



Corrosion during seabed storage - PPCoN Pipe Testing Programme

RF-1998/274



Our reference: 649/654459/4	Authors, Paulsen, J. E., Westerlund, S., Ågotnes, N. O., Hovdan, H., and Myhrvold, A. N.	Version No. / date: Vers. 1 /27 sept.,98
No. of pages: 34	Project Quality Assurance. Tor Hemmingsen	Distribution restriction: Open
ISBN: 82-490-0391-8	Client(s): Phillips Petroleum Company Norway	Open from (date): 27.09.2003
Research Program:	Project title: MIC Pipe Testing Programme	

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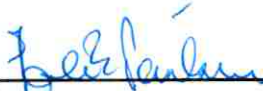
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Summary

Three steel pipe specimens were stored on the seabed at the Ekofisk area. The pipes were stored with seawater confined inside. After each of three, six and nine months one specimen was respectively collected for examination. Analyses of the confined seawater, the steel surface and measurement of corrosion rate were used to assess changes that had developed with reference to analyses taken the first day of the storage period. The data is relevant for North Sea conditions.

Results showed that the chemistry of the confined seawater changed as different chemical and microbiological processes came into play with increased storage time. The redox potential became increasingly more reduced; starting from 371 mV SHE for fresh seawater and ending at -243 mV SHE after 9 months confinement. This development lead to a shift in the microbial population as different conditions favoured different species of bacteria. The pH increased from 7.95 to 8.73 during the same period.

After six months storage period sulphide deposits were detected on the surface of the pipeline, and a slight increase in planktonic sulphate reducing bacteria numbers were detected. Surface growing bacteria were not monitored since no steps had been taken to facilitate such sampling when the sample pipes were prepared. It is still speculated that sessile SRB were active and generated the sulphide that were deposited in the layers that were observed firstly after six months.

After nine months the number of planktonic SRB had increased significantly and outcompeted other bacteria. During the period from six to nine months only a small increase in sulphide was detected. This may be attributed to the low concentration of available nutrients in the system.

The corrosion damage was insignificant, even after nine months storage period. Based on the results seabed storage of steel pipelines without chemical treatment is regarded as a realistic alternative to the current practice where preservative chemicals are added to reduce the risk of possible corrosion damage. How far in time a “safe period” stretches, is thus tentatively proposed based on the evolution of biogenic sulphide formation and measured corrosion rate.

Objectives

To possibly evaluate what may be considered a “safe period” of seabed storage for steel pipelines, full scale pipe specimens were deposited on the seabed at the Ekofisk area. One specimen was retrieved after each period of three, six and nine months to assess possible damage developing as a consequence of leaving the pipe exposed to seawater without using preservative chemicals. Changes of the confined seawater chemistry, the microbiology and surface corrosion processes as read from analyses should facilitate interpretation of which processes were driving the reactions. Based on the result a tentative recommendation for a “safe period” without chemical treatment should be given.

Conclusions

Dissolved oxygen in the pipe water was consumed rapidly; probably within a few days. Oxygen depletion was mainly driven by corrosion processes. The redox potential decreased continuously throughout the storage period paving the way for a boost of sulphate reducing bacteria (SRB) numbers.

Dissolved sulphide was not detected during the period. Precipitated sulphide was measured after six and nine months storage.

Nutrients supporting bacteria growth, measured as fatty acids, were detected at very low concentrations, and changes in levels through the incubation period could not validly be related to numbers of planktonic bacteria.

Surface growing bacteria (sessile) were not possible to monitor with the applied techniques. The sulphide layer covering the inner surface of the pipes originated most likely from sessile SRB activity.

Corrosion damage was not identified by visual inspection, even after nine months exposure to seawater. The inspected pipe specimens were considered to be in excellent condition, based on a total view of the performed analyses.

Identified precipitation on the surface may nevertheless contribute to an increased corrosion rate if the pipes were to be put into production after the nine month storage period. This is inferred from the fact that sulphide layers are electrical conductive and contribute to an increased area for corrosion processes to occur.

A safe period of seabed storage without chemical treatment is difficult to pinpoint exactly in this case. Three months storage was not sufficient to establish conditions that lead to sulphide production, and measured corrosion rate was very low. Three months storage is therefore considered as being non-controversial with respect to risk of corrosion damage. Six months storage lead to development of sulphide deposits, but only a small increase of planktonic SRB was detected. Somewhere in the period between three and six months the conditions became explicitly favourable for sulphide production, assumingly closer to six than three months.

Recommendations

- Three month storage without chemical treatment *in situ* is considered as non harmful for the steel pipes. This statement is based on the assumption that storage is performed at the same conditions as what were prevalent during the experiment.
- Six month storage is believed to be close to what is considered as not safe with respect to sulphide generation. But corrosion damage is still under no circumstances a problem.
- Nine month storage without chemical treatment *in situ* is not recommended based on the lack of empirical data. Corrosion damage during seabed storage is no problem even in this case.

- The pipes should be mechanically pigged and treated with chemicals to remove the sulphide layers before put into production after nine month storage period without chemical treatment. The same recommendation is given for pipes that have been stored for six months.

Further work

With respect to sampling procedures the design of the sample pipes was not optimal. Sampling of sessile bacteria was regarded as important information that was not possible to attain during the experiment. It is therefore suggested that in similar future experiments this problem is solved by applying retrievable corrosion coupons that allow for enumeration of sessile bacteria. In retrospect we therefore recommend that a new experiment is prepared where the following improvements are taken care of :

- the storage period is extended allowing end point estimation of possible sulphide generation.
- retrievable corrosion coupons are installed, allowing enumeration of sessile bacteria.
- replicate corrosion probes are fitted to ensure that corrosion data is collected properly.
- design a follow up experiment that allows estimation of the possible influence different exposure periods may have on corrosion rate after hook up and put in production.
- corrosion damage in welding is important to assess, therefore the welding should be performed according to specifications when hooked up to allow for representative measurements to be carried out.

Introduction

Currently there are constraints related to the period of which steel pipelines may be left exposed to seawater without treatment with chemicals. The constraints are ultimately linked to the risk of damage that the pipelines may suffer during storage before put into production. Common practice during seawater storage involves the use of chemicals to preserve the pipes. Such practice implies higher cost and environmental considerations as the chemicals eventually have to be disposed of. For this reason it is worth considering a “no treatment option”.

Defining a safe period for exposure of production pipelines to seawater before put into production appear as possible by acquiring relevant data to be used as a basis for decision making. In early 1997 Phillips Petroleum Company Norway (PPCoN) decided to examine the possible impact of corrosion, including bacteria impact, on submersed and exposed pipelines during long time storage on the seabed. The test was planned to be performed at field scale.

During the storage period assessment of what was considered to be relevant parameters were carried out in order to disclose possible causes for processes developing, and to monitor damage/corrosion at the inside pipe-surface. This was afforded by retrieving samples for closer examination and analysis at regular periods.

Experimental approach

Three sample pipes were placed on the seabed at the Ekofisk II field September 14. 1997, 77 m below sea level. Each pipe consisted of two pipe sections welded together and closed at both ends by welded steel plates (Fig.1). One end was fitted with a NPT ball valve. The three pipes were linked together by steel wire and attached to a pipeline marker buoy for easy recovery without the use of remote operated vehicle (see figure A.4. in appendix). The air inside the pipes was exchanged with Argon and the valves were shut before they were lowered to the sea bottom to collect sea water. After sea water was collected the pipes were lifted to the surface vessel again and water samples were collected. Then they were re-lowered to rest on the seabed. After periods of three, six, and nine months, one sample pipe was retrieved for examination. Sampling of pipe water was facilitated by inserting a polypropylene tube through the ball valve, which was fitted with an adapter and a pressurised gas container allowing the drained water to be replaced with argon.

Material and Methods

Corrosion assessment: Corrosion measurements were performed on-site. Each pipe was fitted with a corrosion probe (LPR, see Fig 1a.) before placed on the seabed. The probes were fitted at 6 o'clock position (see Fig. 1b.). The cathodic polarisation measurements were performed with a portable computer, and from ambient corrosion potential to 300 mV below with a scan rate of 2.0 mV /sec. The electrochemical polarisation curves were obtained by Gamry CMS 100.

Corrosion probes were fitted into the test pipes before they were placed on the seabed. Figure 1a. shows the shape of the probe. The inner disc is the working electrode with the reference ring outside. The outer ring / body is the counter electrode. The material of working and reference electrode is UNS G10180 (AISI 1018) carbon steel while the body is made of UNS S31600 (AISI 316). The area of the working electrode was approximately 0,78 cm² for the 6 and 9 months exposure pipe and 0,07 cm² for the 3 months exposure pipe.

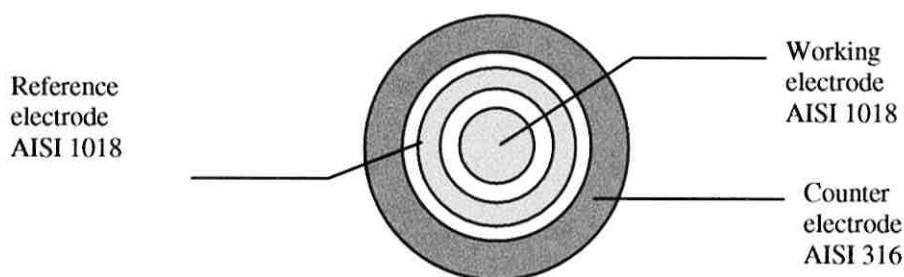


Figure 1a. Sketch of the corrosion probe.

Preparation of the test electrodes: abrasion with emery paper (500 mesh) before rinsed with distilled water, and dried in acetone before mounted on the test pipes. This was done at the laboratory on-shore. The test electrode fitted to the 3 month pipe was prepared on-site, and treatment with acetone was therefore not carried out in this case.

The inner surface of the pipes, as well as the weld seams were visually inspected for corrosion attack, and pipe pieces were cut for closer examination with scanning electron microscopy (SEM) analysis. X-ray fluorescence analysis with an energy dispersive multichannel detector (SEM-EDAX) was used for identification of specific elements. Debris and suspended solids in the pipe waters were collected for analysis of element composition.

Chemical parameters: The pipe water chemistry was monitored by measuring several parameters, in some cases with different methods on-site;

Dissolved oxygen; 1) immersible oxygen sensitive electrode, 2) titration of dissolved oxygen (Winkler method), 3) colorimetric analysis (Chemometrics kit). Experience showed that low oxygen concentrations and discolouring of water by suspended iron favoured the use of the oxygen electrode.

Dissolved sulphide; 1) sulphide electrode, 2) spectrophotometric method¹, 3) Chemometrics kit. The electrochemical data proved to be most reliable as the sulphide concentrations were low and the waters were heavily discoloured.

Precipitated sulphides (surface deposited): samples cut from the pipe were put in jars with distilled water and gas tight lids. Hydrochloric acid was added to volatilize sulphide (pH < 1). The solution was stripped with N₂ for 5-24 hours (recovery efficiency 90%). The effluent gas was lead through a solution of 1 M zinc acetate to provoke sulphide precipitation (ZnS↓). Sulphide was then quantified with the *Munson* spectrophotometric method.

The pH was measured with a Metrohm combination electrode (Ag/AgCl). Standardisation were performed against the NBS- pH scale.

The Redox-potential (Eh) was measured with immersible electrodes (Platinum and Calomel).

Organic carbons; Confined pipe-water were collected for total organic carbon analysis. These samples were immediately acidified with sulphuric acid and stored for later analysis. The organic carbons (TOC) were oxidised to CO₂ by addition of a strong oxidising agent (40 mM H₂SO₄), followed by ultra violet radiation. Quantification of carbon dioxide was then allowed by IR-spectroscopy.

Total suspended solids (TSS) were determined by filtration of water through pre-weighed membrane filters (0.45 µm cut off).

Alkalinity was determined by a standard method².

Analysis of short chain organic acids (acetic-, propanoic-, butanoic-, and higher acids) was performed by isotachopheresis (ITP), standard procedure³ (i.e. direct determination at pH 5.5, and conductivity detection). Collected samples were acidified with sulphuric acid.

Trace metal determination; Triplicate waters samples were taken for metal analysis, two of which were unfiltered and one filtered through 0.45 µm cartridge filter. The samples were preserved with nitric acid according to procedures for seawater analysis. Then analysis was performed with a VG PQ2+ ICP-MS. Seawater collected on site was analysed after treated with solvent extraction⁴ and following ICP-MS. Waters collected from the pipes were diluted before ICP-MS analysis. Matrix matched standards were

1 Munson, D. A., 1977: Simplified Method For The Determination Of Acid-Soluble Sulfides In Marine Sediments. *Marine Biology*, 40. pp 145-150.

2 Norwegian Standard, NS-EN ISO 9963-1.

3 Ref. Dr. Tanja Barth, University of Bergen, Dept. of Chemistry.

4 L.-G. Danielsson, B. Magnusson, S. Westerlund and K. Zhang, 1982. Trace metal determination in estuarine waters by atomic absorptionspectrometry after extraction of dithiocarbamate complexes into freon. *Anal. Chim. Acta*, 144, 183-.

used for quantification. Multi-element analysis of the filters was performed with a semi-quantitative procedure on the digested filters. For the quantification of iron a standard was used.

Microbiological parameters : Total number of micro organisms (i.e.: eubacteria and archaeobacteria, usually < 2µm in diameter) was determined with a modified⁵ fluorescence microscopy technique (DAPI)⁶. Fresh water samples collected on site were conserved with glutardialdehyde.

Two physiological different groups of micro organisms were monitored; chemo-heterotrophic bacteria (bacteria that generate acidic products, referred to as GHB), and sulphate-reducing bacteria, referred to as SRB.

Growth medium for GHB: 1 g glucose, 0.5 g of tryptone peptone and yeast extract, phenolic red, 0.2 l deionized water, 0.8 l filtered sea water (0.45µm). Aerobic incubation.

Growth medium for SRB : 1 g NH₄Cl, 1 g yeast extract, 0.5 g acetate, 2.5 mg FeSO₄ x 7 H₂O, 2.5 mg lactic acid, 2 mg resazurin, 50 mg dithionite, 0.8 l filtered seawater, and 0.2 l deionized water. Anaerobic incubation.

Enumeration of the micro organisms was carried out according to standard MPN (most probable numbers)-method⁷. Inoculated samples were incubated in dark, at 4 °C. Sessile micro organisms were enumerated by retrieving samples of the inside surface of the pipe wall and immersing these in vessels containing anoxic, sterile seawater. Then treated with ultrasonic sound (sonication) for 120 seconds. Water samples were taken for bacteria enumeration using the MPN-method.

Table 1. Overview of analyses applied and respective executive laboratory.

Analysis	Method	Executive laboratory
Corrosion	Polarisation curve / LPR SEM and EDAX	Stavanger College of Science and Technology
Metals	ICP-MS	RF
Microbiology	Microscopy (bright-field, phase contrast and fluorescence), MPN method	RF
Chemistry	Ref. text for different methods	RF
Fatty acids	Isotactophoresis	University of Bergen, Dept. of Chemistry

5 Yu, W., W.K. Dodds, M.K. Banks, J. Skalsky and E.A. Strauss., 1995. Optimal staining and sample storage time for direct microscopic enumeration of total and active bacteria in soil with two fluorescent dyes. *Appl. Environ. Microbiol.* 61:3367-3372

6 Porter, K.G., & Y.S. Feig. 1980. The use of DAPI for identifying and counting aquatic microflora. *Limnol. Oceanogr.* 25: 943-948.

7 J.C. de Man., 1977: MPN Tables for More Than One Test. *European J. Appl. Microbiol.* 4, 307-316

Results and discussion

After periods of three, six, and nine months pipe specimens were recovered for examination of both the pipe water and the inside pipe-surface. Assembled data are presented with reference to the respective field trips: 1) **"0" reference**, the first field trip; September 14 1997, where the pipe samples were positioned on the seabed, 2) **3 month**, the second field trip; December 15 1997, 3) **6 month**, the third field trip; March 13 1998, 4) **9 month**, the fourth field trip; May 27 1998. Topical reports have been prepared after the three first field trips, and the data were discussed elaborately in these. Tables, figures and micrographs are assembled in the appendices, only well arranged shortened versions are used in the following to substantiate the topics being discussed.

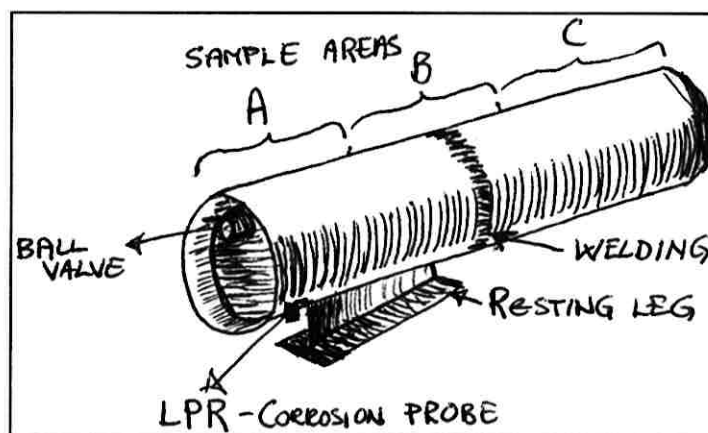


Figure 1b. Schematic drawing showing exterior attributes of test pipes.

Physical data pertinent to the pipes : 8 m total length/ 7.4 m length exposed to contained water, 3 cm wall thickness, inside diameter 34 cm, inside surface area 808.2 dm², bulk water volume 671.5 litres. The drawing (Fig.1) shows the positioning of the corrosion probe and the ball valve. The pipes were mounted on a resting leg for practical purposes. Samples recovered for surface analyses were labelled with reference to sample area A, B and C, and their clock position.

Applied cutting method allowing for pipe inspection and sampling after each period :

- The 3 month pipe sample was first machined down at selected positions and samples were collected for surface analysis. Then pieces of the pipe wall were cut out while the pipe still contained the seawater.

Following, the pipe was drained and divided in to two pieces before inspected for corrosion damage

- The 6 month pipe was machined down at the selected samples areas in a similar way as for the 3 month pipe. To avoid generation of too much heat the final sampling of the pipe wall was made by a hole-saw with a 1 or 2 inch hole diameter. This procedure was carried out while the pipe still contained water. The only visual inspection that were performed on the 6 month pipe was on the selected sample areas.

- For the 9 month pipe sample sessile bacteria was not sampled as it had proven impossible to collect representative samples. The pipe samples were retrieved by hole-saw on the full pipe wall thickness. After this the pipe were cut in 4 sections which allowed visual inspection of the total inside pipe surface.

Water samples were recovered successfully at each field trip. Corrosion measurements were also accomplished without problems. In some cases additional pipe-water samples were collected onshore to check if changes that would affect the onshore analysis had occurred during transportation from the field.

Originally data collection included examination of sessile bacteria thriving on the inside pipe surface. After several efforts we learned that this was not possible to execute without damaging the sample to the extent that almost all microbial life was extinguished. For this reason no data for sessile microbes is presented.

Chemical analyses: The pipe-water chemistry reflected clearly changes that occurred during the seabed storage period. Pipe-water was sampled after the pipes had been retrieved onboard the surface vessel and had rested for a short period to allow particulate matter to settle. For this reason temperature measurements differ slightly between seawater and pipe-water. From the starting point the chemical properties were measured to be very much the same in each pipe, and therefore it seemed legitimate to claim that the sample pipes should be regarded as three parallels. At time "0", the values of oxygen and redox potential differed less than 15% for the three sample pipes. Accordingly, the pH of the three pipe waters differed by less than 0.1 unit. The changes measured during the experiment period (Table 2) were caused by pure chemical reactions and the activity of the micro-organisms. The measured reduction in the redox potential (Fig. 2) was a clear indication of that the system became chemically more reduced as the incubation period progressed.

Table 2. Results of chemical analyses.

	seawater 70m ¹	pipe-water ³ "0"- ref.	pipe-water 3 month	pipe-water 6 month	pipe-water 9 month
Eh (mV SHE)	371	249	-20	-123	-243
pH		7.95	8.42	8.78	8.73
O ₂ (ppm)	5.5	4.8	<0.1	<0.1	<0.1
H ₂ S (ppm)		n.m. ⁴	<0.1	<0.1	<0.1
Temp. (°C)		12	11	8	15
Alkalinity	2.29 ²	n.m. ⁴	n.m. ⁴	n.m. ⁴	1.81

¹Sampled Dec. 97.

²Sampled 27 May 98.

³average of all three pipe samples

⁴n.m. = not measured.

As expected dissolved oxygen totally disappeared in the pipe waters, as measured after 3 months. The exact time taken for the oxygen level to drop below the detection limit can not be determined; the sampling intervals were too long and few. We speculate that this process was proceeding at a high rate due to the large exposed steel area provided. Measurements of dissolved sulphide indicated that there was no dissolved sulphide in the pipes during the whole experimental period. However, while measuring dissolved oxygen

after 9 months the electrode was poisoned; which could suggest traces of sulphide /precipitation of sulphides on the membrane. Any produced sulphide would assumingly

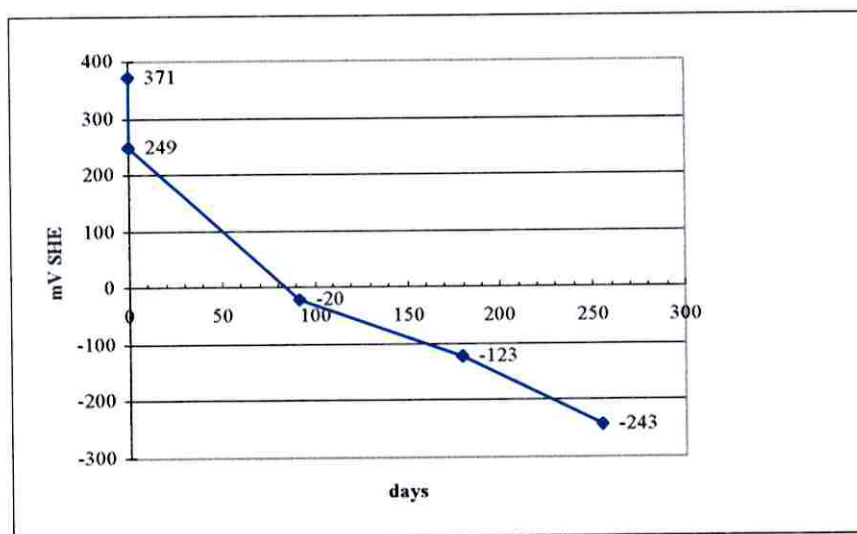


Figure 2. Redox potential (mV vs. SHE) as a function of time. 0-time shows redox potential of raw seawater (371 mV) and mean value (249 mV) of water collected from the pipes.

react with M^{2+} -ions and come out of solution as precipitate. The pH gradually increased, from typical seawater value 7.95 to 8.73 after 9 months. Apparently the pH stabilised in the period between 3 and 6 months. An increase in alkalinity was observed during the experimental period. This increase was expected as the pH had increased. However the alkalinity increase cannot have been the result of increase in total carbonate as there was no large available carbon source that could support this increase.

Fatty acid (FA) analyses: FAs were measured to monitor changes that could be ascribed to microbial consumption. Low molecular weight fatty acids are the preferred nutrients for sulphate reducing bacteria⁸. The level of FAs were in general very low, and often close to or beyond the detection level. Samples of seawater were analysed for FAs content at the second, third and fourth field trip. Table 4 tells us that there were minor differences between samples collected at different depths and at different times. The level in the pipes were comparable to what was found at 70 m depth at the site. Comparing the figures of FAs in pipe water after 9 months with the “0”-ref. (Table 3) indicated that acetic and formic/oxalic acids had accumulated and that higher and total acids had decreased. The complete analytical protocols from the fatty acid analysis are found in the Appendix 3.

8 Widdel, F., and Bak, F. (1992). Gram-Negative Mesophilic Sulfate-Reducing Bacteria. The Procarvates. A. Balows, H.G. Truper, M. Dworkin, W. Harder and K-H Schleifer, Springer-Verlag. **183:** 3352-3379.

We cannot conclude from these measurements that the microbes utilised this nutrient pole, but it may be expected that higher acids were degraded and thus could explain the rise of low molecular FA levels. The variations in the FA readings during the different phases of the experiment indicated a rather low analytical precision.

Table 3. Pipe-water FA-analyses.

Fatty acid (mM)	"0"-ref.	3 month	6 month	9 month
Formic/oxalic		0.06	≤0.05	0.13
Acetic acid	≤0.05	≤0.05	0.27	0.10
Propanoic acid	≤0.2	≤0.05	≤0.05	0.15
Butanoic acid	≤0.2	≤0.05	≤0.05	≤0.07
Higher acids	0.4	≤0.2	0.4	0.15
Total acids	0.7	≤0.2	0.7	0.5

Table 4. Seawater FA-analyses at the experimental site.

Fatty acid (mM)	30m depth ¹	70m depth ¹	70m depth ²	30m depth ³
Formic/oxalic	≤0.05	≤0.05	≤0.05	0.09
Acetic acid	≤0.05	≤0.05	0.18	0.16
Propanoic acid	≤0.05	≤0.05	≤0.05	0.23
Butanoic acid	≤0.05	≤0.05	≤0.05	0.10
Higher acids	≤0.2	≤0.2	0.5	0.3
Total acids	≤0.2	≤0.2	0.9	1.0

¹sampled field trip 2
²sampled field trip 3
³sampled field trip 4

Suspended solids: The amount of suspended solids found in the pipes was to a large extent influenced by the handling procedures and lap time on the ships deck, as well as the sampling. The data in Table 5 indicated that no fine grained, i.e. colloidal fraction, that would stay in suspension was generated during the experiment.

Table 5. Suspended solids (mg/L) found in pipe-waters .

3 month	6 month	9 month
83	154	86
101	166	112
29	142	
mean value : 72	mean val.: 155	mean val.: 99

In table A.11. (appendix) element composition of suspended matter determined for the three different sample pipes are shown. The colour of the filtered material sampled from the 3 and 6 month pipes were reddish; a typical colour of iron compounds (iron-III-hydroxide). The colour of the filtered material sampled from the 9 month pipe was black. The black colour may have indicated presence of FeS. Suspended materials were run through the sulphide stripping procedure, described below, to determine the sulphide content. The results showed that the sulphide content of the suspended matters found in the 9 month pipe water were < 1 %.

The data of the multielement analysis (table A.11., appendix) indicated a change in metal distribution within the suspended matter , as measured after 6 and 9 months. Iron content increased significantly.

Metals: To make sure that the data were interpreted correctly, background levels of the metals found in seawater on site were determined. Seawater samples were therefore collected and analysed after 3 months (Table 6). The concentrations shown in Table 6 coincides with what may be expected at the Ekofisk area, with reference to typical North Sea waters data⁹. Concentration of metals found in the pipe waters, deviating from these figures, can only be explained by factors that were exclusively linked to the particular environments that were created within each pipeline. In this respect we have reason to believe that some of the elements identified in the pipe waters may have been introduced during open air storage periods or during cutting and welding of the pipes.

Table 6. Trace metals in seawater at the test site in the Ekofisk area

Metal	30 m (µg/l)	70 m (µg/l)
Cr	<10	< 10
Mn	< 0.3	0.45
Fe	2	2
Co	0.007	0.070
Ni	0.33	0.39
Cu	0.35	0.35
Zn	0.55	0.86
Cd	0.030	0.024
Pb	0.074	0.095

Concentrations of metals found in the pipewater at time “0”, were higher for most of them, compared to the Ekofisk area bottom water. The source of these metals were most likely urban fall-out deposited during the open air storage period. The Zn metal is a typical representative of such. Metals like Mn and Fe originated most likely from the pipe material.

Manganese, in our view, was an interesting “indicator metal” in the test systems. The behavior in anoxic environment is well documented^{10,11}. Manganese is the first element that changes the oxidation state when the environment becomes anoxic. It changes from the +4 to +2 oxidation level. The solubility of the +2 oxidation state is considerably higher than for the +4, and as a consequence we anticipated to see an increase in dissolved manganese concentrations as oxygen was consumed in the system. From the data in Tables 7 a-c, it was apparent that this occurred somewhere in the period between three to six months. After six months most of the manganese was found in the filtered samples. Another interesting change that occurred between month 3 and 6 was that a large part of the manganese was integrated in the suspended solids (the difference

9 L.-G. Danielsson, B. Magnusson and S. Westerlund, 1985. Cadmium, copper, iron, nickel and zinc in the north-east Atlantic. *Mar. Chem.*, 17, 23-41

10 C. Haraldsson and S. Westerlund, 1988. Trace metals in the water column in the Black sea and the Framvaren. *Mar. Chem.* 23, 417-

11 B. Sundby, L. Anderson, P. Hall, Å. Iverfeldt, M. Rutgers van der Leoff and S. Westerlund, 1985. The effect of oxygen on release and uptake of cobalt, manganese, iron and phosphate at the sediment-water interface. *Geochim. Cosmochim. Acta*, 50,

between unfiltered and filtered samples in Tables 7a-c. Since manganese was one of the main components of the pipe material this observation might indicate that the time period between 3 and 6 months was important for the development of these processes. The same trend was also seen from the data of the filter analyses (Table A.11); the concentration of Fe and Mn in the solid material increased.

Table 7 a-c Trace metals ($\mu\text{g/l}$) in the pipe-water at deployment and after different periods.

Metal	"0" ref.	3 month	3 month
	unfiltered	unfiltered	filtered
Al	137	< 100	< 100
Cr	< 50	< 10	< 10
Mn	493	1619	2
Fe	1510	25094	5978
Co	1.2	2.12	0.78
Ni	59	372	11
Cu	164	7	1
Zn	401	8	5
Mo	< 5	< 5	< 5
Cd	3.2	0.03	0.02
Pb	32.5	1.9	0.1

Table 7 b.

Metal	"0" ref.	6 month	6 month
	unfiltered	unfiltered	filtered
Al	< 100	< 100	< 100
Cr	< 50	27	8
Mn	344	3285	2391
Fe	1755	67117	3520
Co	0.2	2.5	< 1
Ni	16	30	< 10
Cu	24	21	4
Zn	108	64	7
Mo	< 5	< 10	< 10
Cd	< 1	< 0.2	< 0.2
Pb	< 5	2.5	0.0

Table 7 c.

Metal	"0" ref.	9 month	9 month
	unfiltered	unfiltered	filtered
Al	< 100	< 100	< 100
Cr	< 50	32	< 5
Mn	600	4635	2366
Fe	5510	211325	10813
Co	0.8	16	0.42
Ni	32	77	< 10
Cu	23	39	3
Zn	155	122	7
Mo	< 5	28	7
Cd	< 1	4.0	< 0.2
Pb	< 5	6.0	< 1

Iron also goes through a redox change when the environment turns anoxic. Anticipated redox change would be between +3 to +2. However, as opposed to manganese FeS precipitate is formed either on the pipe walls or in solution if sulphide is available. The solubility of FeS is low, consequently dramatic changes in dissolved iron concentrations were unlikely to find.

Sulphide: The measurements of sulphide deposits on the inside surface of the pipes (Table 8) corroborated with the period when the chemical environment shifted towards the anoxic state, the 3-6 month period. According to the sulphide measurement performed on metal samples after 9 months the amount of sulphide deposited was not much different than what was found after six months.

Table 8. Sulphide deposits on the inside surface.

3 month sample		6 month sample		9 month sample	
sample	S ²⁻ (µg/cm ²)	sample	S ²⁻ (µg/cm ²)	sample	S ²⁻ (µg/cm ²)
A, 12 o'clock	< 18	C, 12 o'clock	521	A1	685
B, 6 o'clock	< 18	C, 3 o'clock	504	A2	617
weld seam	< 18	C, 6 o'clock	118	A3	202
		B, 12 o'clock	238	B1	346
		B, 3 o'clock	429	B3	277
		B, 6 o'clock	451	C1	445
				C2	255
				C3	509
Average	< 18		377		417

Microbiology: The applied MPN method allowed a quick and practical monitoring of trends in the microbe numbers. The accuracy of the method is dependent on several factors, and the finite range of error was, for practical reasons, not determined in this case. In general the confidence limit is a statistical calculated value that has to be adjusted by the extra errors introduced during sampling and pipetting. From experience we know that it is a rough, but fairly reliable method given that the sampling and dilution is performed by the same person each time. Additional microbe counting using the DAPI technique was believed to produce reliable figures of maximum number of microbes present in each sample.

A marked change in the balance between GHB and SRB numbers was measured during the exposure period (Tables 9-10). In Table 9 the MPN counts for the "0"-reference are shown. The number of SRBs (4 cells per mL) was low, and typical for fresh North Sea waters MPN counts. This also indicated that the water collected near the seabed did not contain unusual high numbers of this bacteria group. Corresponding number for the GHBs was 4.3×10^5 per mL. The figures are the mean value from water samples collected from the 3 pipes, three parallels in each case. The results were considered to be typical for fresh seawater. As the incubation period of the pipes increased the MPN numbers of samples taken at different intervals showed a slight increase of GHBs until the 6 months sampling. Then a dramatic decrease was measured after 9 months. Correspondingly the SRB numbers stayed low until somewhere between 6 and 9 months. The 9 month counts showed a dramatic increase in SRB numbers.

Table 9. Numbers of bacteria detected in the pipe-waters, using the MPN technique.

	"0"-ref.	3 months	6 months	9 months
Bacteria group	cells /mL	cells /mL	cells /mL	cells /mL
GHB	4.3×10^5	4.6×10^7	24×10^5	240
SRB	4	3	93	1.9×10^5

The microbe-counts of 3 months exposed pipe-water indicated that there was no significant change in numbers during the 3 months incubation period compared to the 0-

reference counts. However, we do not know which species were dominating, except that they all had to be anaerobic since oxygen were totally depleted. In Fig. 2 the redox potential is graphically presented. After 3 months the Eh was measured to -20 mV. This potential is a little bit too high to favour the growth of SRBs. SRBs are known to become active when the $Eh \leq -100\text{mV}$. Chemical measurements after 3 months showed no sulphide which also correlate with no SRB growth.

It is still worth keeping in mind that the situation may be different for the sessile SRB. Generally it is difficult to predict sessile numbers from counts of planktonic microbes. The sessile bacteria and the behaviour within a biofilm may be very different than what is seen within the water body. The local chemistry at the interface between a biofilm and steel material may differ substantially from the bulk water phase. The sessile bacteria develop different consortia of microbes that may express different physiological processes. It is thus quite possible that a sessile SRB population may be active although this is not reflected by counting planktonic numbers.

By extrapolation of a line between the readings in Fig. 2 we can see that the -100mV limit is crossed after approximately 160 days (i.e.: 5 months and 10 days). But such inference is not strictly valid, as we know nothing about the redox potential in between the sampling intervals. The microbe counts show that after 6 months the SRB number had increased, and this correlate with the redox potential of -123 mV and an average of 377 μg sulphide per cm^2 steel surface. The 6 month reading shows clearly that a sulfidogenic microbial population had established. This trend was confirmed by the nine month reading where the SRB number had risen two thousand times (to $1.9 \times 10^5/\text{mL}$). It is interesting to note that the amount of sulphide produced between 6 and nine months was minor; 417 μg sulphide per cm^2 was measured after nine months, which is an increase of only 40 $\mu\text{g}/\text{cm}^2$. Theoretically the sulphate pool allowed 723 grams of sulphide to be produced, given that nothing else limited the activity of the SRBs. The amount of sulphide covering the pipe wall was calculated to be less than 5% of the theoretical potential.

The DAPI counts (Table 10) showed that the total number of microbes were about the same in samples collected at different depths of the seawater column, and the pipe waters (3 month data). The total numbers after three and six months exposure were less than estimated with the MPN count, and larger after 9 months. This discrepancy is acceptable, and as stated earlier we rely on the DAPI counts in favour of the MPN counts.

Table 10. Mean values of total bacteria counts (DAPI), cells/mL

Sample	3 month	6 month	9 month
Sea water, 30 m depth	9.01×10^4		
Sea water, 70 m depth	7.55×10^4	3.36×10^5	
pipe-water, sampled offshore	4.64×10^4	4.56×10^5	1.2×10^6
pipe-water, sampled onshore	4.17×10^4		

The temperature is a parameter that influence microbial growth rate, and in this respect it may be questioned whether the rate of the microbial processes would have been different given that the temperature was different. This is difficult to predict, but the temperature

is acknowledged as an important parameter as it also governs solubility of gases and ion equilibria. The relevance of the presented data is supported by the recorded data of temperatures at the seabed in the Ekofisk area, which can be read in Figure A.5., found in the appendix.

Corrosion: Visual inspection of the pipe after 9 months exposure revealed no severe corrosion damage to the inside of the pipe. Corrosion products covered the entire internal surface area and indicated that the attack was general and not localised. The surface cover was mainly brown, but some black cover was observed as well. A thick layer of black deposit was observed at the bottom of the pipe. The thickness of this layer varied but in some locations it appeared to be in the range of 1 mm thick. Because of the location it is believed that this product was sedimentation from the sea water and that it was not the result of a localised anodic reaction.

The corrosion products and the corrosion attack on the pipe was also investigated using scanning electron microscopy and conventional optical microscopy after 3, 6 and 9 months exposure. The exposed pipe was examined at three different locations: bottom (6 o'clock), top (12 o'clock) and beside the weld.

The composition of the corrosion product was determined by EDAX analyses showing that there was no sulphur after the first three months exposure. After 6 and 9 months exposure sulphur was detected. Note, the method did not distinguish between different chemical form of sulphur (i.e.: $\text{FeS}/\text{SO}_4^{2-}/\text{S}_0$). The amounts were in the range of 5 to 10 wt %. The results are shown in the tables A.12-15. (appendix).

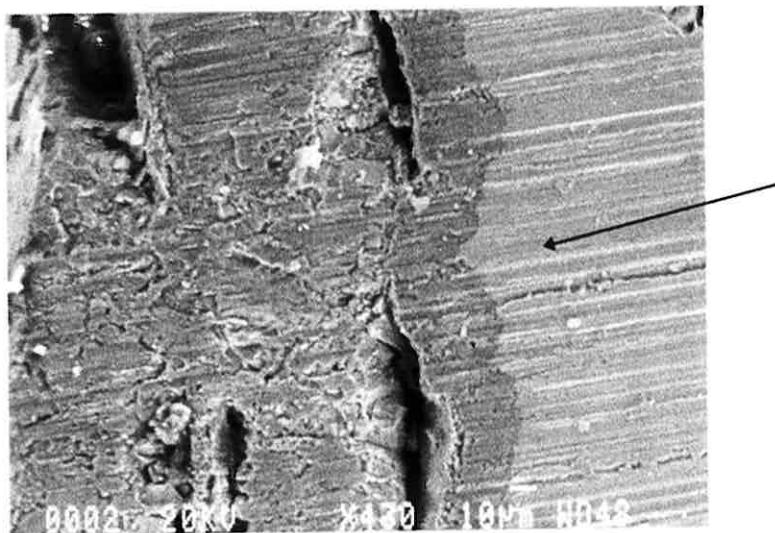


Figure 3. SEM micrograph of a cross section of corrosion product, 9 months exposure. The arrow indicates area of non-infested steel material.

A cross-section micrograph of the corrosion product is shown in Figure 3. The figure shows that the thickness of the corrosion layer was between 0.15 and 0.20 mm. There is also an indication that the surface is covered by two layers of different origin. It is believed that one is formed on the steel surface prior to exposure, while the other is formed during exposure. Some cracks in the products are shown as well. Other micrographs of the corrosion products are shown in appendix, Figures A.22.-26.

Polarisation measurements: The cathodic polarisation curves after day 1 (first field trip), after 3, 6 and 9 months exposure are shown in Figure A.6. The curves were plotted in the same diagram to facilitate interpretation of changes in the shapes of the curves. The measurements showed that the current densities first decreased (after 3 months exposure) and then increased (after 9 months exposure).

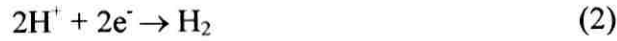
The shape of the curve after 6 months exposure indicated an ohmic resistance suggesting that the probe had been short circuited. Based on this observation the measurements were repeated onshore after the pipe had arrived at PPCoN Tananger. The results from the onshore measurements were exactly the same as found offshore (plotted in the same figure, Figure A.6.).

Some solid material dropped off the corrosion probe when it was removed from the pipe. It was believed that this solid material had short-circuited the counter and reference electrodes on the probe, and the product was taken to the laboratory for analysis to determine whether or not the material was electrically conductive (see Fig. A.10 in appendix to see how the probe was fitted to the inside surface). It was verified that the composition of the surface of this material was similar to that of the other corrosion products sampled (see Appendix) and it was concluded that the material was electrically conductive and this could explain the non-exponential profile of the polarisation curve. Plotting the potential as a function of current gave a linear curve, see Figure A.7. This can only be explained as an artefact of an Ohmic short circuit on the probe. The resistance of the short circuit can be determined from the slope of the curve and is found to be approximately 4 ohms.

Some linearity is also observed for the same probe at day 1 (see Figure A.8.). The slope of this curve represented approximately 1580 ohms.

The polarisation curve after 9 months exposure shows significantly higher current densities than the measurements made at day 1. The shape of the curve shows both a convex and a concave portion indicating that there are at least two different current conducting mechanisms present simultaneously. At the lowest potentials the curve shows Tafel behaviour which is indicative of an activation controlled electrochemical half-cell reaction. The shape of the curve nearer the open circuit potential could indicate either a diffusion controlled reaction mechanism or a short circuiting phenomenon similar to that observed after 6 months exposure. It is believed that in this case the explanation is a short circuit. For low current densities the short circuit path will be the dominating current path, while at higher current densities, the electrochemical electron transfer will be the dominant path. This is illustrated in Figure A.9. which shows the curve measured after 9 months exposure compared with a theoretical polarisation curve constructed from a hypothetical ohmic resistance and an electrochemical activation controlled reduction reaction mechanism.

The different electrochemical reduction reactions involved at the different time exposure might be oxygen reduction (Eq.1) for day one and hydrogen reduction (Eq.2) or reduction of water (Eq.3) for the other exposure time.



In case of H_2S the following reactions will occur:



The dissolved iron will immediately react with S^{2-} and form iron sulphide.



The amount of H_2S (<0.1 ppm) and the increasing pH in the water inside the pipe (pH 8.7) suggest that the main cathodic reaction is hydrogen reduction or reduction of water.

The current densities after 9 months exposure are relatively high compared to the other valid measurements. As far as we can tell, there are no new reduction reactions that can account for this increase in current density. Therefore we cannot find any other explanation than a significant increase in the surface area where the cathodic reduction takes place. This could be caused by an electrically conducting corrosion product, such as iron sulphide or Fe_3O_4 , settling on the corrosion probe.

After exposure lasting 9 months, the corrosion damage to the pipe itself was insignificant. However, the corrosion process had produced corrosion products containing, among other elements, sulphur (not elemental), and these products appeared to have electrical conductivity and to be capable of supporting electrochemical reactions. It is conceivable, therefore, that the corrosion products formed during the test could affect the corrosion rate in a future production phase by enhancing the rate of the cathodic reactions. A thorough cleaning process would reduce this effect.

Appendix 1, Tables

Table A. 11. Suspended material collected on the 0.4 µm filters. No traces (<0.001%) of Li, Be, B, Sc, Y, Zr, Nb, Mo, Ru, Ag, Cd, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Tu, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, Th, U, Ir could be found.

	3 month	6 month	9 month	3 month	6 month	9 month
	%	%	%	µg/l	µg/l	µg/l
	Composition of the suspended material			Concentrations of suspended metals in the pipe water		
Al	0.111	0.034	0.034	44.6	56.1	37.7
Ti	0.24	0.045	0.05	96.5	74.3	55.5
V	0.021	0.000	0.000	8.4	0.0	0.0
Cr	0.009	0.006	0.004	3.6	9.9	4.4
Mn	0.46	0.299	0.426	185	493	473
Fe	37.3	40.9	53.2	15000	67500	59000
Co	0.007	0.002	0.003	2.8	3.3	3.3
Ni	0.074	0.026	0.023	29.7	42.9	25.5
Cu	0.015	0.008	0.005	6.0	13.2	5.6
Zn	0.098	0.048	0.04	39.4	79.2	44.4
Ga	0.003	0.002	0.001	1.2	3.3	1.1
Ge	0.002	0.001	0.002	0.8	1.7	2.2
As	0.004	0.001	0.002	1.6	1.7	2.2
Se	0.006	0.002	0.004	2.4	3.3	4.4
Rb	0.001	0.000	0.000	0.4	0.0	0.0
Sr	0.006	0.004	0.026	2.4	6.6	28.9
Pd	0.002	0.001	0.001	0.8	1.7	1.1
Sn	0.002	0.001	0.001	0.8	1.7	1.1
Te	0.001	0.000	0.001	0.4	0.0	1.1
Ba	0.032	0.03	0.018	12.9	49.5	20.0
Hg	0.005	0.000	0.000	2.0	0.0	0.0
Pb	0.004	0.001	0.001	1.6	1.7	1.1
Bi	0.001	0.000	0.000	0.4	0.0	0.0
Sum	38.43	41.43	53.80			

Table A.12 : Chemical composition of the 3 month pipe specimen, and corrosion product for the unexposed and exposed pipe using SEM / EDAX (wt. %).

Element (wt%) Sample	O	Al	P	Si	Ca	Cr	Mn	Fe	Scan-area EDAX	Micrograph #
Pipe				0.45			1.39	98.16		
Unexposed		0.89		0.93	0.54	0.36	1.51	95.76	0.06 mm ²	4.2
Exposed, 3 month, 6 o'clock, a			1.98		3.03		0.98	94.01	0.06 mm	4.3
- " -, b	35.24							64.76		4.4
- " -, c	42.6							57.4		4.5
12 o'clock			6.36		7.20		1.58	84.86	0.06 mm ²	
Weld			3.20		5.68		1.19	89.93	0.06 mm ²	4.6
Corrosion product	36.65							63.35		4.7
- " -	38.58							61.42		4.8

Table A.13. Chemical composition of the corrosion product for the 6 months exposed pipe; analysed with SEM /EDAX (wt. %, scan area 0.48 mm²).

Element (wt%) Sample reference	Na	Mg	Si	P	S	Cl	K	Ca	Mn	Fe	Fig. #
1	1.52	3.80	0.74	0.86	3.25	0.27		4.93	1.58	83.06	4.4
9 o'clock, band 1	4.43	2.20	0.62		11.41	6.51		1.55	0.28	69.98	
9 o'clock, band 1			0.52		5.59	2.05		0.56	0.91	90.38	
9	15.61	3.92	0.51		2.95	42.11	1.10	2.25		31.56	
13*		0.81	0.45	1.58	3.01			2.74	1.27	90.13	4.5 , 4.6
17			0.40		6.71			3.12	0.52	89.25	4.7
17**			0.21		14.14	0.29		2.30		83.16	
20	5.48		0.78		6.55	13.83	0.54	2.05	0.69	70.09	
Solid species	1.56	1.40	0.43	0.10	6.05	2.91	0.26	0.28	0.84	86.16	

* washed with tap water before analyses

** scan-area 0.0015 mm²

Table A.14. Chemical composition of the corrosion product for the 9 months exposed pipe using SEM / EDAX (wt%, scan area 0.48 mm²).

Element (wt%) Sample	Na	Mg	Si	P	S	Cl	K	Ca	Ti	Mn	Fe
WE, Corrosion probe			0.83		1.17	3.81	0.27	0.74		0.82	92.36
WE, Corrosion probe	0.74	0.40			2.23	4.72		0.50		0.42	90.98
RE, Corrosion probe		8.38	1.15		5.48	6.37		3.58		0.39	74.64
CE, Corrosion probe	2.00		0.22		6.01	8.20	0.17	0.53		0.62	82.25
A1	0.44	4.75	2.19	3.79	3.27			7.01	0.93	4.72	72.89
A3	0.28	2.32	0.88	5.61	3.47			7.77	0.25	1.21	78.20
A3	1.23	1.33	0.47	0.12	6.86			1.29		4.11	84.58
Corrosion product					0.75	0.92		0.51	0.39	0.74	96.69
C3 in Cu epoxy*	0.83			1.84				2.07			95.26
Filter **			1.88		4.02	1.35		2.49		1.08	89.19

* Analyses of product near the steel, Fe and Mn, analyses of product near the Cu epoxy, Fe and Mn

** The filter was covered by carbon before analyses.

Appendix 2, Figures.

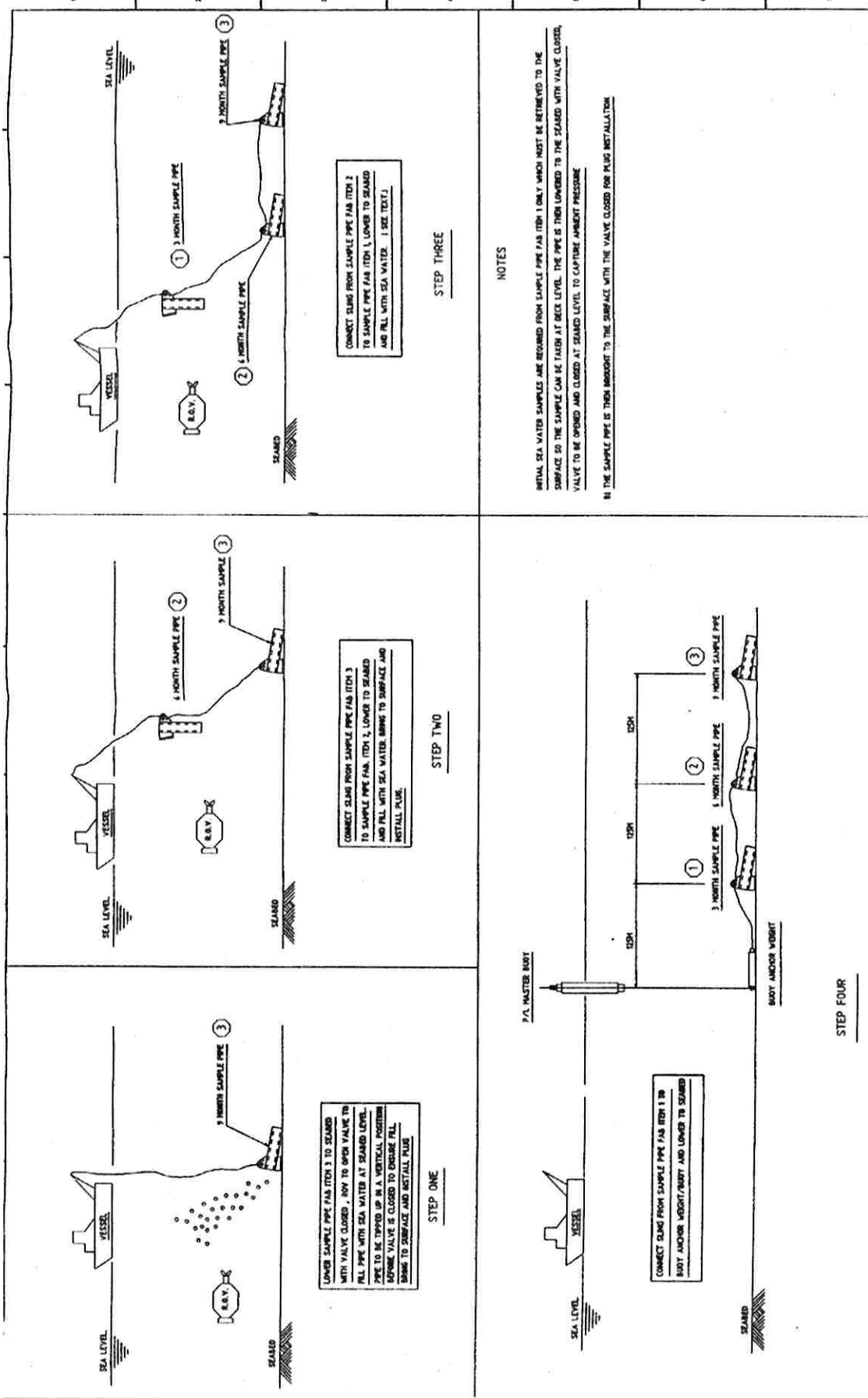


Figure A.4. Experimental setup

DEGREES CENTIGRADE

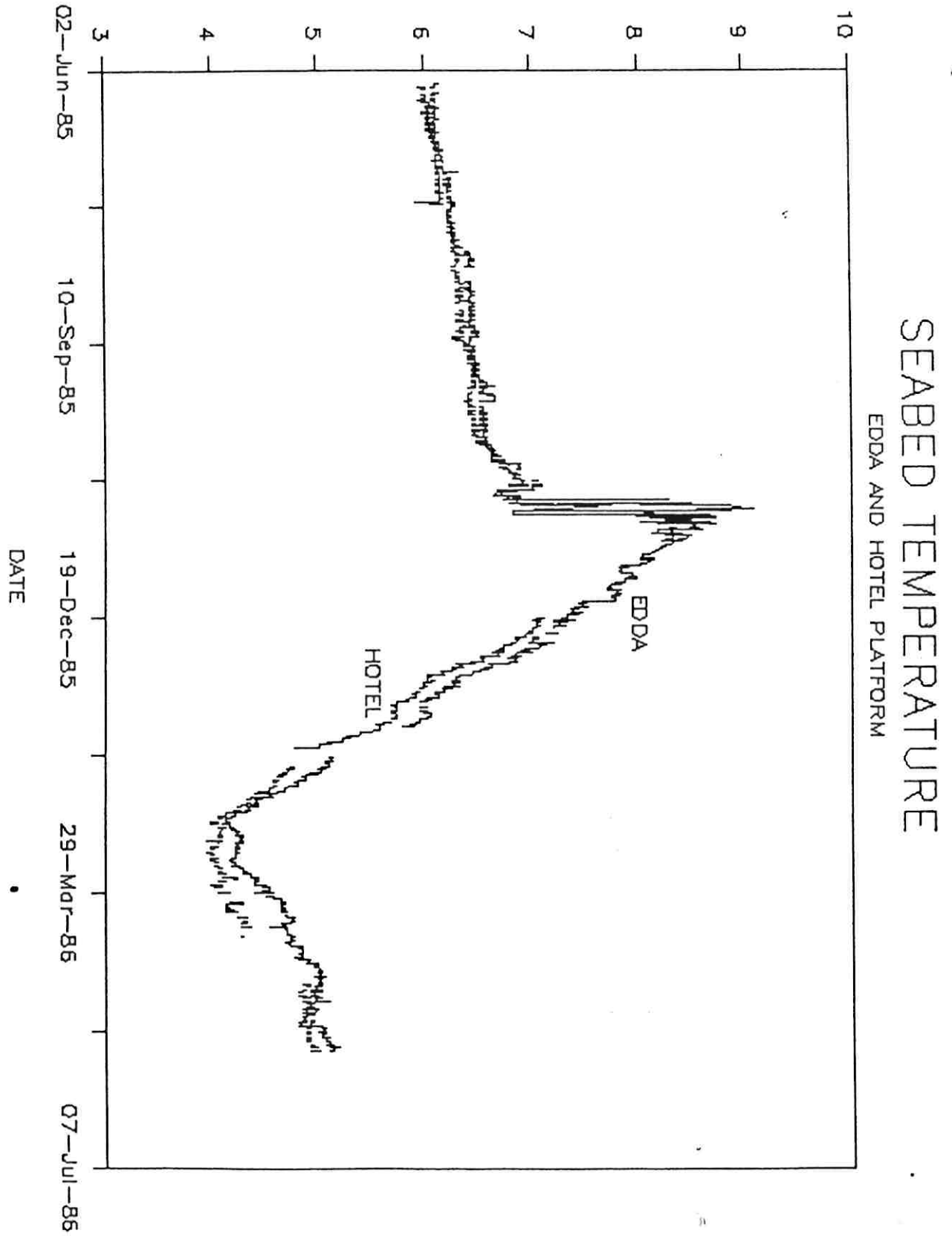


Figure A.5. Temperature cycle at the experimental area

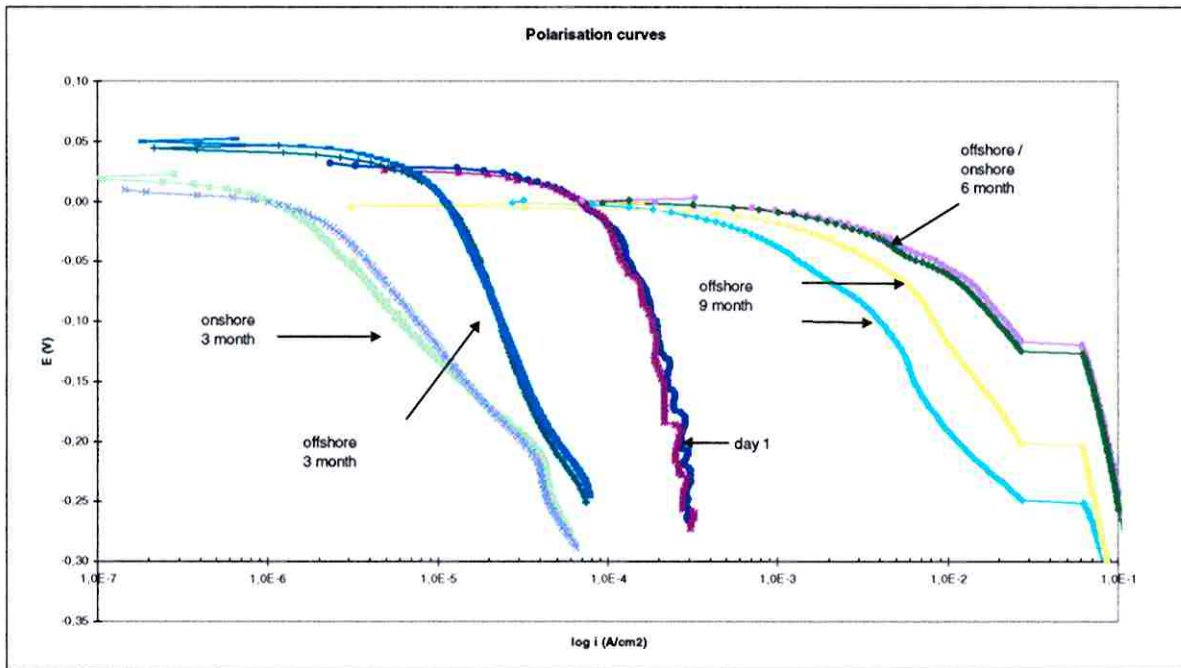


Figure A.6: Polarisation curves for day 1 (hours), 3 months, 6 months and 9 months exposure.

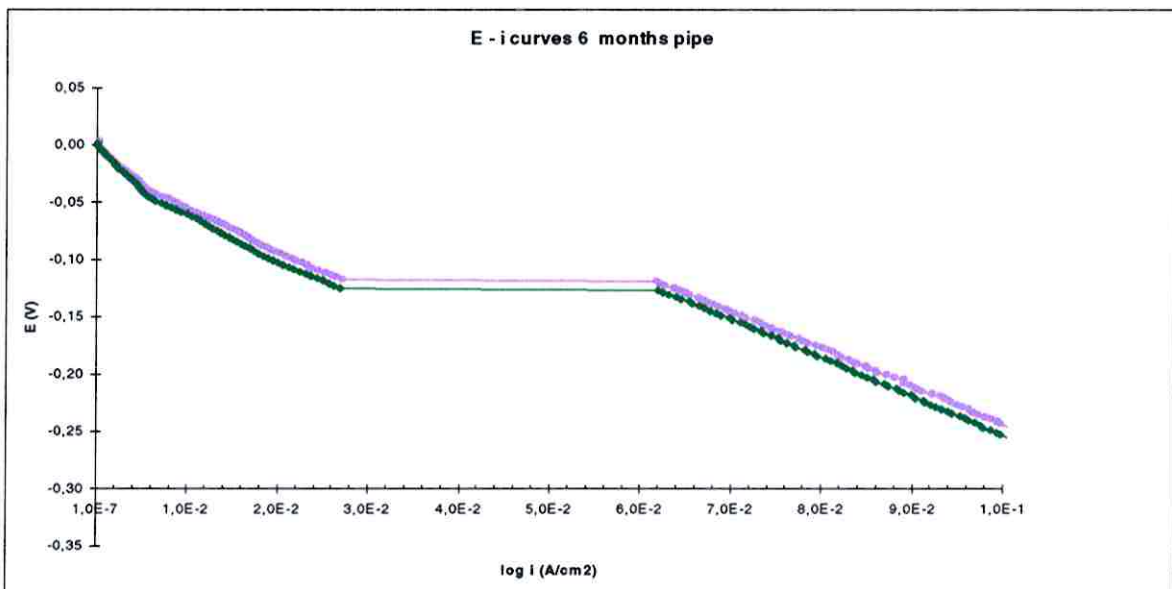


Figure A.7. Potential as a function of current for 6 months exposure.

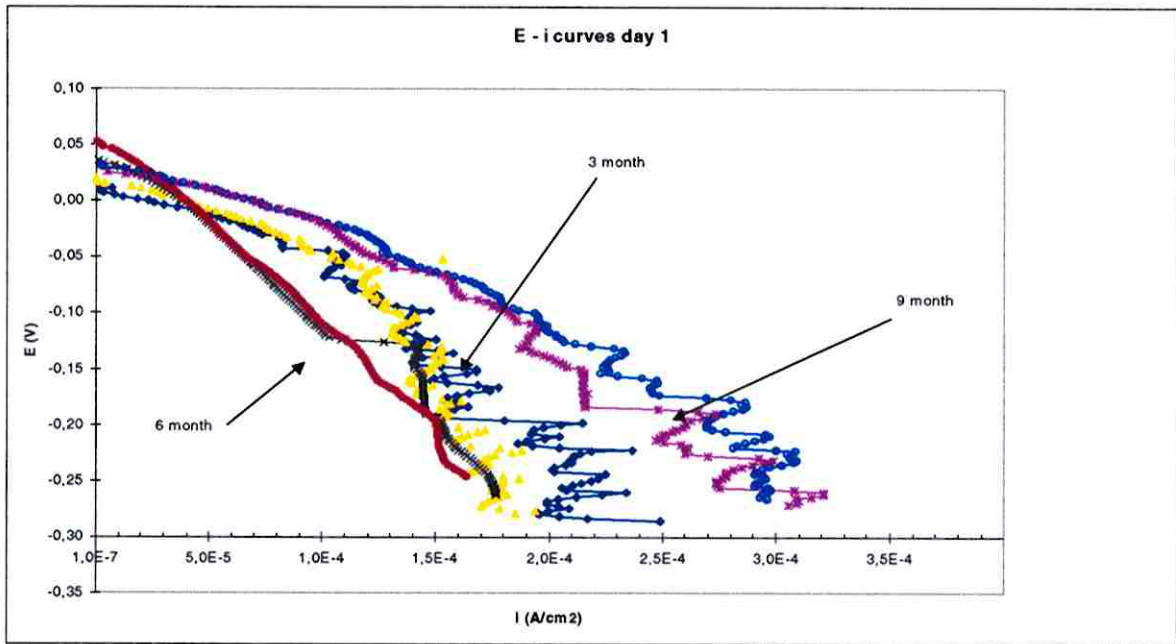


Figure A.8. Potential as a function of current for the different probes for day 1 (hour exposure).

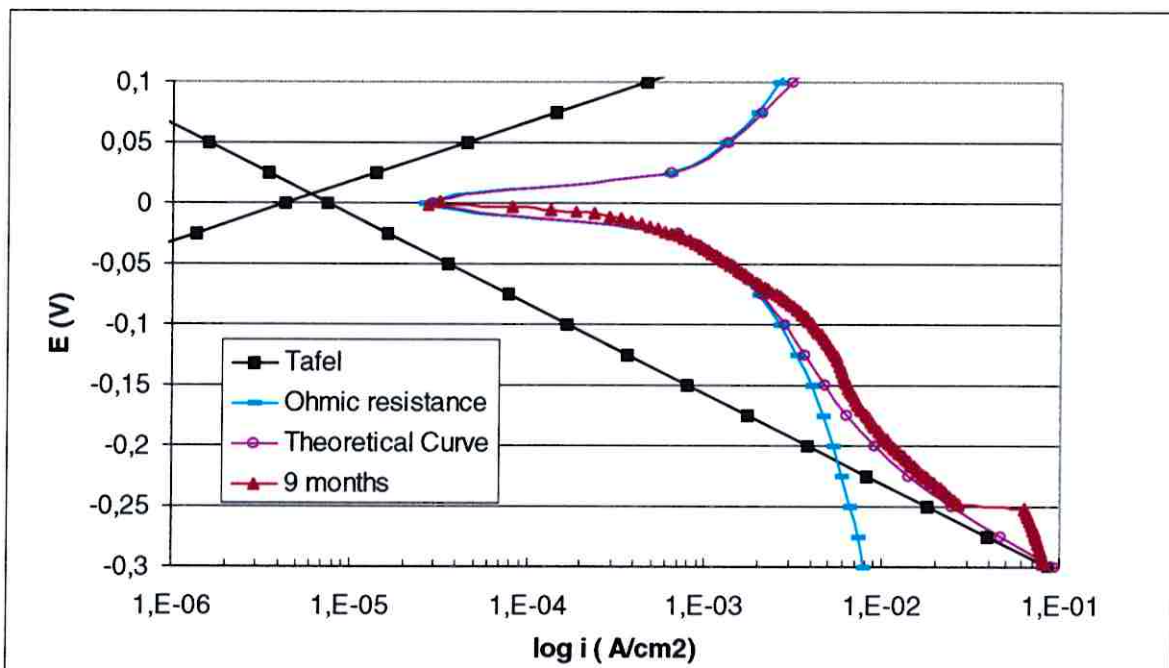


Figure A.9. Polarisation curve for 9 months compared with the theoretical reduction reaction based on activation controlled reaction (Tafel) and short circuit reaction.

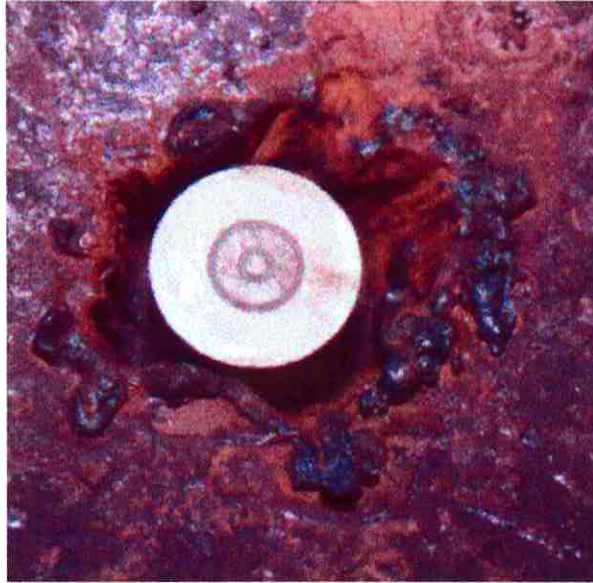


Figure A.10. The corrosion probe; close up as viewed from the inside of the pipes.

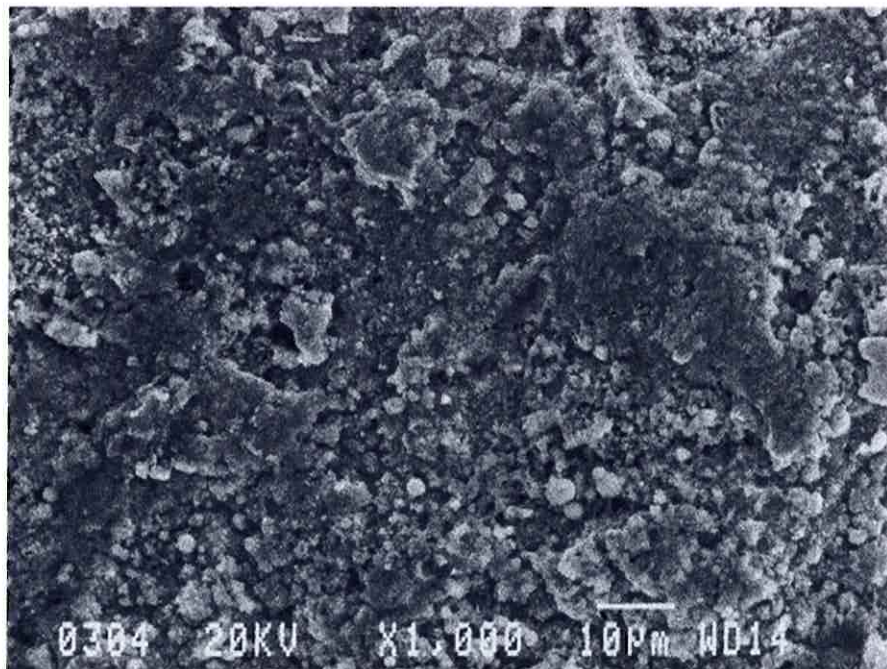


Figure A.11. SEM micrograph of the surface/corrosion product of unexposed pipe (magnification 1000X).

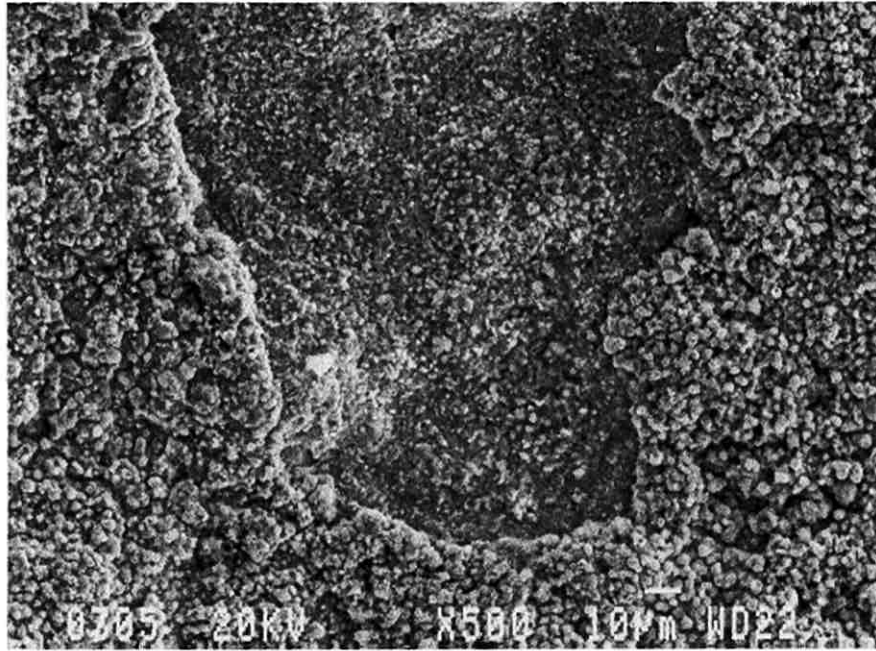


Figure A.12. SEM micrograph of the surface/corrosion product (magn. 500X), bottom of pipe, 3 months exposure).

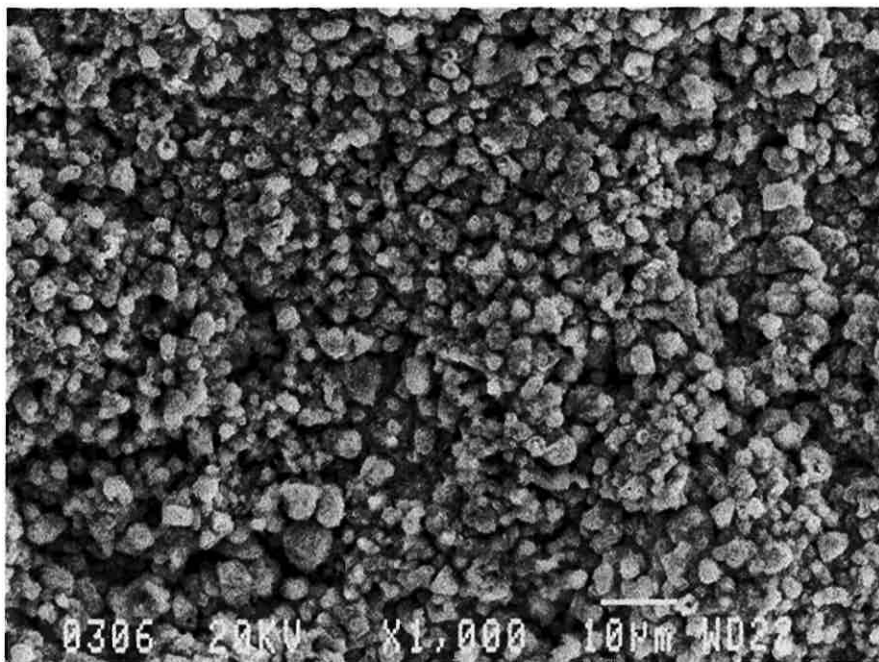


Figure A.13. SEM micrograph of the surface/ corrosion product (magn. 1000X), bottom of pipe, 3 months exposure

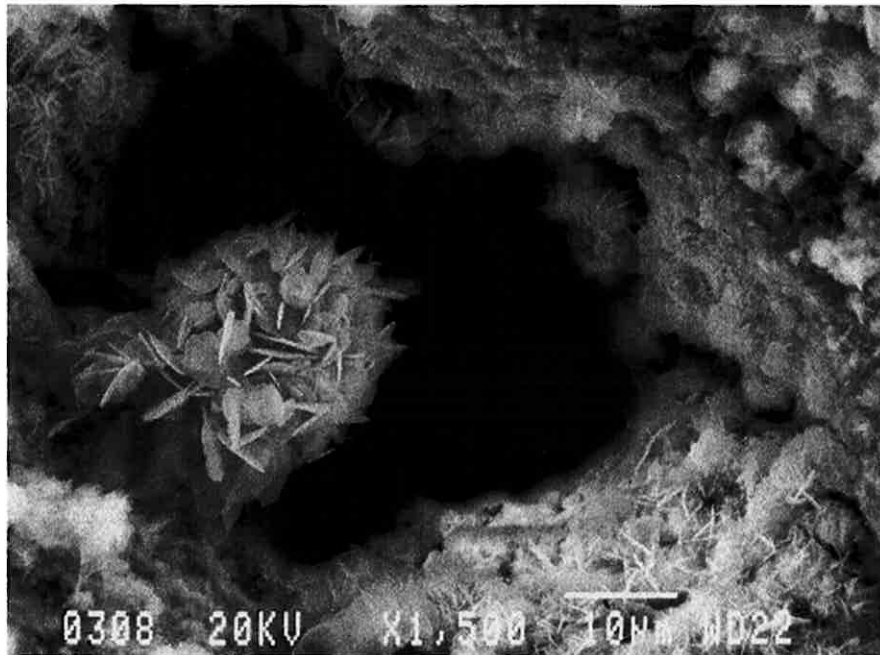


Figure A.14. SEM micrograph of surface deposits ("cactus"), bottom of pipe, 3 months exposure (magn. 1500X).

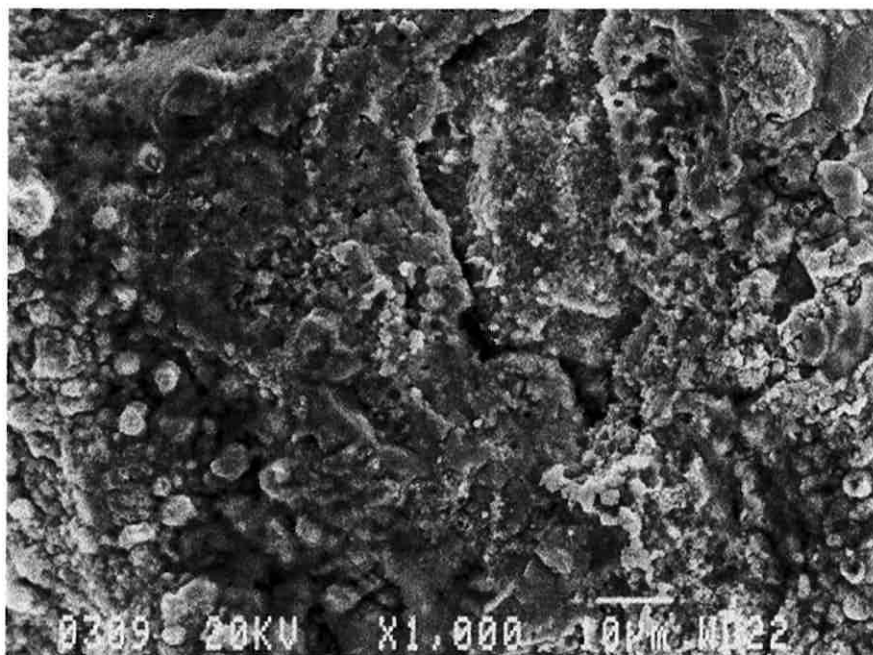


Figure A.15. SEM micrograph of the surface/corrosion product adjacent to the weld (2 halves were welded to one pipe length), 3 months exposure (magn. 1000X).

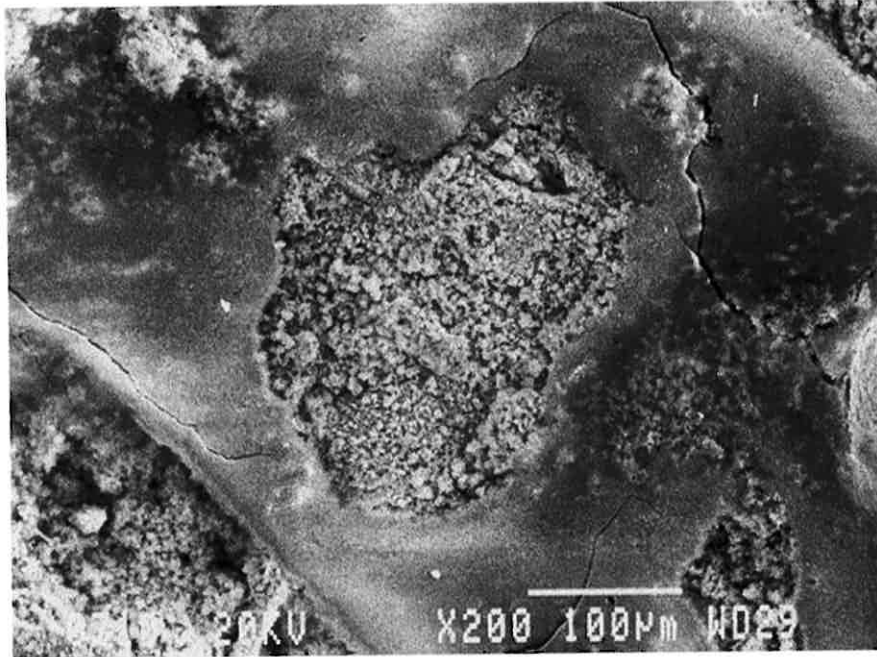


Figure A.16. SEM micrograph of corrosion products/deposits removed from the pipe; 3 months exposure (magn. 200X).



Figure A.17. SEM micrograph of a generic corrosion product; sampled from the pipe 3 months exposure (magn. 150X).

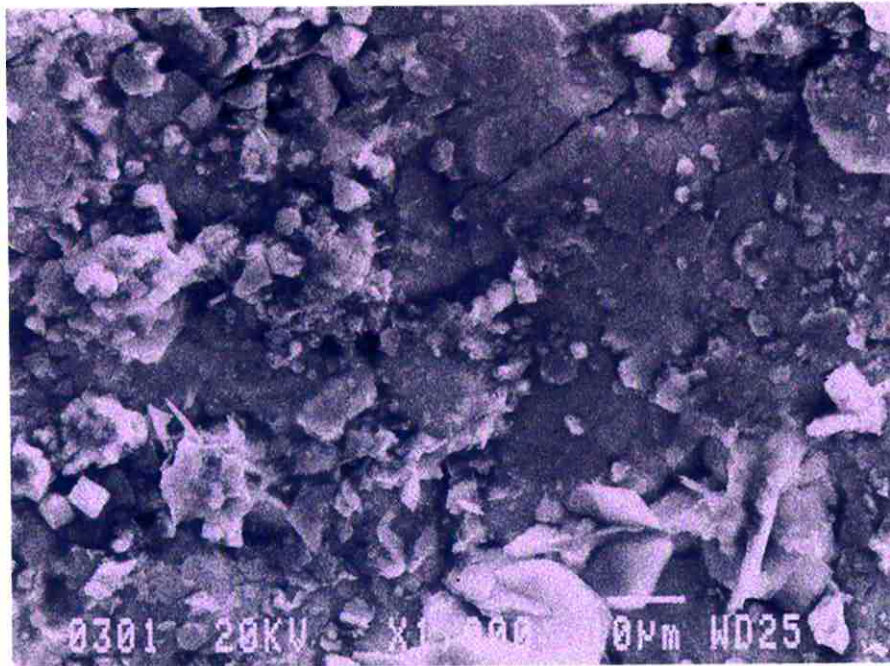


Figure A.18. SEM micrograph of the surface/corrosion product, 12 o'clock, 6 months exposure.

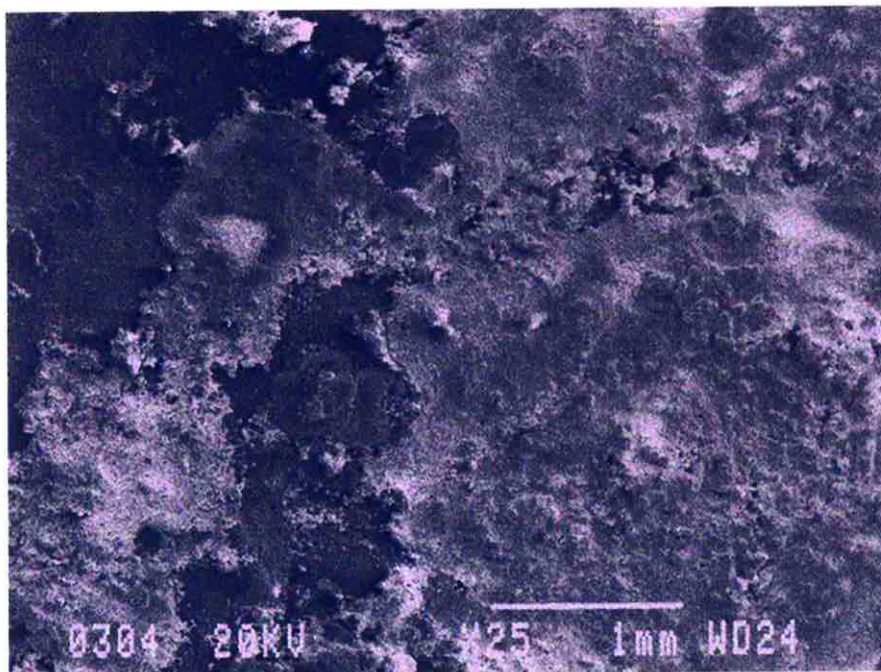


Figure A.19. SEM micrograph of the surface/corrosion product, 12 o'clock, 6 months exposure.

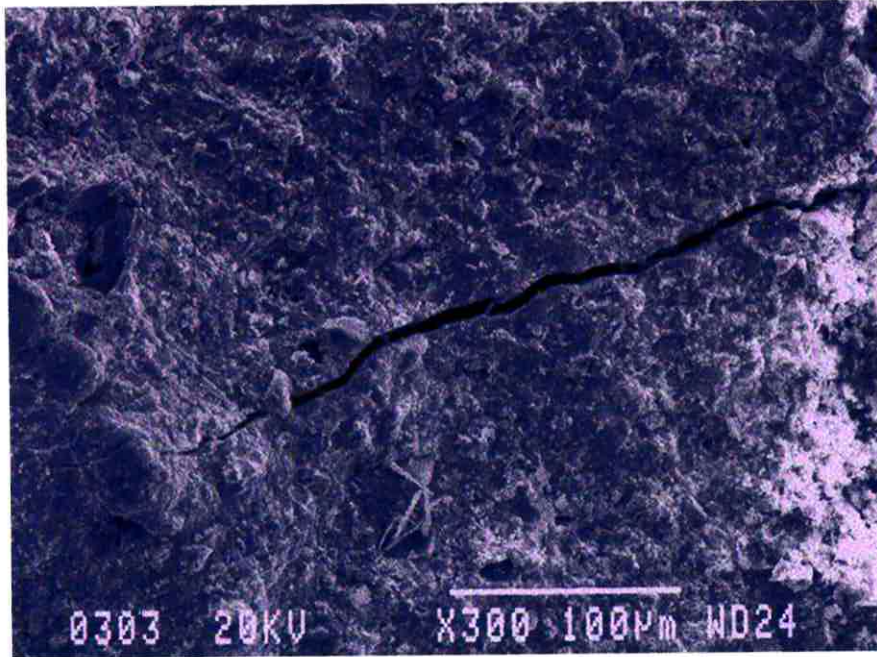


Figure A.20. SEM micrograph of the surface/corrosion product, 12 o'clock, 6 months exposure.

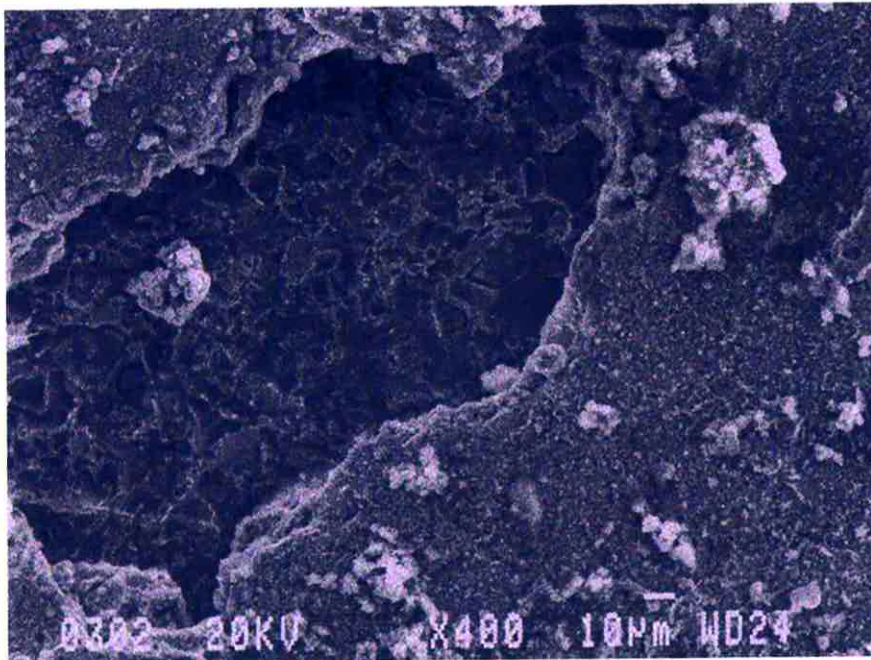


Figure A.21. SEM micrograph of the surface/corrosion product, 3 o'clock, 6 months exposure.

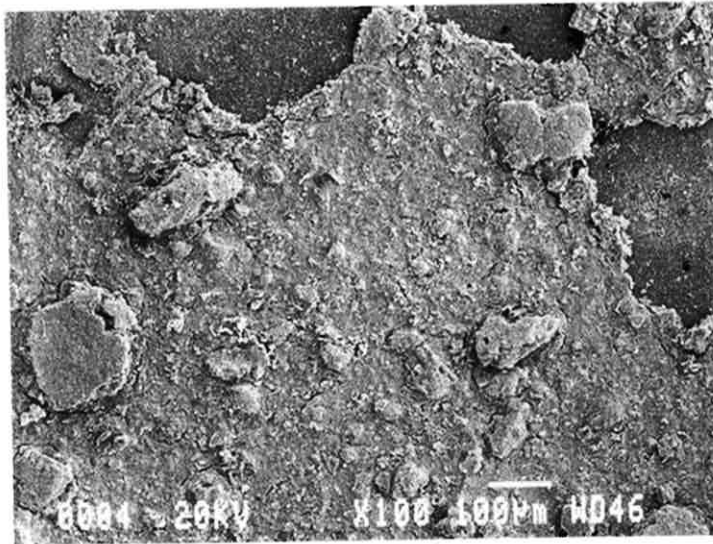


Figure A.22. SEM micrograph of the filter covered with Au, magnification X100 (9 months)

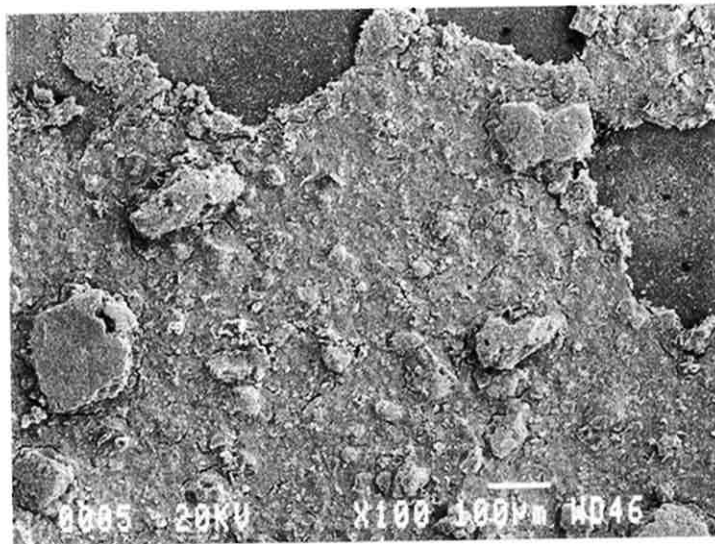


Figure A.23. Same image as in figure A.22, only this time without Au cover.

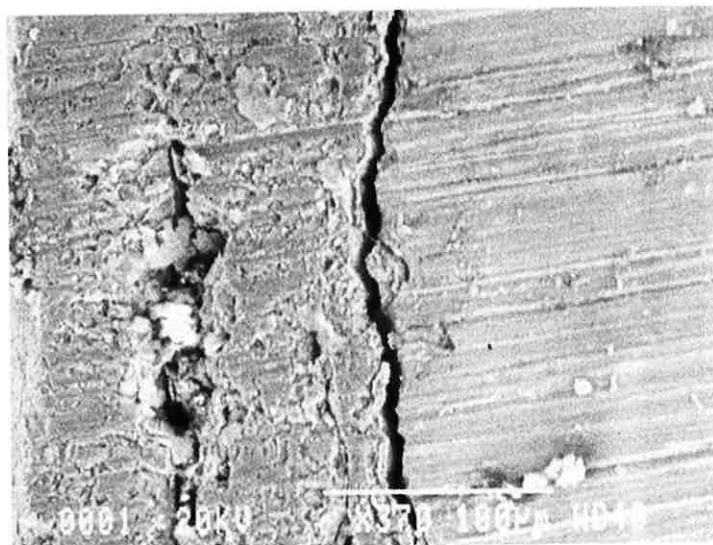


Figure A.24. 9 month / sample C3, cast-in copper (Cu); cross-sectional view 1.

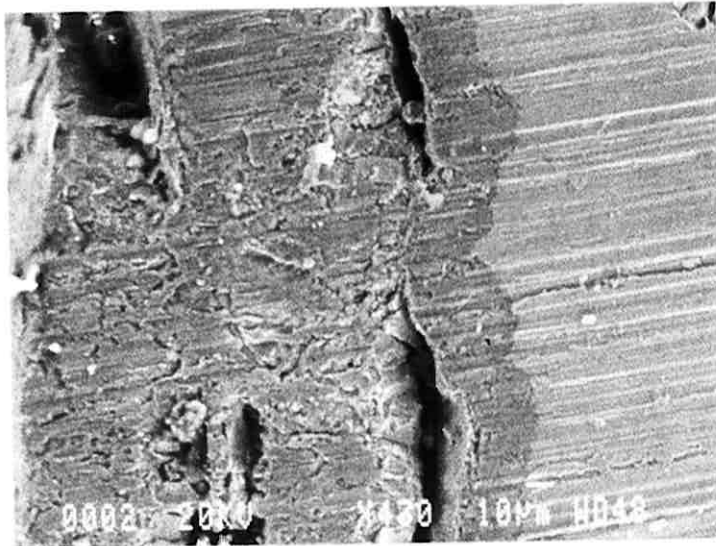


Figure A.25. 9 month / sample C3, cast-in copper (Cu); cross-sectional view 2.

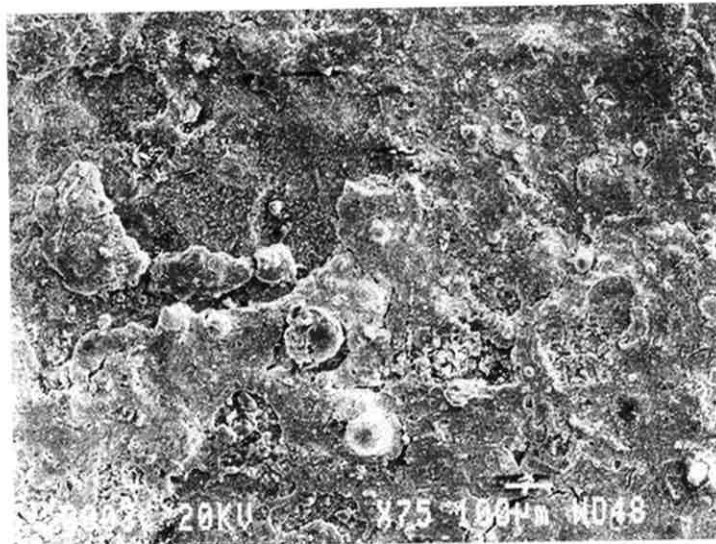


Figure A.26. 9 month / sample A3; corrosion product, some cracks in the layer.

APPENDIX 3 Analytical protocol

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7. October 1997

Rogalandsforskningen
Att. Anne.N. Myrvold
P.O.Box 2503 Ullandhaug
5004 Stavanger

Re: Analysis of water sample for short chain organic acids by ITP.

Three samples of formation water, labelled 97247-1, 97247-2 and 97247-3, have been analysed for content of short chain organic acid by isotachopheresis (ITP) using the standard procedure (i.e. direct determination at pH 5.5, with conductivity detection).

The results of the analysis was as follows, given in millimolar concentrations:

Acid	Concentrations:		
	3 month Sample 1	6 month Sample 2	9 month Sample 3
Acetic acid	0.05 mM	0.05 mM	0.05 mM
Propanoic acid	trace	trace	trace
Butanoic acid	trace	trace	trace
Higher acids *	0.3 mM	0.4 mM	0.4 mM
Total acids	0.7 mM	0.8 mM	0.6 mM

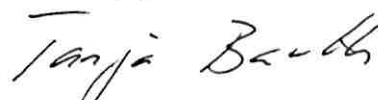
* Diffuse zone probably containing many components at low concentrations.

The results are based on two parallel determinations with different amounts of sample injected to reduce the risk of calibration curve errors.. The measurement uncertainties are ± 0.05 mM for acetic acid, and ± 0.2 mM for the remaining quantities. The total acid concentration is a separately calculated concentration that includes all registered compounds in the sample, quantified by the acetic acid calibration. The "higher acids" group includes weak acids and higher molecular weight acids (more than 8 carbon atoms) that could not be individually separated, quantified by the calibration for octanoic acid.

The content of acetic acid in the samples are close to the minimum detection level. Otherwise, the samples contain a normal background level of unseparated higher acids (probably of biological origin) typical for seawater.

I hope these results are satisfactory and will be pleased to provide further details on the analytical procedure or results if required.

Sincerely yours


Tanja Barth



ARKIVERT DOK. SENTRET	
DATE MOTTATT: 26.1.98	KOPI TIL: KN
ORIGINAL: ANM	

21. January 1998

Rogalandsforskningen
Att. Anne.N. Myrvold
P.O.Box 2503 Ullandhaug
5004 Stavanger

Re: Analysis of water sample for short chain organic acids by ITP.

Three water samples labelled FA 1, FA 2 and FA 3 have been analysed for short chain organic acids by isotachophoresis (ITP) using the standard procedure (i.e. direct determination at pH 5.5, with conductivity detection).

The results of the analysis was as follows, given in millimolar concentrations:

Acid	Concentrations:		
	30 m Sample 1	70 m Sample 2	3 month Sample 3
Formic/oxalic*	0.02 mM	0.05 mM	0.06 mM
Acetic acid	0.01 mM	0.05 mM	0.05 mM
Propanoic acid	0.01 mM	0.06 mM	0.05 mM
Butanoic acid	-	-	-
Higher acids**	n.r.	n.r.	n.r.
Total acids	0.07 mM	0.16 mM	0.06 mM

* Uncertain identification due to low levels.

** Diffuse zone probably containing many components at low concentrations.

The results are based on two parallel determinations with different amounts of sample injected to reduce the risk of calibration curve errors.. The measurement uncertainties are ± 0.05 mM The total acid concentration is a separately calculated concentration that includes all registered compounds in the sample, quantified by the acetic acid calibration. The present analysis was optimised for low molecular weight compound analysis, and no higher acids were registered. The detection minimum for these componens are 0.2 mM, so trace amounts may be undetected, and the total value correspondingly lower. The "higher acids" group includes weak acids and higher molecular weight acids (more than 8 carbon atoms) that could not be individually separated, quantified by the calibration for octanoic acid.

I hope these results are satisfactory and will be pleased to provide further details on the analytical procedure or results if required.

Sincerely yours

Tanja Barth



Rogalandsforskningen
Att. John Eirik Paulsen
P.O. Box 2503 Ullandhaug
5004 Stavanger

BOKSENTERET	
16.4.98	KOPITIL: KN
RFMN	
JEP	

27. March 1998

Re: Analysis of water sample for short chain organic acids by ITP.

Two water samples labelled 1 and 2 have been analysed for short chain organic acids by isotachopheresis (ITP) using the standard procedure (i.e. direct determination at pH 5.5, with conductivity detection).

The results of the analysis was as follows, given in millimolar concentrations:

Acid	Concentrations:	
	6 month Sample 1	70 m Sample 2
Formic/oxalic*	trace	0.04 mM
Acetic acid	0.27 mM	0.18 mM
Propanoic acid	trace	trace
Butanoic acid	-	-
Higher acids**	0.4 mM	0.5 mM
Total acids	0.7 mM	0.9 mM

* Uncertain identification due to low levels.

** Diffuse zone probably containing many components at low concentrations.

The results are based on two parallel determinations with different amounts of sample injected to reduce the risk of calibration curve errors. The measurement uncertainties are ± 0.05 mM for the individual component and ± 0.1 mM for the composite groups (Higher and total acids). The total acid concentration is a separately calculated concentration that includes all registered compounds in the sample, quantified by the acetic acid calibration. The "higher acids" group includes weak acids and higher molecular weight acids (more than 8 carbon atoms) that could not be individually separated, quantified by the calibration for octanoic acid.

I hope these results are satisfactory and will be pleased to provide further details on the analytical procedure or results if required.

Sincerely yours

Tanja Barth

Tanja Barth



12. June 1998

Rogalandforskningen
Att. John Eirik Paulsen
P.O.Box 2503 Ullandhaug
5004 Stavanger

Re: Analysis of water samples for short chain organic acids by ITP.

Two water samples labelled "SW 26/-98" and "9 mnd 27/5-98" have been analysed for short chain organic acids by isotachopheresis (ITP) using the standard procedure (i.e. direct determination at pH 5.5, with conductivity detection).

The results of the analysis was as follows, given in millimolar concentrations:

Acid	Concentrations:	
	SW	9 mnd
Formic/oxalic*	0.09 mM	0.13 mM
Acetic acid	0.16 mM	0.10 mM
Propanoic acid	0.23 mM	0.15 mM
Butanoic acid	0.10 mM	0.03 mM
Higher acids**	0.3 mM	0.15 mM
Total acids	1.0 mM	0.5 mM

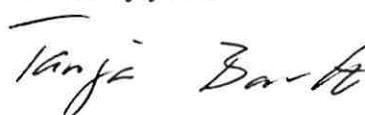
* Uncertain identification due to low levels, quantified as formic acid.

** Diffuse zone probably containing many components at low concentrations, quantified as octanoic acid.

The results are based on two parallel determinations with different amounts of sample injected to reduce the risk of calibration curve errors. The measurement uncertainties are ± 0.07 mM for the individual component and ± 0.1 mM for the composite groups (Higher and total acids). The total acid concentration is a separately calculated concentration that includes all registered compounds in the sample, quantified by the acetic acid calibration. The "higher acids" group includes weak acids and higher molecular weight acids (more than 8 carbon atoms) that could not be individually separated.

I hope these results are satisfactory and will be pleased to provide further details on the analytical procedure or results if required.

Sincerely yours


Tanja Barth

SEABED TEMPERATURE

EDDA AND HOTEL PLATFORM

