

CORROSION RESISTANCE OF COPPER IN SWEDISH SOILS

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ABSTRACT

The corrosion of copper and other metals is being investigated in a systematic long-term field study. Test panels have been buried in trenches at nine test sites above and below the ground water table. The soil at the test sites is rather homogeneous and it is representative of Swedish and northern European geology. The soil types are: clay (two types), gyttja (muddy) clay (two types), clay with high sulphide content, peat, sand and till (two types). The soils have been characterised by measurement of several chemical and geotechnical parameters. The effects of soil composition, embedment of test panels in sandfill and position of test panels in respect to groundwater table on the uniform and local corrosion and on the corrosion potential of copper are given based on up to 7 years' exposure.

INTRODUCTION

The corrosion resistance of copper and other metals in soil is being investigated in a systematic and unique long-term field study. The reason why including copper in the exposure programme is that copper is widely used as a material for buried structures in the Scandinavian countries.

Non-coated copper structures, which exist in a very large amount in the ground in Sweden, are: water service pipes, rods and wires for local electrical earthing and very long earthing wires, which are buried along the high voltage transmission power line routes. The function of these extremely long copper wires is to improve the electrical grounding of the power line steel towers. It is estimated that there are in total in Sweden approx. 150 000 single copper service pipes (corresponding to an estimated total length of ca. 3 700 km) and approx. 11 200 km copper earthing wires in the power line routes. There is no corresponding figure available for local earthing rods and wires. With respect to the large amount and economical value of these buried copper structures, reliable knowledge about the corrosion behaviour of copper in various types of soil is of great importance. To achieve this the long-term exposure program was started in the beginning of the 1980's. The exposure program is still going on. The aim is to chart the corrosion resistance of different metals in typical Swedish soils during very long periods and to investigate the effects of different soil parameters on the corrosion. This report presents the results after up to seven years' exposure of copper panels. The corrosion rates for every single test panel in all three withdrawals of panels at all nine test sites have been reported earlier (ref. 1 and 2).

EXPERIMENTAL

Test sites

Nine test sites in soil have been established in different parts of Sweden. See **figure 1**. All test sites were established in flat terrain, which means that there are no strong ground water movements. The soil at the test sites is given in table 1.

The soil at the sites is naturally stratified, relatively uniform and has never been dug over. There is no risk of stray-current corrosion. The ground water table in the test trenches is

roughly 1 m below ground level in the early autumn and has moderate seasonal variations. Specimens could thus be placed both above and below the groundwater table for study of its effects on corrosion. An exception are the test sites nr.8 and 9 where there is only one test level and where the ground water table is far below the test level.

For practical reasons, the specimens above and below the groundwater table at the test site nr.7 (sand) had to be placed at two locations about 100 m apart. As a result, both the upper and the lower test levels are about 0.7 m below the ground level. At the lower test level at this test site the groundwater table stands above the test panels and close to the ground level. The pH value and the carbonate concentration differ somewhat but otherwise the soils are similar at the two locations.



Figure 1. Location of the test sites in soil.

The soil types at the test sites

The clay at test site nr.1 (Enköping) is a pure glacial clay with low content of organic matter, sulphur compounds and chloride. The site is situated on cultivated land. The clay at test site nr.2 (Sollentuna) is post-glacial clay. This site is situated on cultivated land and very close to the shoreline of a lake, which probably explains the quite high content of organic matter and sulphur compounds. The clay at test site nr.3 (Kramfors) is a post-glacial black silty clay with an extremely high sulphide content and an anaerobe soil environment. The test site is situated on cultivated land near the large river Ängermanälven, which is originating in the manganese and iron sulphide rich mountains in the northern part of Sweden. This may explain the high sulphide content in the clay. When this clay is aerated its colour changes rapidly from black to light grey and the sulphides are oxidised to sulphate resulting in a lowering of the pH- value one or two pH-units.

The clay at test site nr.4 (Gothenburg) is a marine clay. The site is situated on cultivated land near the seawater, which explains the very high chloride content. Since the organic content is high this clay has the prefix gyttja (mud). The clay at test site nr.5 (Stockholm) is a post-glacial gyttja (muddy) clay. The site is situated on cultivated land and not far from the shoreline of Lake Mälaren, which probably explains the high content of organic matter and sulphur compounds. The soil at test site nr.6 (Laxå) is a pure peat soil consisting of almost only organic matter. The organic matter and the sulphur compounds is the result of the historic pu-

trerefaction of plants and animals during the formation of this soil. The site is situated in forest land.

The soil at test site nr.7 (Linköping) is a homogenous and well aerated sand with quite high resistivity. The soils at test sites nr.8 (Falun) and nr.9 (Lund) are similar to each other with the exception of the soil resistivity. Both soils are till soils, which is a coarse, inorganic non-sorted type of soil that is encountered in moraine terrain. Both soils are well aerated. The test sites 7, 8 and 9 are situated in forest land.

All these soils are representative of Swedish and northern European geology. They are also encountered quite often further down south in Europe.

Soil analysis

The characters of the soils can be seen in **table 1**. The analyses were carried out on samples taken from the disturbed soil in the test trenches at a depth corresponding to the location of the metal specimens. Because of very high water content and the lack of heavy mineral particles in the organic peat soil at test site 6, the content of chloride and sulphur compounds is illusory high in this soil. The soil resistivities and pH values of the sandfills that surround some of the specimens at test sites nr. 1 - 7, measured about three years after start of exposure, are shown in **table 2**. All analyses at test sites 1-7 represent conditions in the autumn of 1986 and at test sites 8-9 in the autumn of 1987. The soil resistivity was measured in a naturally moist sample using a soil box. In the pH measurements, the naturally moist samples were shaken in deionized water at a mass ratio of 1:2,5.

Table 1. Characterization of the soil at the Swedish Corrosion Institute's test sites.

Test site	Depth of test level m	Type of soil	Resis- tivity ohm- cm	Water content wt% of wet soil	Organic content wt% of dry soil	pH value	Carbon- ate wt% CaCO ₃ of dry soil	Chloride mg Cl ⁻ /kg dry soil	Sulphur compounds mg S/kg dry soil		
									Sul- phide S ²⁻ - S	Sulphate SO ₄ ²⁻ - S	Total sulphur
1. Enköping	0.7	Heavy clay	3 290	31	1,6	6,6	0,18	20	7	21	190
	1.7	Very heavy clay	3 450	32	0,7	6,9	0,16	20	7	29	150
2. Sollentuna	0.7	Heavy clay	3 770	41	2,9	4,3	0,32	34	8	202	2 090
	1.7	Heavy clay	1 170	48	2,2	6,3	0,32	22	288	526	10 300
3. Kramfors	1,2	Silty clay	2 570	33	0,9	6,2	0,19	50	238	49	2 030
	2,2	Silty clay	1 430	30	1,9	6,8	0,19	60	347	47	1 240
4. Gothenburg	0.7	Heavy muddy clay	1 710	41	3,7	4,4	0,16	170	8	412	1 480
	1.7	Heavy muddy clay	345	54	4,6	7,4	0,22	2 200	82	322	14 600
5. Stockholm	0.7	Heavy muddy clay	5 220	43	2,8	4,2	0,18	30	8	188	1 840
	1.7	Muddy clay	1 050	51	4,5	5,4	0,15	140	19	758	6 400
6. Laxå	0.7	Fibrous peat	7 160	85	75	4,3	< 0,10	180	61	36	120
	1.7	Pseudo- fibrous peat	13 100	92	61	4,2	< 0,10	220	31	41	550
7. Linköping	0.7	Sand	262 000	7	0,5	5,7	0,12	20	< 5	6	90
	1.7	Greavelly sand	17 900	13	0,2	8,0	3,0	20	< 5	8	140
8. Falun	0,4	Sandy till	331 000	17	0,8	5,5	0,34	22	-	29	285
9. Lund	0,4	Sandy till	21 500	15	1,9	4,4	0,27	22	-	50	238

TABLE 2. Resistivity and pH value in the sandfills used at the test sites 1-6 measured about 3 years' after start of exposure.

Test site	Depth m	Resistivity ohm-cm	pH-value
1. Enköping	0,7	10 300	6,5
	1,7	13 500	7,1
2. Sollentuna	0,7	18 500	6,8
	1,7	10 900	8,1
3. Kramfors	0,7	14 900	5,9
	1,7	12 000	6,7
4. Gothenburg	0,7	3 660	7,2
	1,7	1 670	8,2
5. Stockholm	0,7	30 700	5,1
	1,7	2 260	5,6
6. Laxå	0,7	56 900	6,4
	1,7	45 500	7,0

Tested material and specimen design

The material tested is pure, phosphorus-desoxidized copper corresponding to Swedish Standard SS 50 15-04 with the chemical requirements: Cu (+Ag) min 99.85 mass-% and P 0.015 - 0.040 mass-%. The compositions of the copper can be seen in **table 3**. The test specimens consist of copper panels with dimensions 150x100x1 mm. Triplicate specimens are being used throughout. Exposure began in 1983 except at the Kramfors test site where it started in 1985.

TABLE 3. Chemical composition (mass-%) of the copper test specimens.

P	Ag	Pb	Ni	Sn	Zn	As	Fe	Sb
0.034	0.008	0.008	0.007	0.006	0.006	0.004	0.003	0.003

Position of the specimens in the soil

The test panels have been buried in trenches at the test sites - one trench for each planned withdrawal of samples. At test site nr.1 – 7 there are in total five test trenches at each test site. In each trench there is an upper test level at a depth of about 0,7 m and a lower one at about 1,7 m. See **figure 2**. When the trenches were refilled, an attempt was made to return as far as possible the excavated soil according to its original stratification. The groundwater table fluctuates with the season of the year between these two levels. During the period from late autumn with frequent rainfall to early spring after the snowmelting the groundwater table is high at test sites with clay soil. The upper test level may then be covered with groundwater and thus the soil at the upper level periodically is water saturated.

The test panels are exposed standing in a vertical position in a row in the original soil above and below the groundwater table. Furthermore, a set of panels above and a set below the groundwater table have been entirely embedded in a sand-fill. When the specimens were buried at the test site nr. 3 the upper and the lower rows of test panels were placed rather deeply (1,2 m and 2,2 m respectively) by mistake, so that the groundwater table stands at or above the upper row of panels during long periods of the year.

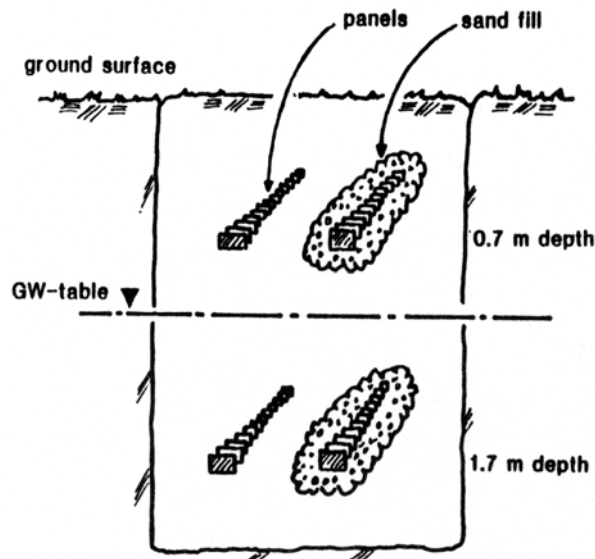


Figure 2. Position of the test panels in the trenches at the soil test sites no.1-7.

At test site nr.8 and 9 there are only three test trenches and only one test level in each trench. In these trenches the copper panels were pushed into position in the trench wall at a depth of 0,4 m below ground surface. At these two test sites the ground water level is, as already mentioned, far below the test levels.

Evaluation of corrosion rate

The corrosion rate of all the specimens has been determined as mass loss and is expressed as average penetration. After removal of loose soil, the specimens were pickled in 10 vol.-% H_2SO_4 using repeated pickling at room temperature. To convert mass loss to average penetration a density of 8940 kg/m^3 has been used. The depth of localized corrosion areas was measured throughout with a focusing microscope.

RESULTS

Corrosion rates

The corrosion rate (uniform and localized corrosion) of the test panels after the latest withdrawal of specimens, which were buried in original soil, is shown in **figure 3**. The corrosion rate (uniform and localized corrosion) of the test panels after the latest withdrawal of specimens, which were buried in sand fill at test sites 1-6, is shown in **figure 4**. The exposure period is seven years for panels from test sites 1, 2, 4, 5, 6 and 7 and five years for panels from test sites 3, 8 and 9. The corrosion rate is presented as uniform corrosion, and as localized corrosion. The corrosion rates are given as mean value for triplicate test panels (three test panels having been exposed near each other at the same position in the trench). The corrosion rates are based on evaluation of 48 single test panels. The corrosion rate (uniform and localized corrosion) for each single test panel at each of the three withdrawals has, as already mentioned, been reported earlier for test sites 1 – 7 (1) and for test sites 8-9 (2).

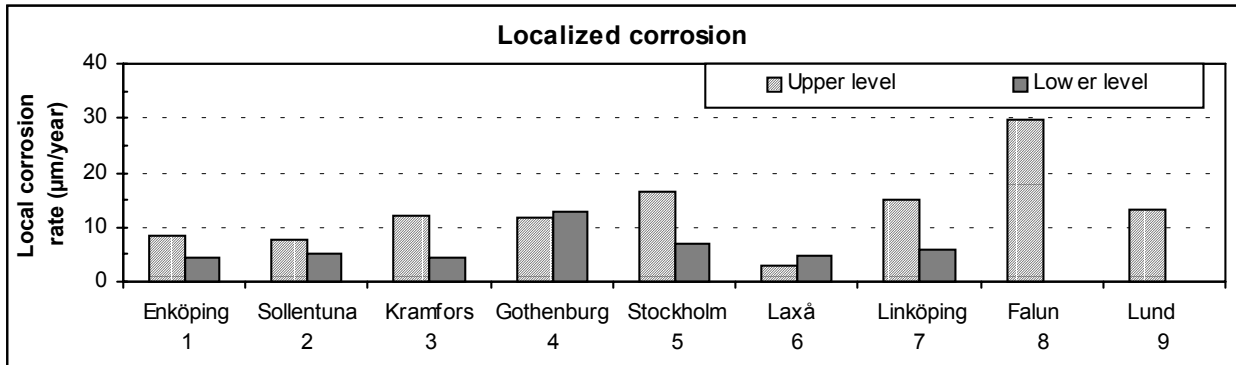
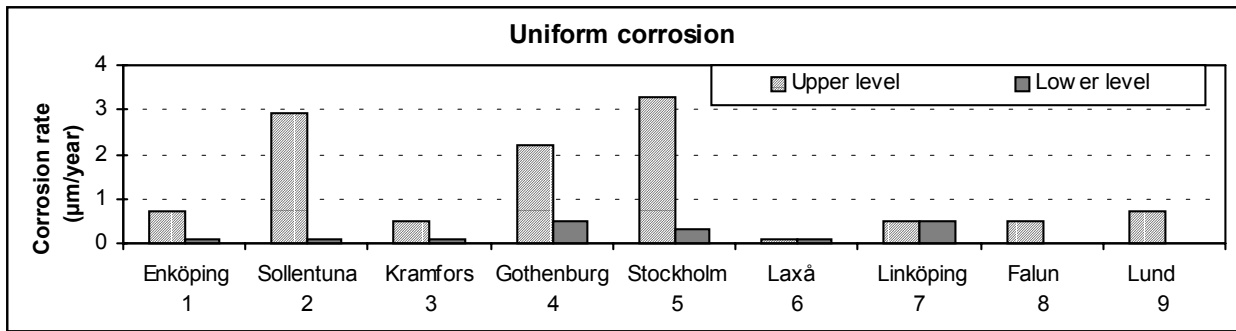


Figure 3. Corrosion rate (uniform and localized corrosion) of the test panels after the latest withdrawal of specimens, which had been buried directly in original soil. At test sites 1-7 test panels had been buried at an upper and at an lower test level. At test sites 8-9 test panels had been buried only at one test level.

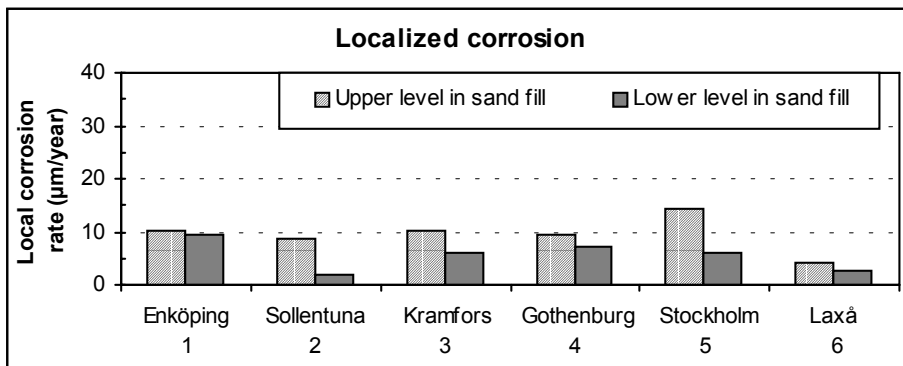
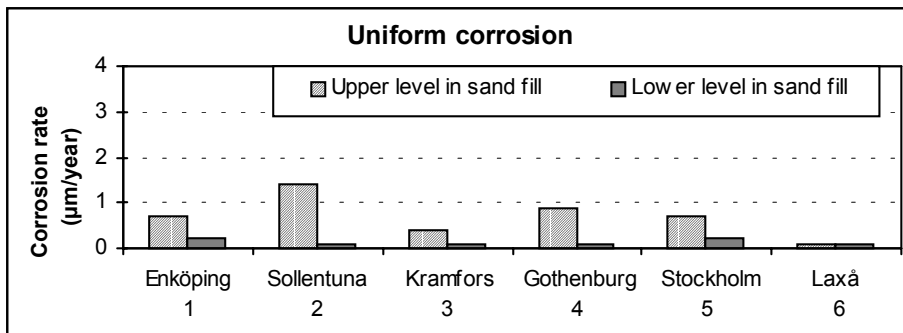


Figure 4. Corrosion rate (uniform and localized corrosion) of the test panels after the latest withdrawal of specimens, which had been buried in sand fill at test sites 1-6. The test panels had been buried at an upper and at an lower test level.

From figure 3 it appears that the uniform corrosion was low and that it varies between $<0,1$ and $3,3 \mu\text{m}/\text{year}$. Only nine of all 48 test panels showed a uniform corrosion higher than $0,5 \mu\text{m}/\text{year}$. Also the localized corrosion was quite low and it varies between ca 1 and $30 \mu\text{m}/\text{year}$. Only twelve of all 48 test panels showed a localized corrosion higher than $10 \mu\text{m}/\text{year}$.

After a comparison with results obtained in systematic field studies carried out in the USA (3) and in Great Britain (4, 5) it appears that the corrosion rates measured in this Swedish study are of the same magnitude as those measured in the American and the British studies. In the latter studies, however, much higher corrosion rates were obtained in some cases, but these were found in not natural soils containing ash and cinder (3, 5).

The appearance of the corrosion

The copper surface of test panels exposed at the upper test level showed a relatively uniform corrosion attack, however, resulting in a slightly rugged surface. This rugged pattern was less pronounced on test panels having been embedded in sandfills. The copper surface of test panels exposed at the lower test level were very little corroded but with localized deeper attacks, in some cases reminding of pitting corrosion. No pronounced pitting corrosion, similar to the pitting that may occur on the inside on copper water tubes, was found.

The corrosion potential of the test panels

The corrosion potential of each separate panel at test sites 1-7, measured when the panels were taken in after three years' exposure, is shown in **figure 5**. During the measurement, the reference electrode (saturated Cu/CuSO_4) was placed in the soil close to the test panel. Metal contact was achieved by carefully uncovering and cleaning a corner of the test panel. Thereafter the test lead was connected to the panel with a crocodile clip.

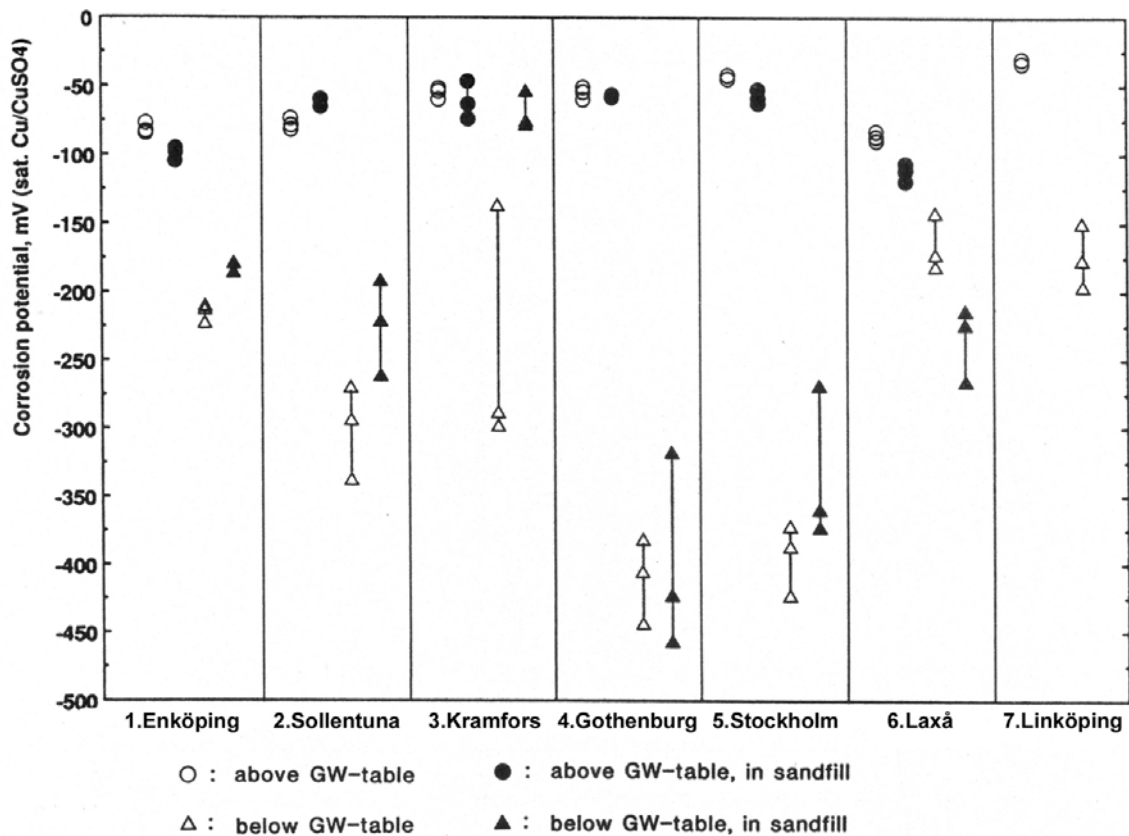


Figure 5. Free corrosion potential of copper test panels after ca. 3 years exposure in soil.

DISCUSSION

In this discussion, the emphasis is placed on an attempt to distinguish factors, which have an influence on the corrosion.

Influence of the chemical composition of the soil

An attempt has been made to distinguish a relationship between the corrosion rate and the chemical composition of the soil. It is found from figure 3 that the highest uniform corrosion (mean value of triplicate specimens) appeared on test panels exposed in the original soil at the upper test level at the test sites no. 2 (2,9 $\mu\text{m}/\text{year}$), nr. 4 (2,2 $\mu\text{m}/\text{year}$) and no. 5 (3,3 $\mu\text{m}/\text{year}$). At the remainder sites and panel positions the average penetration was 0,7 $\mu\text{m}/\text{year}$ or less, with the exception of the test site no. 2, upper test level in sandfill, where the corrosion rate was 1,4 $\mu\text{m}/\text{year}$.

The highest localized corrosion also appeared on test panels exposed in original soil at the upper test level, at the test sites no. 3 (12,0 $\mu\text{m}/\text{year}$), no. 4 (11,7 $\mu\text{m}/\text{year}$), no. 5 (16,5 $\mu\text{m}/\text{year}$) and no. 7 (15,0 $\mu\text{m}/\text{year}$). At the lower test level at these test sites the local corrosion rate was ca 10 $\mu\text{m}/\text{year}$ or less, with the exception of test site no. 4 where it was 12,7 $\mu\text{m}/\text{year}$. Further, high localized corrosion appeared at test sites no. 8 (29,7 $\mu\text{m}/\text{year}$) and no.9 (13,3 $\mu\text{m}/\text{year}$).

Characteristics concerning the chemical composition of the soil at the upper test level, table 1, at the test sites where the highest corrosion appeared are:

Test site	Characteristics
No. 2:	Very low pH, high sulphate and organic content
No. 3:	High sulphide content
No. 4:	Very low pH, high sulphate, chloride and organic content
No. 5	Very low pH, high sulphate and organic content
No. 7	Low pH
No. 8:	Low pH
No. 9:	Very low pH

Thus, common for the soils are a low pH-value and/or a high content of organics, chlorides, sulphides and/or sulphates. These observations are in accordance with those made in the mentioned American and British field studies.

Gilbert (6), however, points out that it seems not to exist any direct relationship between the corrosion rate and any single chemical component in the soil. Ekbom (7) could not either find any statistical relationship. Sederholm and Vinka (8, 9) found in a laboratory study in water saturated soil that the average corrosion was very low in the pH-interval 4-7, but that it increased at a pH-value lower than 4.

Thus, in all studies, the Swedish one included, there are examples showing that a low pH-value or high contents of sulphides, sulphates or chlorides not necessarily result in an increased corrosion.

After another systematization made in the present Swedish study it appeared that common for the position of panels having increased corrosion was aerated cracked clay soils (upper test level) with a rather high organic content. The exception is the large local corrosion at the upper test level at test site Linköping (sand soil).

It is known that copper ions may be adsorbed on surfaces of clay particles and on organic material in the soil and that copper ions may form metal-organic complex ions together with humic substances (products from the decomposition of humus) in the soil, especially with the most soluble component fluvic-acids (10). These two circumstances imply that copper ions may be transported away from the copper surface, which counteracts the formation of a protective layer of corrosion products.

A conclusion which complements the traditional view on corrosion of copper in soil concerning the influence of the pH-value and the sulphur and chloride content would thus be that increased copper corrosion could also be expected in aerated soil, especially clay soil, containing high amount of organic matter.

Influence of the groundwater table

The uniform corrosion and the local corrosion are in most cases higher above the groundwater table (upper test level) than below it. The reason to this is probably, as already hinted at, that the oxygen transport to the metal surface is faster in the non-water saturated soil above the groundwater table. A more detailed description of the influence of the groundwater table has been given elsewhere (12).

Influence of micro-aeration cells

As already mentioned increased localized corrosion appeared in the sand soil at the upper test level at test site no.7 and in the till soils at test sites no.8 and 9, **figure 3**. The sand and the till soils are the most aerated soils in the test program. The reason to the increased localized corrosion might be that the sand was unevenly packed towards the copper surface during the burial resulting in the formation of micro-aeration cells. Till is per se a non-uniform type of soil. Such corrosion cells can be quite effective in aerated soils since the oxygen transportation to the cathodic areas is effective in loose soils. Increased localized corrosion was found also on carbon steel and aluminium in this test position, given the cause of micro-aeration cells (11, 12, 13).

The corrosion rate as function of exposure time

In an earlier evaluation (1, 2) it was found that in those cases where the local corrosion rate was high after 1 years exposure it had decreased considerably after 5 and 7 years' exposure respectively. The uniform corrosion on the other hand was almost constant during the whole exposure periods.

The corrosion potential as function of the test panel-position

In practically all cases the free corrosion potential was more positive on test panels exposed at the upper test level with more efficient soil aeration. The most negative corrosion potentials were measured on test panels exposed in water saturated clay soil with a high sulphide content.

CONCLUSIONS

- Copper has a good corrosion resistance in soil. After 5 and 7 years' exposure respectively the maximum uniform corrosion was 4 $\mu\text{m}/\text{year}$, and the maximum local corrosion rate was 30 $\mu\text{m}/\text{year}$. No pronounced pitting was found of the type that may occur on the inside of copper water tubes.

- ❑ The highest corrosion rates (uniform corrosion) appeared in aerated soils, especially clay soils with a high content of organics, accompanied by increased levels of sulphides, sulphates and/or chlorides and low pH-values.
- ❑ Micro-aeration cells may have contributed to the increased localized corrosion in sand, sandfills and till soils.
- ❑ Both uniform and local corrosion rates were higher above than below the groundwater table at the test sites where there exist two test levels.
- ❑ In cases where high local corrosion rates appeared after 1 year's exposure a considerable decrease was found after 5 and 7 years' exposure respectively.
- ❑ Corrosion potentials were more positive in well aerated than in poorly aerated soils. The most negative potentials were measured in water saturated clay soils with high sulphide content.

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REFERENCES

1. Camitz, G & Vinka, T-G: Corrosion of copper in Swedish soils. 12th Scandinavian Corrosion Congress & Eurocorr '92. Helsinki, Finland. 1992.
2. Vinka, T-G: Corrosion of metals in acidic till soils. Report to the Swedish Council for Building Research. Stockholm, 1997. (in Swedish). (Also available from the Swedish Corrosion Institute).
3. Denison, I A & Romanoff, M. Research Paper RP 2096. Journal of the National Bureau of Standards 44(1950) p 259-289.
4. Gilbert, P T. Journal of the Institute of Metals 73(1947) p. 139-174.
5. Gilbert, P T & Porter, F C.: Special Report No. 45. Iron and Steel Institute, London 1952 p 55-74.
6. Gilbert, P T. In: Corrosion (L L Shreir, ed.), Volume 1. 2nd edition. Newnes -Butterworths, London 1976. p. 4:33-4:67.
7. Ekbohm, L. In: KBS Technical Report 90. Nuclear Fuel Safety Project, Stockholm 1978. Appendix.
8. Sederholm, B & Vinka, T-G. In: Miljörapport (Environmental Report) 1990:9 (V Kucera, ed.). Nordic Council of Ministers, Copenhagen 1990. p 150-169.
9. Sederholm, B & Svenson, T & Vinka, T-G. Report R7: 1992. Swedish Council for Building Research, Stockholm 1992 (in Swedish).
10. Förstner, U & Wittmann, G T W: Metal pollution in the aquatic environment. 2nd edition. Springer-Verlag, Berlin 1981. Chapter E.
11. Camitz, G & Vinka, T-G: Corrosion of steel and metal coated steel in Swedish soils – Effects of soil parameters. In: ASTM STP 1013 (V Chaker & J D Palmer, eds.) American Society of Testing and Materials, Philadelphia 1988. p. 37-53.
12. Camitz, G & Vinka, T-G: Influence of some soil parameters on the corrosion of steel in Swedish soils. Proc. CEOCOR 2nd International Conference on Corrosion, Napoli 1989. p. 77-90. CEOCOR, c/o CIBE, Rue aux Laines 70, B-1000 Bryssel, Belgien.
13. Camitz, G & Vinka, T-G: Corrosion of aluminium in Swedish soils. Proc. 11th Scandinavian Corrosion Congress, Stavanger 1989. Högskolesenteret i Rogaland, Stavanger 1989. Paper F-33.