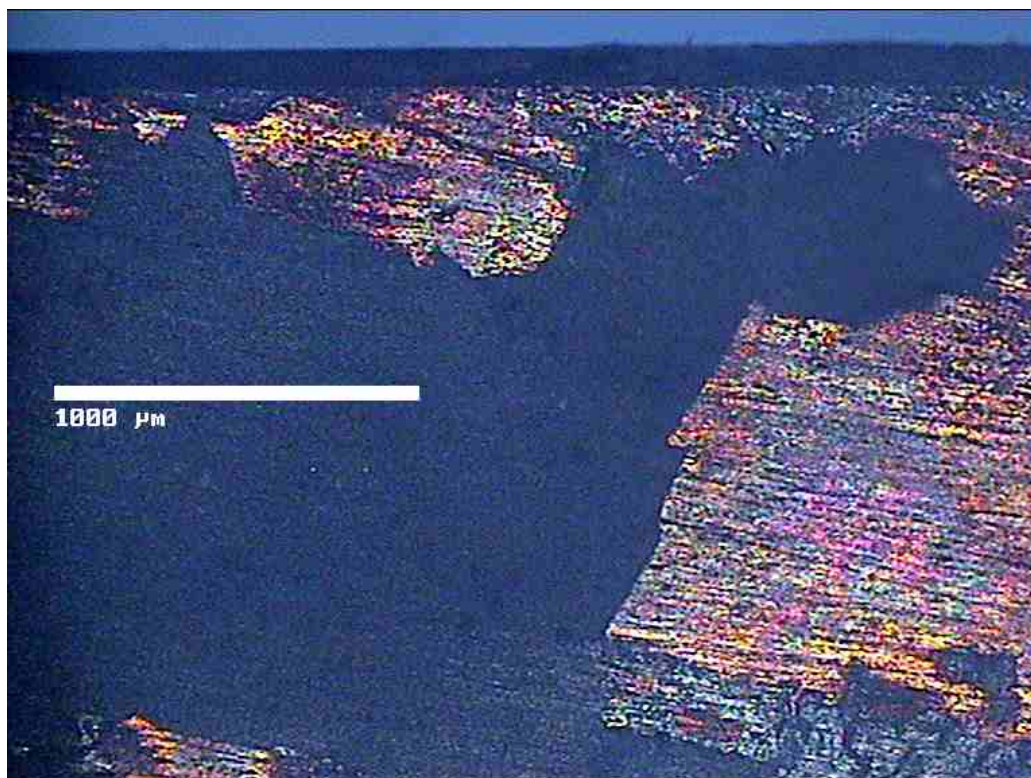


Figure 6 Microscope image of a coupon exposed in the sulphide rich water. Before pickling.

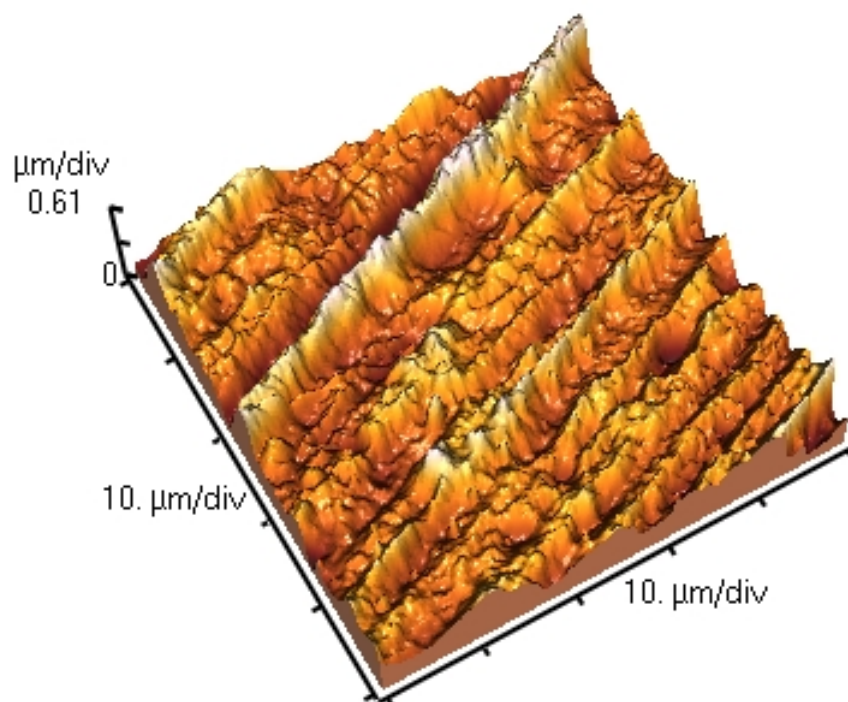


Figure 7. Surface morphology from AFM of a copper coupon exposed in bore Hole 2880, Chloride rich water (Cl⁻ 11 000-13 000 mg/l).

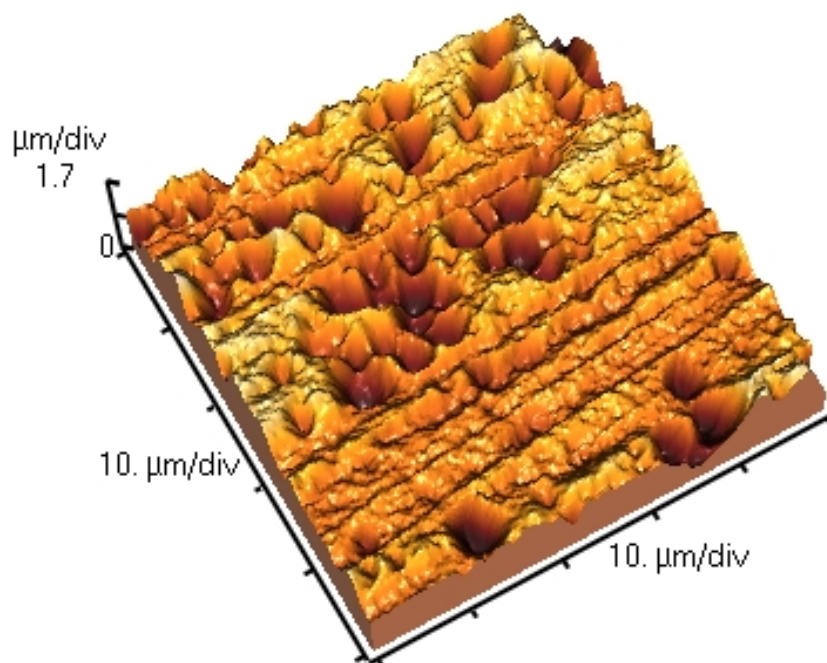


Figure 8. Surface morphology from AFM of a copper coupon exposed in bore Hole 1440, Sulphide rich water (HS⁻ 0.1- 0.4 mg).

Discussion

Copper coupons exposed to the sulphide rich water in bore hole 1420 show characteristics normally associated with this type of corrosion. A black deposit of insoluble corrosion products at the copper surface seems to be present in figures 4 and 6. The uneven coverage of the copper coupon, visible in both figures, also indicates that the deposit easily cracks and falls off the underlying metal. It seems likely that the relatively thick and more or less adherent corrosion products have provided some degree of barrier between the underlying copper metal and free sulphide in the water, during the exposure. This barrier may have been a limiting factor for the corrosion of the copper coupons exposed at bore hole 1420.

Copper coupons exposed in the chloride rich water in bore hole 2880 show, to the naked eye, no signs of corrosion. During the exposure period a large amount of ground water has passed through the container with the copper coupons. Assuming a constant flow of 1 litre per minute, approximately 1.3×10^6 litres have passed the copper coupons during the whole exposure period. The average corrosion corresponds to about 6.9 mg Cu per coupon. With 6 coupons in the container, the average copper concentration in the outgoing water would be about $6 \times 6.9 / 1.3 \times 10^6 = 3.2 \times 10^{-5}$ mg Cu per litre. In molar units, the average concentration of copper would be 5×10^{-10} M. With the strong complex forming capacity of the chloride contents of the local ground water, $\sim 13\,000$ mg Cl/litre, the activity of the free Cu^+ ion is so low that the results are consistent with reducing conditions. Thus, the mass loss is consistent with reducing conditions. But there was a mass increase observed after exposure but before pickling. Can the observed mass increase be consistent with reducing conditions? The mass increase could indicate solid corrosion products. Solid corrosion products such as Cu_2O and CuCl would explain the mass increase but their formation is not consistent with reducing conditions and they are so soluble that their presence at the surface does not seem to be consistent with the very low copper concentration in the water. It is possible that the mass increase is due to deposits or sediments from the ground water that has nothing to do with copper corrosion. However, the microscope image in figure 5 shows some rainbow coloured patterns on the copper coupon that are similar to the patterns that can be observed in figure 4 for the coupon exposed in sulphide rich water. The local ground water in bore hole SA2880A is nominally free of sulphide as shown in table AII in appendix I. The measurement uncertainty is given as 0.1 mg/litre. The composition of the sulphide rich water in bore hole SA1420A in table AI in appendix I shows that the sulphide concentration varies from one analysis to another. The variations are very high in relative terms. In absolute terms and in relation to the measurement uncertainty, the sulphide concentrations may be considered low. The reported values are in several instances lower than the measurement uncertainty. Yet we conclude that the sulphide contents in the water from bore hole SA1420A is responsible for the corrosion of the copper coupons exposed to this water. It would be consistent with observations if sulphide present, in the water from bore hole SA2880A, at concentrations below reporting level, is the cause for the observed corrosion of the copper coupons exposed to this water.

Conclusions

Copper coupons exposed to flowing ground water with sulphide concentrations in the order of 0.1 mg S per litre at bore hole SA288A show the characteristics of sulphide corrosion. The mass loss and the presence of the black corrosion products are consistent with the formation of Cu_2S as the major corrosion product.

The corrosion of the copper coupons exposed to flowing ground water with chloride concentrations in the order of 10000 mg Cl per litre at bore hole SA1420A is consistent with several scenarios. It is possible that the major corrosion product has been aqueous chloride complexes of Cu(I) and that the observed mass gain after exposure is caused by inert deposits from the ground water. An alternative explanation is that Cu_2S is the main corrosion product also in this case. The source of the sulphide would be its presence in the ground water at concentrations below reporting level.

For both bore holes, the waters are so aggressive and the corrosion is so slight that the observed corrosion can be explained by hydrogen evolution as the cathodic process. Sulphide binds the Cu^+ -ion so strongly in the solid Cu_2S that the free Cu^+ ion activity lies within a range where hydrogen evolution is possible. For the chloride rich water with aqueous chlorides as corrosion products, the flowing water prevents the build up of significant copper concentrations and the strong complexation of the Cu^+ ion by chloride causes the free Cu^+ ion activity to be within the range where hydrogen evolution is possible.

Your sincerely
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Appendix 1

Table AI. Water composition at bore hole SA1420A.

Idcode			SA1420A	SA1420A	SA1420A	SA1420A	SA1420A	SA1420A	SA1420A	SA1420A	SA1420A	SA1420A
Secup	m		6	6	6	6	6	6	6	6	6	6
Seclow	m	Measurement uncertainty:	50	50	50	50	50	50	50	50	50	50
Sample			2318	2330	2358	2395	2440	2492	2656	2895	2999	3331
Sampling	date		18/05/1995	11/10/1995	21/05/1996	11/03/1997	30/09/1997	04/03/1998	01/10/1998	13/04/1999	05/10/1999	18/09/2000
Na	mg/L	0.05	1347.5	1334.4	1315.8	1392.6	1500	1530	1360	1420	1370	1450
K	mg/L	0.05	20.5	20.3	21.1	25.91	30.9	27	23.5	27.3	25.3	31.5
Ca	mg/L	0.05	284.4	247.3	245.4	210	245	246	214	203	228	216
Mg	mg/L	0.05	135.8	129.4	119.1	136.6	161	157	123	135.1	140.8	152
HCO3	mg/L	0.05	199	205	214	189	194	204	198	205	200	203
Cl	mg/L	0.05	2900.1	2721	2676.7	2507.8	2972.5	3050	2530	2690	2720	2860
SO4	mg/L	0.1 xx		267.44	280.88	300.78	390	324	258	292	299	292
SO4-S	mg/L	0.05	100.6	97.5	87.97	99.16	110	108	91.7	97	98	100
Br	mg/l	0.1 xx		13.73	0	9.08	11.6	10.2	8.5	9.6	10.2	9.5
F	mg/L	0.1 -	-	-	-	-	-	-	1.68	0.83	1.15	1
Si	mg/L	0.05	6.3	5.6	6	6.2	5.6	5.6	5.3	5.4	6.8	5.5
Fe-ICP	mg/L	0.05	1.853	1.522	1.446	1.712	1.76	1.57	1.2	1.401	1.7	1.49
Fetot	mg/L	0.1	1.867	1.637	1.538	1.584	1.855	1.56	1.34	1.438	1.45	1.546
Fe2+	mg/L	0.1 xx		1.633 xx		1.572	1.855	1.55	1.34	1.44	1.48	1.536
Mn	mg/L	0.05	0.8	0.69	0.69	0.7	0.73	0.72	0.56	0.61	0.78	0.64
Li	mg/L	0.05	0.072	0.059	0.076	0.052	0.052	0.046	0.052	0.06	0.047	0.044
Sr	mg/L	0.05	3.68	2.9	3.45	2.6	3.01	2.96	2.26	2.2	2.8	2.7
pH	pH unit	0.1 unit	7.3	7.5	7.4	7.36	7.4	7.37	7.51	7.3	7.5	7.5
El. Cond.	mS/m	0.05	900	815 xx		783	878	914	729	690	930	960
Smpl Flow	L/min		1.55	2	1.8	0.5	0.5	10	1.1	10	10	24
Drill water	%	-	-	-		0.16	0.27	0.06 -		0.4	0.34	0.08
DOC	mg/L	0.1 mg/L	4.8	5.1	8.4	7.9	5.5	7.2	7.9	9	8.7	6
S2	mg/L	0.1 -		0.15	0.05	0.03	0.2	0.1	0.12	0.24	0.12	0.07
NH4-N	mg/L	0.2	2.128	2.16	0.2	0.638	2.951	0.1	2.56	0.773	0.831	2.73

Table AII. Water composition at bore hole SA2880A.

Idcode			SA2880A	SA2880A	SA2880A	SA2880A	SA2880A	SA2880A	SA2880A	SA2880A	SA2880A	SA2880A
Secup	m		11.92	11.92	11.92	11.92	11.92	11.92	11.92	11.92	11.92	6
Seclow	m	Measurement uncertainty:	13.92	13.92	13.92	13.92	13.92	13.92	13.92	13.92	13.92	19.5
Sample			2338	2349	2384	2449	2505	2651	2906	2938	2989	3344
Sampling	date		25/10/1995	12/04/1996	06/03/1997	01/10/1997	06/03/1998	30/09/1998	14/04/1999	21/09/1999	01/10/1999	20/09/2000
Na	mg/L	0.05	2846.8	3156.4	3180.7	3338.4	2990	3080	3110	2890	3140	3370
K	mg/L	0.05	12.1	13.64	11.78	12.93	12.8	12.5	12.7	12.8	13.8	14.8
Ca	mg/L	0.05	3812.5	4378.1	4447.8	4651.3	3980	4250	4398	3912	4252	5130
Mg	mg/L	0.05	46.4	41.1	45.9	41	44.2	38.9	39.8	36.3	44.5	33
HCO3	mg/L	0.05	30	22	27	20	40	39	37	37	41	18
Cl	mg/L	0.05	11371.5	12956.3	13011.6	13524	12500	12300	12930	12490	12430	14500
SO4	mg/L	0.1	609.39	651.79	672.48	632.17	638	613	687	554	565	643
SO4-S	mg/L	0.05	188.47	208.71	213.49	210	195	192	198	184	198	194
Br	mg/l	0.1	81.33	96	99.2	83	102	94.5	109.6	98.8	95	113.3
F	mg/L	0.1	-	-	-	-	-	-	1.03	-	1.2	1.4
Si	mg/L	0.05	4.4	4.8	5.1	3.6	4.3	4.4	3.9	4.6	5.3	4.4
Fe-ICP	mg/L	0.05	0.183	0.211	0.239	0.169	0.184	0.175	xx	0.21	0.206	0.176
Fetot	mg/L	0.1	0.245	0.232	0.213	0.199	0.232	0.207	1.005	-	0.223	0.189
Fe2+	mg/L	0.1	xx	0.211	0.214	0.201	xx	0.205	0.959	-	0.223	0.189
Mn	mg/L	0.05	0.35	0.38	0.44	0.32	0.36	0.37	xx	0.28	0.41	0.29
Li	mg/L	0.05	2.382	3.189	2.739	2.979	2.79	2.81	2.7	2.827	3.106	3.21
Sr	mg/L	0.05	56.95	72.3	70.88	78.12	64	61.3	57.65	51.4	68.4	86.1
pH	pH unit	0.1 unit	7.61	7.5	7.41	7.2	7.28	7.5	7.4	7.3	7.4	7.5
El. Cond.	mS/m	0.05	2850	3200	3390	3550	3250	2880	2500	2760	3210	3670
Smpl Flow	L/min		1.36	-	1.1	1.26	1.3	0.82	0.921	0.6	1.05	1
Drill water	%		-	-	0.05	0.11	0.01	-	0.08	-	0.08	0.05
DOC	mg/L	0.1 mg/L	0.9	0.3	1	0.2	1.3	1.1	1.5	-	1	1
S2	mg/L	0.1	-	-	-	-	-	-0.01	-	-	-	-0.01
NH4-N	mg/L	0.2	0.048	-	-	0.048	0.06	0.086	0.061	-	0.062	0.05