CSIR

Division of Mining Technology

Report to the

WATER RESEARCH COMMISSION

on

A STUDY ON A MINE WATER RECLAMATION TEST PLANT

by

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EXECUTIVE SUMMARY

This study was aimed at quantifying the influence of individual water treatment processes on the corrosion of various metals. The ultimate aim was to define the most cost-effective method of minimizing corrosion in mine waters of varying quality, i.e. materials selection vs water treatment. A water reclamation plant with eight parallel corrosion and water quality monitoring lines was designed, built and operated. Two water chemistries, one typical of a Witwatersrand gold mine and the other typical of a Klerksdorp gold mine were treated. After each unit process (e.g. neutralization, filtering, disinfection etc.) the water was passed through a water quality and corrosion monitoring line.

Major technical difficulties were experienced during the course of the study and it was not possible to achieve a constant water chemistry for each unit process. Evaluation of the data indicated that the most sensible approach would be to correlate corrosion data with measured water quality parameters rather than with the effect of each unit process per sé.

The corrosion rate of mild steel tended to increase with increasing levels of dissolved solids. The chemistries of the various waters tested were such that an increase in total dissolved solids was accompanied by an increase in the concentration of all the corrosive anions. It was therefore not possible to quantify the corrosive effect of individual anions. Galvanised steel coupons also followed the trend of increasing corrosion with increasing levels of total dissolved solids.

No correlation between Langelier or corrosivity indices and corrosion rate could be established for any of the metals tested and the use of these indices to predict the corrosivity of mine waters have to be questioned seriously.

In this study no microbial corrosion was detected. Microbial corrosion by sulphate reducing bacteria in particular is a very common phenomenon in mine waters and the importance of controlling this form of corrosion by using biocides for instance cannot be over emphasized.

Although corrosion of copper and copper-nickel coupons did occur in many of the waters tested, no satisfactory correlation between corrosion rate and water quality parameters were found.

No corrosion was observed on any of the AISI 316 stainless steel coupons. The corrosion resistant steel 3CR12, was also immune to corrosive attack in many of the waters. Significant corrosion of 3CR12 only occurred in three waters having relatively low levels of total dissolved solids and more significantly, low chloride levels compared to other water chemistries in which no corrosion of 3CR12 occurred. This phenomenon was ascribed to the inhibiting effect that sulphate and nitrate have on the pitting of stainless steels, with the high TDS waters having a more favourable ratio of sulphates and nitrates to chlorides.

Due to the difficulty of correlating a particular water treatment condition or process to a corrosive effect it was not possible to reach the ultimate aim of the project. However, it is apparent that it is not possible to predict the corrosivity of a particular mine water from chemistry alone. The relationship between ions in the water is complex and does not lend itself to simple empirical relationship.

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1. INTRODUCTION

The gold mining industry uses large quantities of mine service water underground for dust suppression, watering down of working areas, water jetting and cooling purposes. These activities, as well as the ingress of saline fissure water and drainage of water from old worked out areas, result in a significant deterioration in quality of the water gravitating to the bottom of the mine.

Poor water quality results in problems such as erosion, corrosion, scale formation and fouling. In order to maintain salt concentrations at a constant level, mine service water circuits are supplemented with good quality water (eg. Water Board water) and approximately 220 Mℓ/d (2500 ℓ/s) of Water Board water is being consumed by the gold mining industry. The high cost and limited availability of Water Board water are strong incentives to treat and re-use mine water wherever practically feasible.

Although drainage water is treated underground, the harsh conditions and very limited monitoring and control of water treatment processes result in the treated water still being of poor quality. In addition, very little reliable data regarding the cost benefits associated with improved water treatment exists.

In 1990, COMRO initiated a research project aimed at obtaining reliable data to establish the cost benefits associated with water treatment unit processes. The ultimate aim of the project is to define the optimum cost-effective water treatment process configuration which enables large scale water re-use for different mine water qualities. The project was jointly funded by COMRO and the Water Research Commission.

The project entailed treatment of ERPM Gold Mine Water at the Hercules Shaft using a water reclamation test plant. After various stages in the process the treated water was pumped through corrosion and bio-fouling test rigs. Feed blending and product blending was proposed in order to simulate various mine waters and various slip-stream desalination scenarios. In this way the contribution of each water treatment unit process (eg. neutralization, settling, disinfection) to the feasibility of cost-effective water reclamation would be tested.

During the course of the project various difficulties and technical stumbling blocks were experienced which necessitated modifications to the original project proposal. Before final completion, COMRO was integrated into the CSIR (as the Division for Mining Technology) and it was decided to draw on corrosion expertise available within the Corrosion and Metallurgical Services Programme of the Division for Materials Science and Technology in order to evaluate and interpret corrosion data. This was deemed necessary as the difficulties experienced and modifications effected during the project complicated interpretation of this data significantly.

The specific aims of this report are:

1. To assess the data generated during the project critically (with particular reference to the technical difficulties experienced).

2. Inclusion of previously unpublished work performed by COMRO on the influence of water quality on the corrosion performance of various materials.

3. To interpret this data relative to the aims of the original project proposal.

4. Assess to which extent the objectives of the project had been achieved and to recommend what further action is required.

The report comprises a description of the water reclamation plant, analysis of all available results, followed by discussion and recommendations.

2. PROJECT DETAILS

A simplified block diagram of the proposed COMRO Water Reclamation Test Plant is given in Figure 1. Eight different waters are tested in terms of corrosion and microbiological fouling. The different water qualities/processes are:

1. Mine Water

2. Neutralized mine water (to a pH of 6,5 to 7,5 using sodium hydroxide)

3. Flocculation and settling using a high rate settling process capable of producing clear water with a suspended solids concentration of less than 25 mg/ℓ.

4. Filtration using a standard upflow sand filter producing a filtered water with a suspended solids concentration of less than 5 mg/ℓ.

5. Disinfection using a chlorine gas disinfection system in order to control bio-fouling and bio-corrosion and also to meet health related requirements.

6. Desalination using the COMRO developed SPARRO process capable of producing water with a total dissolved solids content as low as 500 mg/ℓ.

7. Feed blending with desalinated water or concentrated brine streams in order to simulate various mine waters (West Wits and Klerksdorp).

8. Product blending in order to simulate various slip-stream desalination scenarios by blending desalinated product water with raw mine water.

Water from each of the eight unit processes pass through a line containing corrosion coupons to measure long term general and localized corrosion,

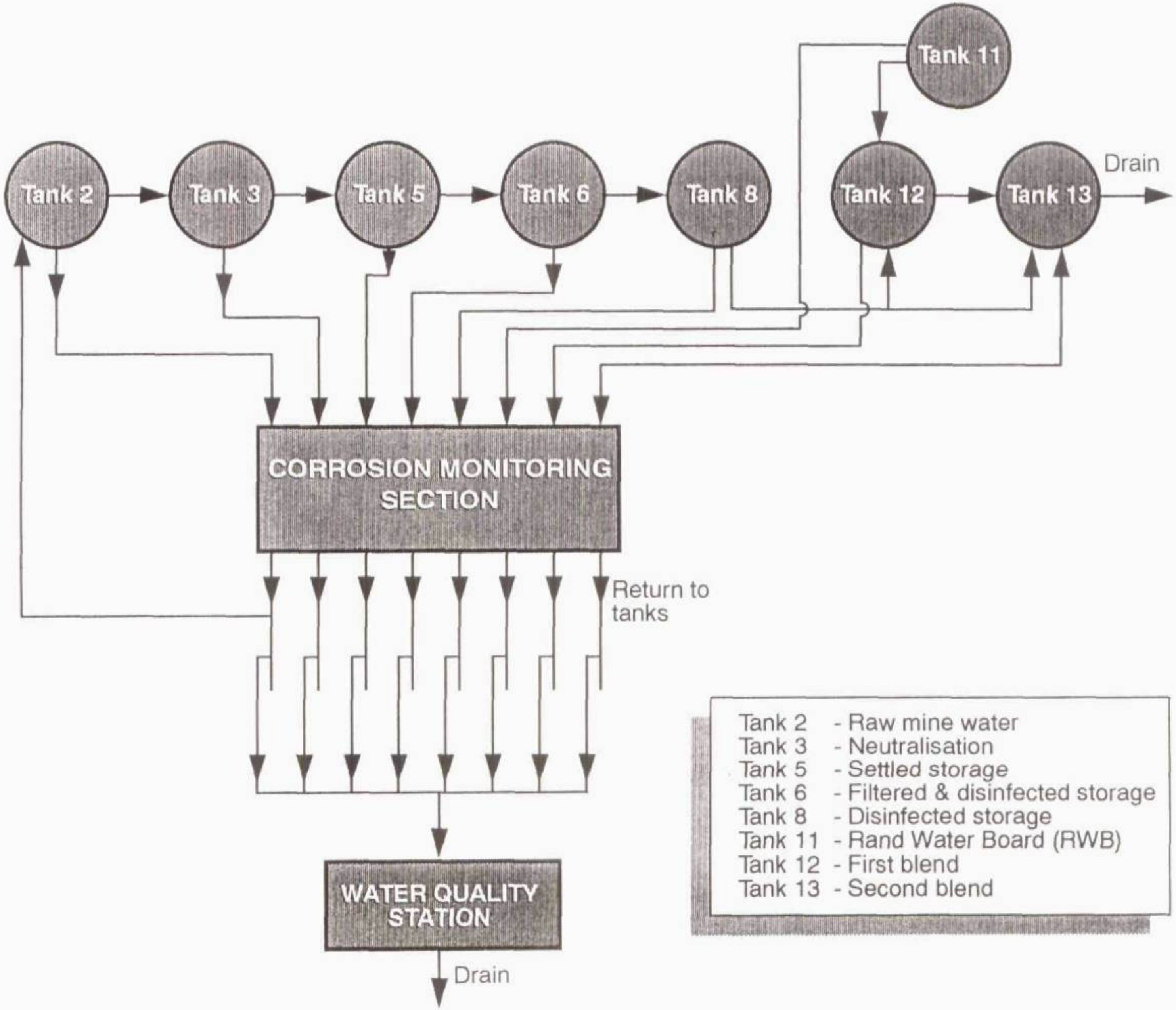

Figure 1: Schematic presentation of the mine water reclamation plant.

Robbins devices to measure bio-fouling and pipe sections to monitor scale formation. The Water Reclamation Test Plant also incorporates a water quality rig for monitoring flow, temperature, pH, conductivity, turbidity and dissolved oxygen for each of the unit process product streams.

In the early stages of the project it was decided to also monitor corrosion rates continuously using Linear Polarization Resistance (LPR) probes. The advantage of this technique is that instantaneous corrosion rates are obtained making it possible to correlate corrosion rates with water quality at any given moment in time.

Initially it was proposed to study the treatment of mine water at a Witwatersrand, a West Wits and Klerksdorp gold mine.

During the course of the project various difficulties were experienced which not only caused delays but also necessitated modifications to what was originally proposed. The difficulties varied from staff reductions at COMRO, problems with equipment typical of a pilot plant of this scale and also equipment failures of a more serious nature influencing the course of the project. Only difficulties affecting the course of the project will be described here in order to explain the final configuration and operating conditions used for the test plant. These difficulties were:

1. Continued fouling of the reverse osmosis membranes in the SPARRO desalination plant which led to the replacement of SPARRO product water with Rand Water Board water.

2. During Phase 1 of the project (treatment of ERPM raw mine water) difficulties with controlling the water chemistry within the design limits were experienced due to equipment failure, high flow rates (2 m/s) and the relatively small volume of the storage tanks. As these difficulties would be compounded when trying to simulate a Klerksdorp or West Wits water by the addition of desalinated water or chemicals to ERPM raw mine water, it was decided to run the Water Reclamation Test Plant as a closed loop system for the subsequent phases. Regular monitoring of water quality with topping up of the storage tanks was proposed in order to keep the water

chemistry within design limits.

3. Unavailability of equipment made it impossible to record corrosion rates electrochemically using LPR probes during Phase 1 (ERPM water). Coupons only were therefore tested during this phase.

4. After completion of Phase 1, the Technical Sub-Committee decided that in view of time pressures, Phase 2 should focus on the simulated Klerksdorp water and that work on the West Wits water should be left out for the time being.

5. During the Christmas period in 1992, the computer, used to capture data was stolen resulting in all the flow data being lost.

The final programme of work therefore consisted of two phases ie.

Phase 1: Treatment of ERPM raw mine water as shown schematically in Figure 1. Desalinated water from the SPARRO plant was substituted with Rand Water Board water.

Phase 2: Simulation of a Klerksdorp water by the addition of chemicals to ERPM raw water. This water was then treated in the Water Reclamation Test Plant in order to fill the various storage tanks. Once filled, the water from each unit was recirculated through each of the monitoring loops. During Phase 2, only seven of the eight corrosion monitoring lines were operational because the settled and filtered waters were combined in one storage tank.

In the next section, the results from these two phases will be presented and discussed. In addition, previous work on the corrosivity of various mine waters performed in the COMRO laboratories will be reported on.

3. RESULTS - PHASE 1

3.1 Water Reclamation Plant Details

During Phase 1, ERPM mine service water was treated in the water reclamation plant described in Figure 1. The plant was operated for a period of 90 days with a 24 hour per day operator attendance. Although flow data was lost due to the computer being stolen, it was reported that flow rates typically varied between 1.6 and 2 m/s for all the lines.

3.2 Water Quality Data - Phase 1

Corrosion is a complex phenomenon and many factors have to be taken into account when interpreting data. During Phase 1, the temperature, dissolved oxygen, turbidity, pH and conductivity of the water flowing through the eight lines were monitored on a continuous basis. In addition, samples were taken from each of the storage tanks on five occasions during the three months of operation and analyzed in the laboratory for pH, conductivity, turbidity, suspended solids, total dissolved solids, alkalinity, total hardness, calcium, magnesium, sodium, chlorides, nitrates, sulphates, iron, zinc, manganese, barium and copper.

The pH of the mine water is shown in Figure 2 for the period 24.02.1992 to 02.05.1992. It is evident that the pH fluctuates through a range from about four to almost twelve over this time period. The pH of the neutralized water over the same time period is shown in Figure 3. The large variations in pH indicate that neutralization of the mine water was not effective. The pH values for the raw mine water and the neutralized water during the period 10.04.1992 to 26.04.1992 are plotted on one graph in Figure 4 and here it is illustrated that excessive amounts of acid was sometimes dosed into the system resulting in low pH values for the neutralized water. Also, for certain periods the pH of the neutralized water follows that of the raw mine water while it is outside the design limits, indicating that neutralization did not always take place when it should have. The analyses performed in the laboratory confirmed these observations because the PH values of

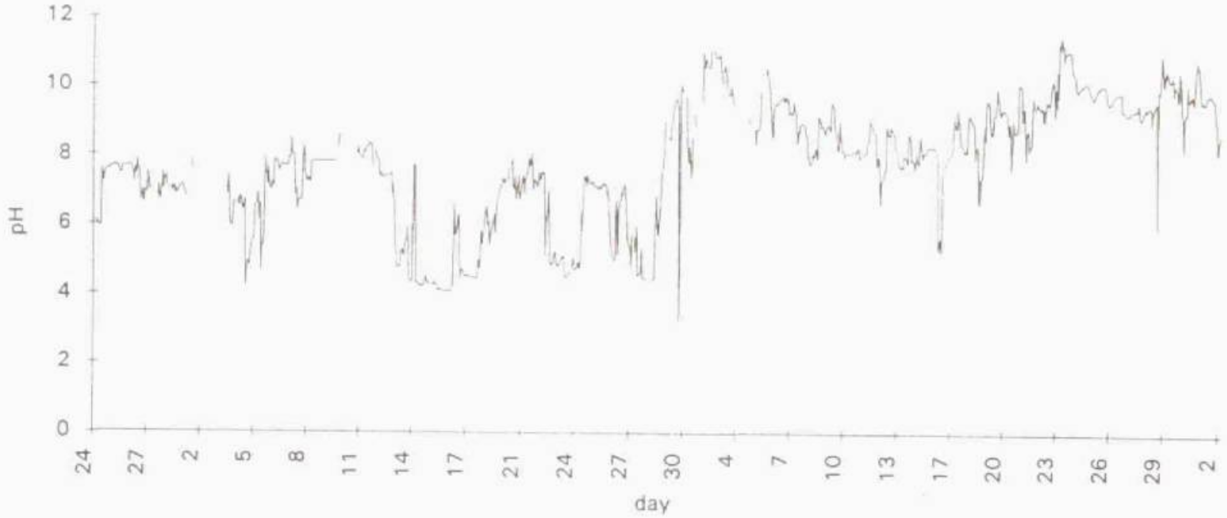

Figure 2: The pH of raw mine water for the period 24.02.1992 to 02.05.1992 (Phase 1).

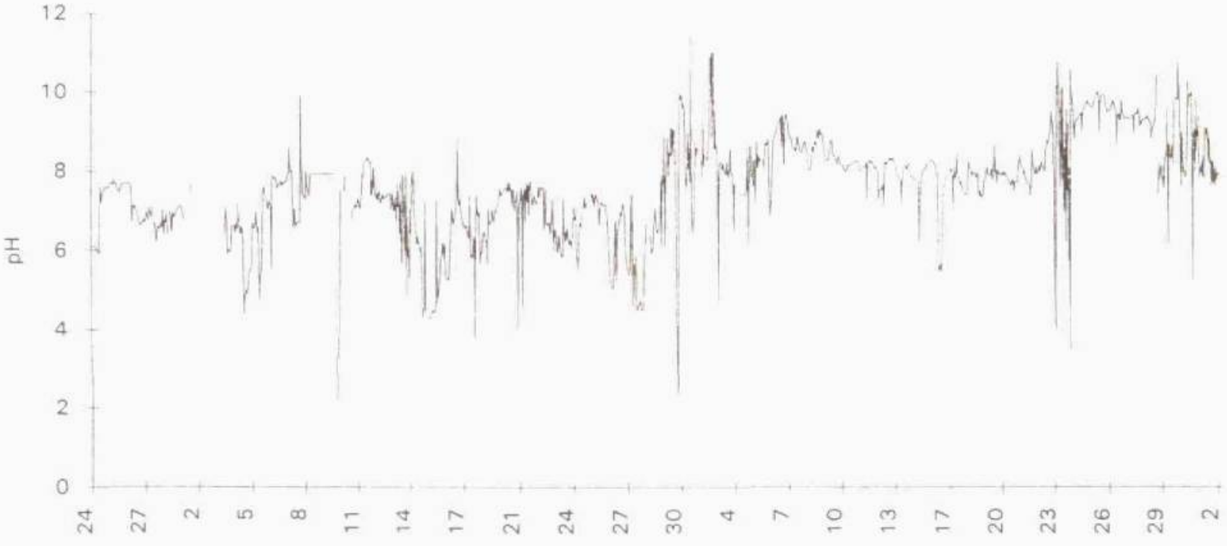

Figure 3: The pH of neutralized water over the period 24.02.1992 to 02.05.1992 (Phase 1).

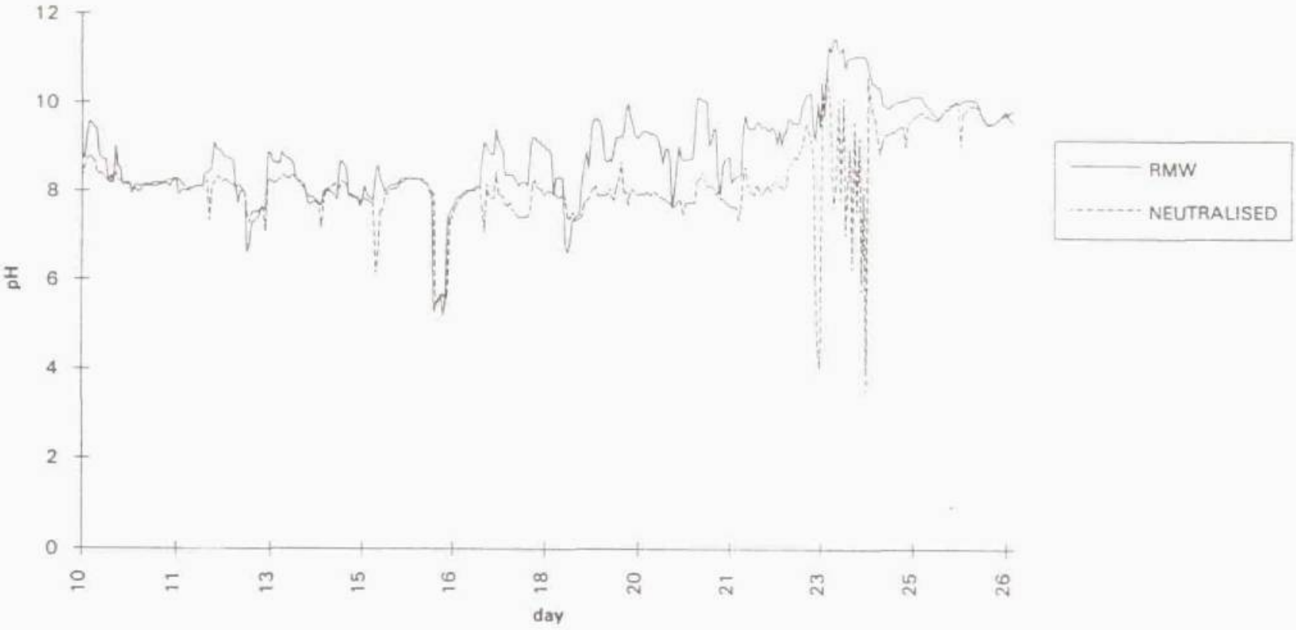

Figure 4: The pH of raw mine water and neutralized water (Phase 1) for the period 10.04.1992 to 26.04.1992.

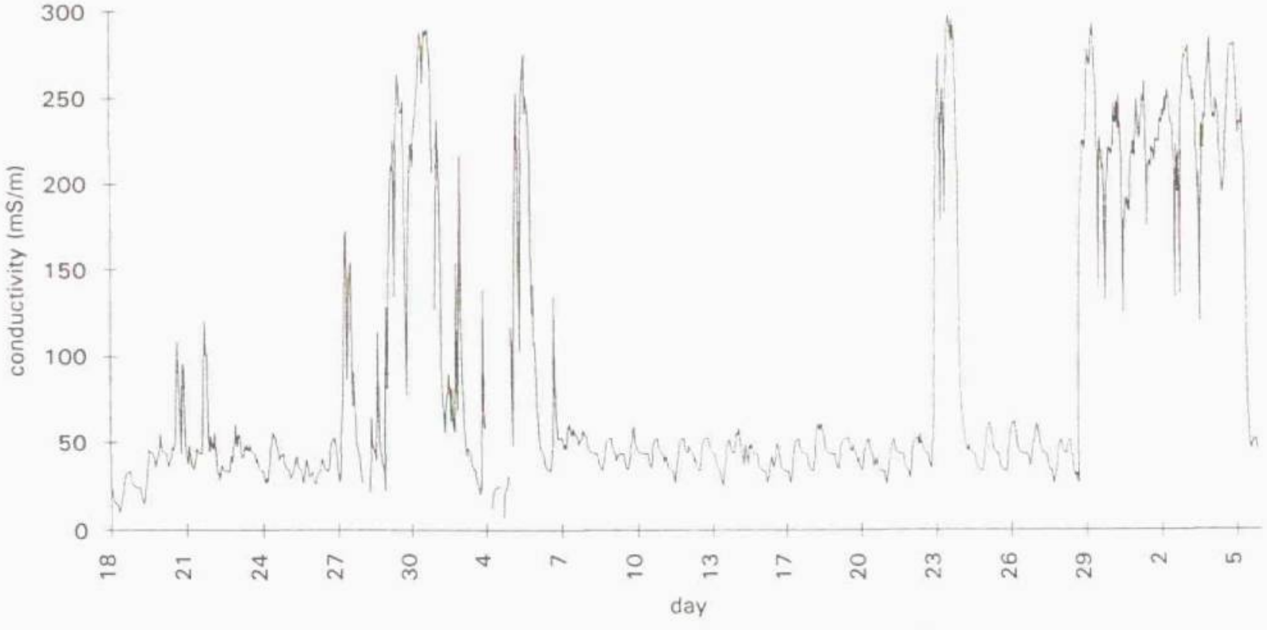

Figure 5: The conductivity of neutralized water for the period 18.03.92 to 05.05.92 (Phase 1).

"neutralized water" samples tested in this way varied between five and eleven rather than between 6,5 and 7,5 (pH 7 ± 0,5) as was intended in the first place.

A further indication of the problems experienced with neutralizing the raw mine water is given by the data in Table 1. (The analyses of a raw mine water sample and a sample of the neutralized water taken on 16 April 1992). It is immediately apparent that the total dissolved solids (and therefore also the conductivity) of the neutralized water is much higher than that of the raw mine water. It is also clear that this difference in TDS is a result of the sodium and sulphate contents of the neutralized water being significantly higher than that of the raw mine water. Sodium hydroxide and sulphuric acid were used as neutralizing agents and the high sodium and sulphate contents are probably indicative of excessive dosing of one of these agents followed by dosing of the other to correct the pH again.

Problems were experienced with continuous conductivity measurements during Phase 1. Figure 5 is the conductivity measurements taken on the neutralized water during the period 18.03.1992 to 05.05.1992. The results of conductivity measurements taken in the laboratory are presented in Table 2. Comparison of this data with that in Figure 5 indicates large discrepancies between the lab data and the plant data. Only the laboratory conductivity data could therefore be used with certainty.

Problems were also experienced with the continuous measurement of turbidity during Phase 1. Of greater importance in terms of interpreting corrosion data is the measurement of dissolved oxygen and temperature. The temperature of the raw mine water during Phase 1 varied between a minimum of almost 5°C to a maximum of almost 40°C (Figure 6). There is a general decrease in the daily minimum temperatures as the winter months approach. Dissolved oxygen is a function of temperature and the dissolved oxygen content and the temperature of raw mine water for the period 08.04.1992 to 18.04.1992 are plotted on one graph in Figure 7. As expected the dissolved oxygen content increases as the temperature decreases. All the tanks showed similar trends as shown in Figure 7 for temperature and dissolved oxygen.

TABLE 1: Analysis results of samples taken on 16.04.1992.

PARAMETER	RMW	NEUTRALIZED WATER
pH	7,94	8,6
Conductivity (mS/m)	211	515
TDS (mg/ℓ)	1876	4299
Alkalinity (mg/ℓ) (as $CaCO_3$)	13	33
Total Hardness (mg/ℓ) (as $CaCO_3$)	941	878
Ca (mg/ℓ)	300	311
Mg (mg/ℓ)	47	24
Na (mg/ℓ)	106	927
Cl (mg/ℓ)	57	54
NO_3 (mg/ℓ)	16	12
SO_4 (mg/ℓ)	1184	2851

TABLE 2: Laboratory conductivity data on neutralized water - Phase 1

DATE	CONDUCTIVITY (mS/m)
18.03.1992	135
07.04.1992	196
16.04.1992	515
23.04.1992	198
04.05.1992	198

TABLE 3: Average temperatures and dissolved oxygen contents of the different waters in Phase 1 - plant data

WATER	AVERAGE TEMPERATURE (°C)	AVERAGE DISSOLVED OXYGEN (mg/ℓ)
Raw mine water	27,7 ± 6,1	5,5 ± 0,7
Neutralized	27,4 ± 5,9	5,5 ± 0,8
Settled	25,3 ± 4,7	5,8 ± 0,8
Filtered	25,6 ± 5,0	5,7 ± 0,8
Disinfected	25,4 ± 4,9	5,8 ± 0,7
RWB	25,2 ± 5,1	5,8 ± 0,8
Blend 1	24,5 ± 5,0	5,9 ± 0,7
Blend 2	25,7 ± 5,1	6,1 ± 1,3

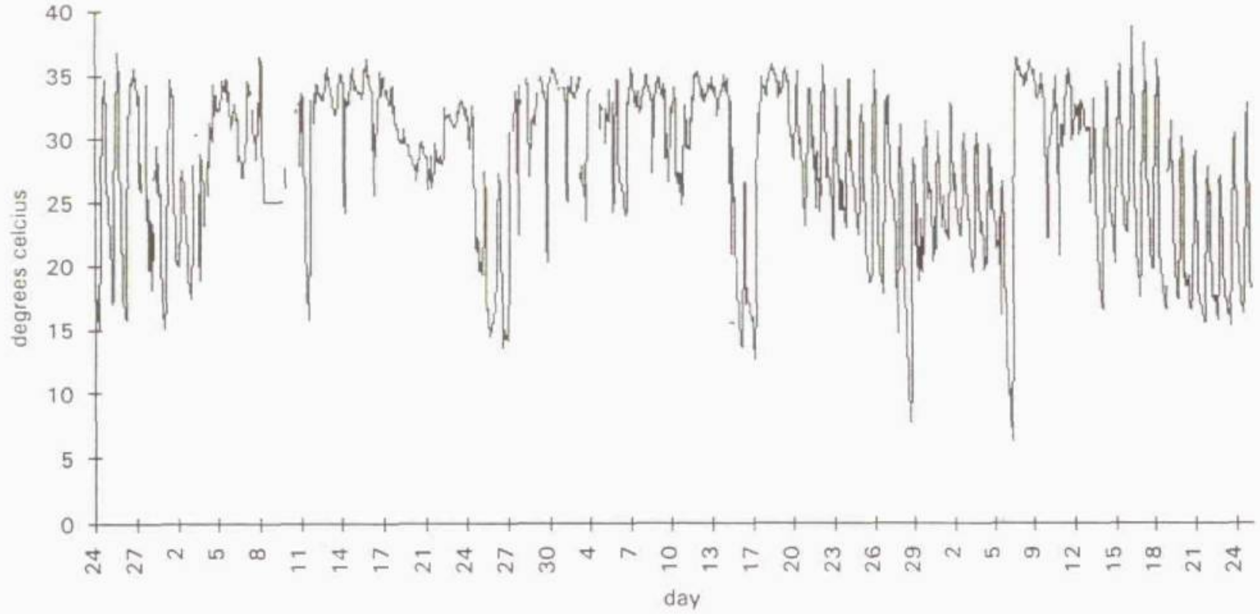

Figure 6: The temperature of the raw mine water during Phase 1.

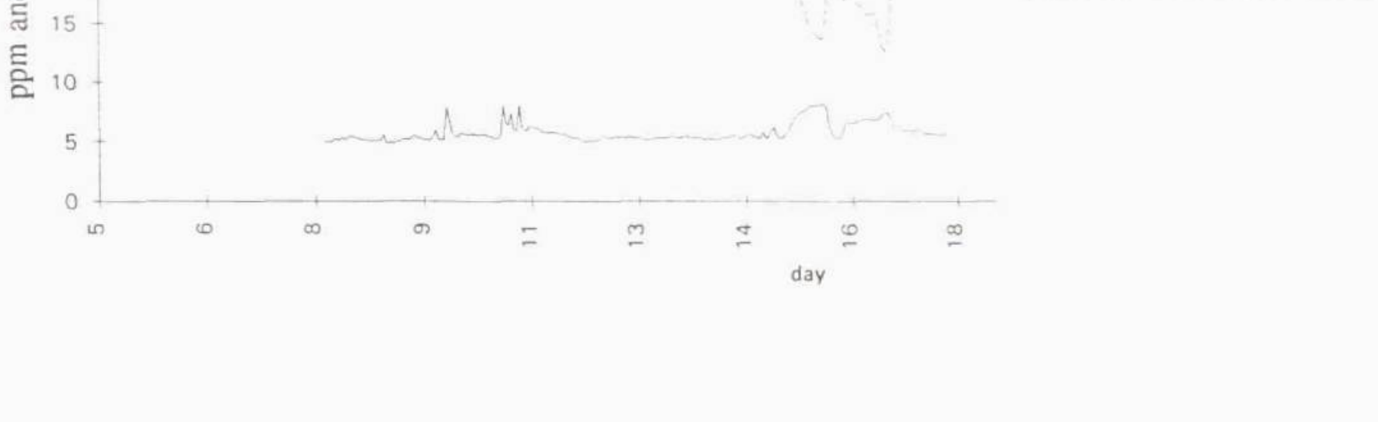

Figure 7: Temperature and dissolved oxygen of raw mine water for the period 8.04.1992 to 18.04.1993.

The average values of temperature and dissolved oxygen content measured during Phase 1 are presented in Table 3. The raw mine water had the highest average temperature of 27,7°C. The average temperature of the neutralized water was slightly lower (27,4°C) and thereafter all the average temperatures are quite constant (approximately 25°C). The average dissolved oxygen contents fall in the fairly narrow range of 5,5 mg/ℓ to 6,1 mg/ℓ.

The results of analyses performed in the laboratory (average values of the 5 samples taken during 3 months of operation) are presented in Table 4. Standard deviations are only reported where this value exceeded 30% of the average value.

3.3 Corrosion Data - Phase 1

After removal the coupons were cleaned and weighed. From the weight loss, a corrosion rate expressed as micro-meters per annum (µm/a) was calculated. Duplicate coupons were removed after one, two and three months and average values are reported.

The corrosion data generated by evaluating coupons removed from the eight parallel monitoring lines are summarized in Tables 5 and 6. Table 5 is the average corrosion rates calculated from the weight loss recorded on duplicate coupons while Table 6 summarizes the appearance of each coupon removed after one, two and three months exposure. The coupons were examined for the presence of general corrosion, pitting corrosion, crevice corrosion under the insulating washer and preferential corrosion of the edges. Localized pitting or crevice corrosion is often more serious than general corrosion as this form of corrosion penetrates at a faster rate than general corrosion occurring over the whole surface. Failure of a critical component will therefore often be due to perforation caused by localised corrosion rather than by general corrosion. For this reason the deepest pit or crevice on each coupon was also measured and reported.

The zinc coating on galvanized steel is a sacrificial coating which cathodically protects the underlying steel substrate. The terms "white rust" and "red rust"

TABLE 4: Average of laboratory analysis results - Phase 1 (mg/l unless otherwise indicated)

PARAMETER	RMW	NEUTR.	SETTLED	FILT. D	DISINF.	BLEND 2	BLEND 1	RWB
pH	9,40	7,99 ± 2,33	7,97	7,80	7,62	8,07	8,20	8,19
Conductivity (mS/m)	183	248 ± 151	192	184	182	120	80 ± 48	26
Susp. solids	822 ± 1496	388 ± 800	8	2,2	4,6	3,4	2,6	0,6
TDS	1742	2164 ± 1221	1778	1640	1657	1023	621	146 ± 43
Alkalinity	412 ± 773	185 ± 366	16	16	18	46	62	80
Total Hardness	877	811	871	793	788	471 ± 209	300 ± 198	83
Calcium	313	280	294	262	257	148 ± 74	92 ± 68	20
Magnesium	24 ± 17	27 ± 16	34 ± 15	34 ± 12	35 ± 12	25 ± 10	17 ± 8	8
Sodium	103	266 ± 369	110	100	98	65 ± 19	44 ± 20	20
Chlorides	53	49	53	52	54	34 ± 10	24 ± 11	15
Nitrates	12 ± 5	13 ± 7	18 ± 14	13 ± 8	18 ± 17	10 ± 14	10 ± 9	1
Sulphates	1100	1362 ± 868	1063	988	979	528 ± 230	282 ± 231	30 ± 9
Iron	0,18	0,24	0,26	0,26	0,28	0,28	0,24	0,24
Zinc	0,08	0,20	0,15	0,17	0,15	0,11	0,08	0,06
Manganese	0,05	0,79	0,85	0,96	0,98	0,60	0,27	0,06
Barium	4,29	4,7	5,1	4,9	3,9	1,3	2,6	0,75
Copper	0,09	0,13	0,08	0,07	0,06	0,06	0,05	0,04

TABLE 5: Corrosion rate based on the coupon mass losses for Phase 1 (MSI = Mild steel removed after one month. Duplicate coupons removed and average values reported)

	R.M.W. Corrosion Rate (μm/a)	Neutralized Water Corrosion Rate (μm/a)	Settled Storage Corrosion Rate (μm/a)	Filtered Storage Corrosion Rate (μm/a)	Disinfected Storage Corrosion Rate (μm/a)	R.W.B. Water Corrosion Rate (μm/a)	First Blend Corrosion Rate (μm/a)	Second Blend Corrosion Rate (μm/a)
MS1	242,49	372,92	326,80	310,80	311,49	326,04	332,71	286,42
MS2	101,10	382,48	211,74	336,88	274,05	166,62	52,06	175,56
MS3	117,79	310,17	243,30	243,36	318,99	164,00	80,75	151,68
GS1	208,40	417,60	90,53	119,12	126,81	70,81	164,99	156,36
GS2	105,76	607,43	310,90	501,47	396,42	45,68	1,13	192,36
GS3	44,06	518,23	315,22	284,76	279,74	18,53	28,35	151,61
316SS1	1,62	1,95	1,97	1,71	1,77	1,70	1,53	1,22
316SS2	1,25	1,07	0,64	0,70	0,36	0,63	1,06	0,73
316SS3	0,69	0,82	0,51	0,62	0,81	0,60	0,66	0,31
CU1	32,54	38,15	26,63	17,64	19,72	25,21	10,34	20,64
CU2	9,51	25,96	8,30	9,18	10,15	19,59	0,14	10,72
CU3	11,74	27,63	12,18	9,06	14,05	7,20	0,72	12,51
CUNI1	34,56	43,85	23,71	16,78	16,95	16,56	8,66	20,47
CUNI2	7,66	35,62	11,39	9,81	11,41	8,20	0,19	10,93
CUNI3	7,54	42,12	11,60	8,96	9,93	5,12	0,77	11,85
3CR12 1	2,65	7,12	0,78	0,95	0,73	1,11	0,86	0,74
3CR12 2	0,19	1,23	4,01	0,07	0,33	0,48	0,70	0,27
3CR12 3	0,919	15,46	3,89	3,56	0,08	0,33	0,15	0,15

TABLE 6: The appearance of corrosion coupons removed after 1, 2 and 3 months during Phase 1 (MS1 = 1 month, MS2 = 2 months etc)

	R.M.W.	Neutralized Water	Settled Storage	Filtered Storage	Disinfected Storage	R.W.B. Water	First Blend	Second Blend
MS1	Loc (0,13) Gen	Gen Gen	Loc (0,06) Gen	Gen Loc (0,010)	Loc (0,12) Gen	Gen Loc (0,05) Gen	Gen Pit (0,39) Edge (1)	Gen Gen
MS2	Gen; Edge (1) Gen; Edge (1)	Gen Gen; Edge	Gen Gen	Gen Gen	Gen Gen	Gen Gen	Gen; Edge Gen; Edge	Gen; Edge Gen; Edge
MS3	Gen Gen	Gen; Loc (0,37 Gen; Loc (0,18)	Gen	Gen Gen	Gen Gen	Gen Gen	Gen Gen	Gen Gen
GS1	St; Gen St; Gen	St;RR(5%);C/C(1); Gen St;RR (30%); Gen	St; Gen St; Gen	St; Gen St; Gen	St; Gen St; Gen	St; Gen St; Gen	St; Gen St; Gen	St; Gen St; Gen
GS2	St; Gen St; Gen	RR (100%); Gen RR (100%); Gen	Gen Gen	St;RR(80); Gen ST;RR(5); Gen	St;RR(80%); Gen ST;RR(10%); Gen	Gen Gen	St;Gen	St; Gen St; Gen
GS3	St; Gen St; Gen	RR(100%); Gen RR(100%); Gen	St;RR(40%); Gen RR(90%); Gen	RR(70%); Gen RR(100%); Gen	St;RR(30%); Gen RR(100%); Gen	St; Gen St; Gen	St; Gen St; Gen	St; Gen St; Gen
316SS1	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected
316SS2	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected
316SS3	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected	Unaffected Unaffected
CU1	St; St	St; St	St; St	St; St	St; St	St; St	St; St	St; St
CU2	St; St	St; St	St; St	St; St	St; St	St; St	St; St	St; St
CU3	St; St	St; St	St; St	St; St	St; St	St; St	St; St	St; St
CUNI1	St; Pit (0,25) St; Pit (0,35)	St St	St St	St St	St St	St; Pit (0,46) St	St St; Pit (0,25)	St St
CUNI2	St St	St St	St St	St St; Gen	St; Loc (0,21) St; Loc (0,20)	St St	St; C/C (1) St	St St
CUNI3	St; Pit (0,15) St; Pit (0,05)	St St	St St	St; Gen St; Gen	St; Gen St; Gen; Pit (0,14)	St St	St; Pit (0,14) St; Gen	St; Gen St
3CR12 1	Unaffected Unaffected	Edge St	St St	St St	St St	Unaffected Unaffected	St St	St Unaffected
3CR12 2	St St	St; Edge (2) St; Edge (2)	St; Edge (1) St; Edge (1)	St; Edge (1) St	St St	St St	St St	St St
3CR12 3	St St	Edge (2); St St	St; Edge (1) St; Edge (1)	St St	St St	St St	St St	St St

are often used to describe corrosion of a galvanized component. White rust refers to zinc corrosion products (eg. zinc hydroxide) while red rust is caused by the formation of ferrous corrosion products (iron oxides and hydroxides). The appearance of red rust on a galvanized component is therefore indicative of a failed zinc coating (ie. the zinc has been corroded away locally and the surrounding zinc no longer affords sufficient cathodic protection to prevent corrosion of the underlying steel substrate). The appearance of red rust and the approximate surface area of the coupon covered by it was therefore also evaluated and reported in Table 6 for each of the galvanized steel coupons.

The following abbreviations have been used in Table 6:

St	- staining
Gen	- general corrosion
Loc	- localized corrosion (depth in mm)
Pit	- pitting corrosion (depth in mm)
C/C	- crevice corrosion (1 = mild, 2 = moderate, 3 = severe)
Edge	- edge attack
RR (%)	- red rust (% of surface affected).

The classifications of the corrosion mechanism and its severity as used in Table 6 are illustrated by the photographs of various coupons presented in Figures 8,9 and 10.

The corrosion rates for mild steel and galvanized steel coupons are presented graphically in Figures 11 and 12. Intuitively, the corrosivity of the various waters are expected to decrease in the order

$$\text{RMW} > \text{Neutralized} \geq \text{Settled} \geq \text{Filtered} \geq \text{Disinfected}$$
$$> \text{Blend 1} > \text{Blend 2} > \text{RWB}$$

and the data is plotted in this order on the x-axis of Figures 11 and 12.

In Figure 11 it is apparent that there is a decrease in corrosion rate for the 2 month exposure compared to the 1 month exposure. It is only in the

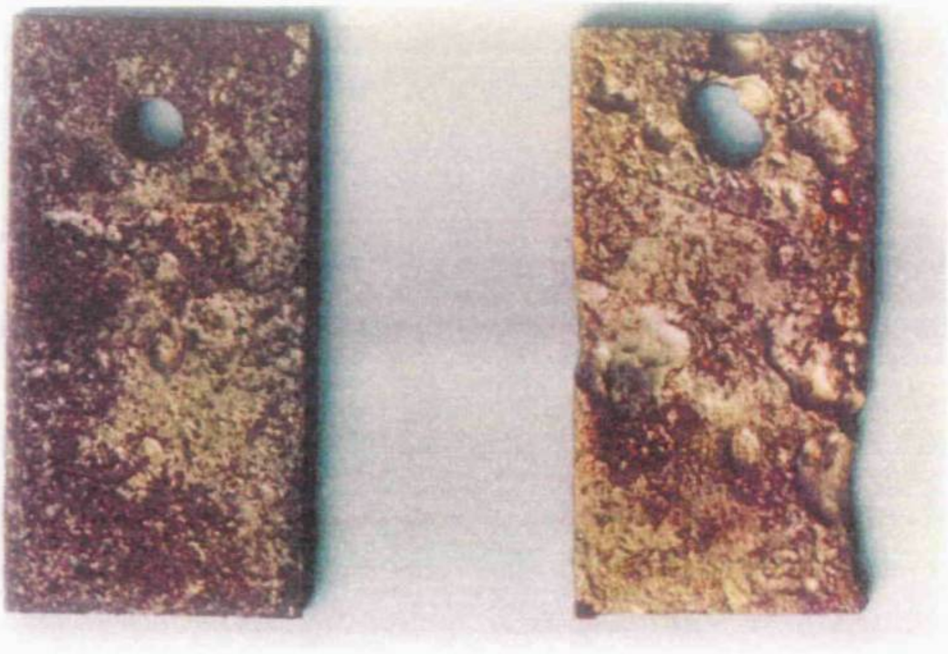

Figure 8: General corrosion of a mild steel coupon (LHS) and localized and pitting corrosion of mild steel (RHS).

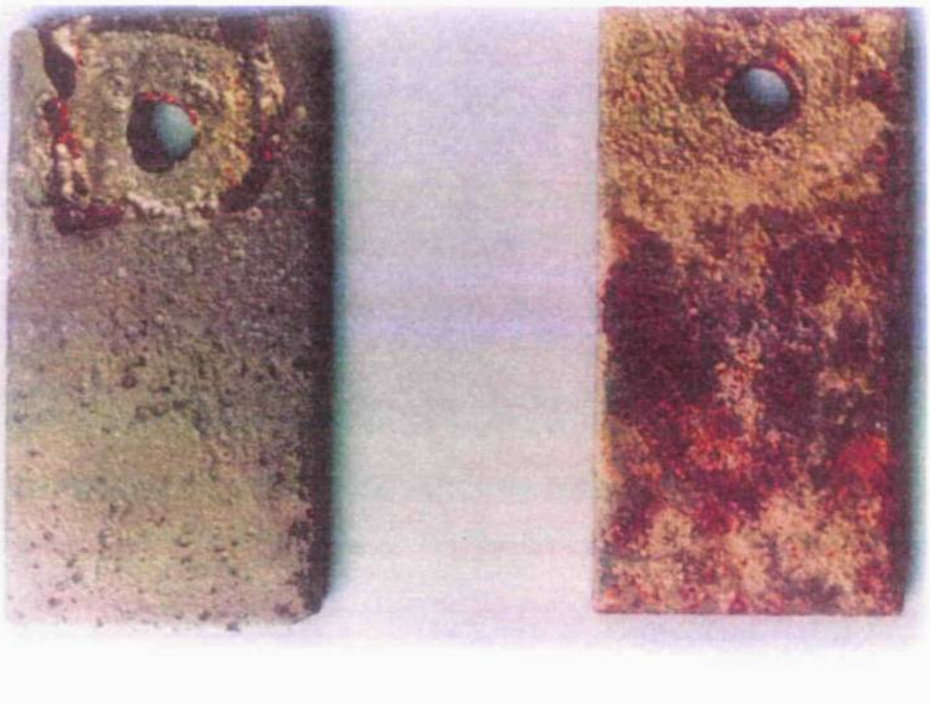

Figure 9: Crevice corrosion around the mounting hole of a galvanized steel coupon (LHS) and red rust on a galvanized steel coupon (RHS).

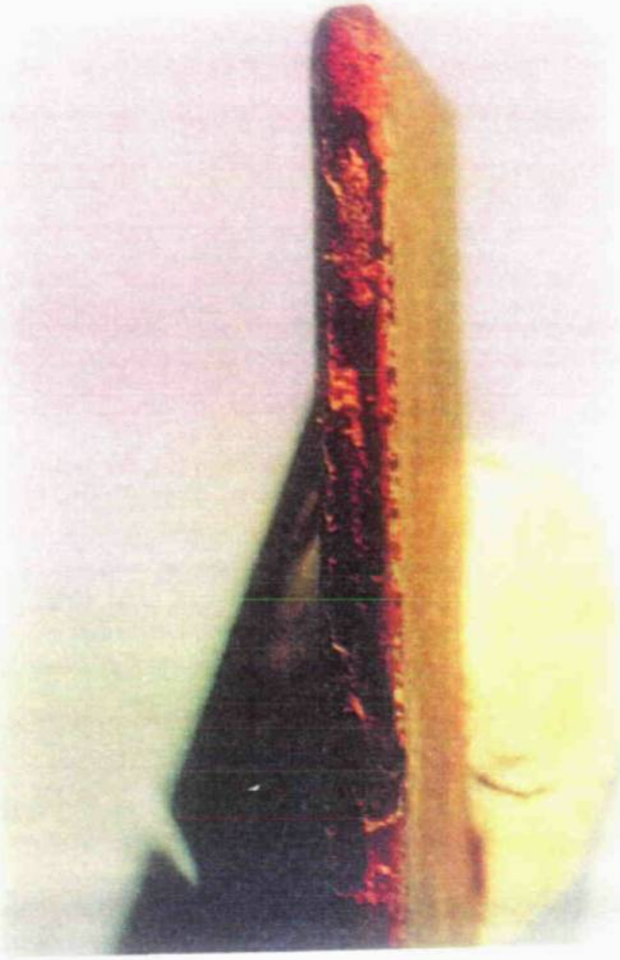

Figure 10: Severe edge attack of a 3CR12 coupon.

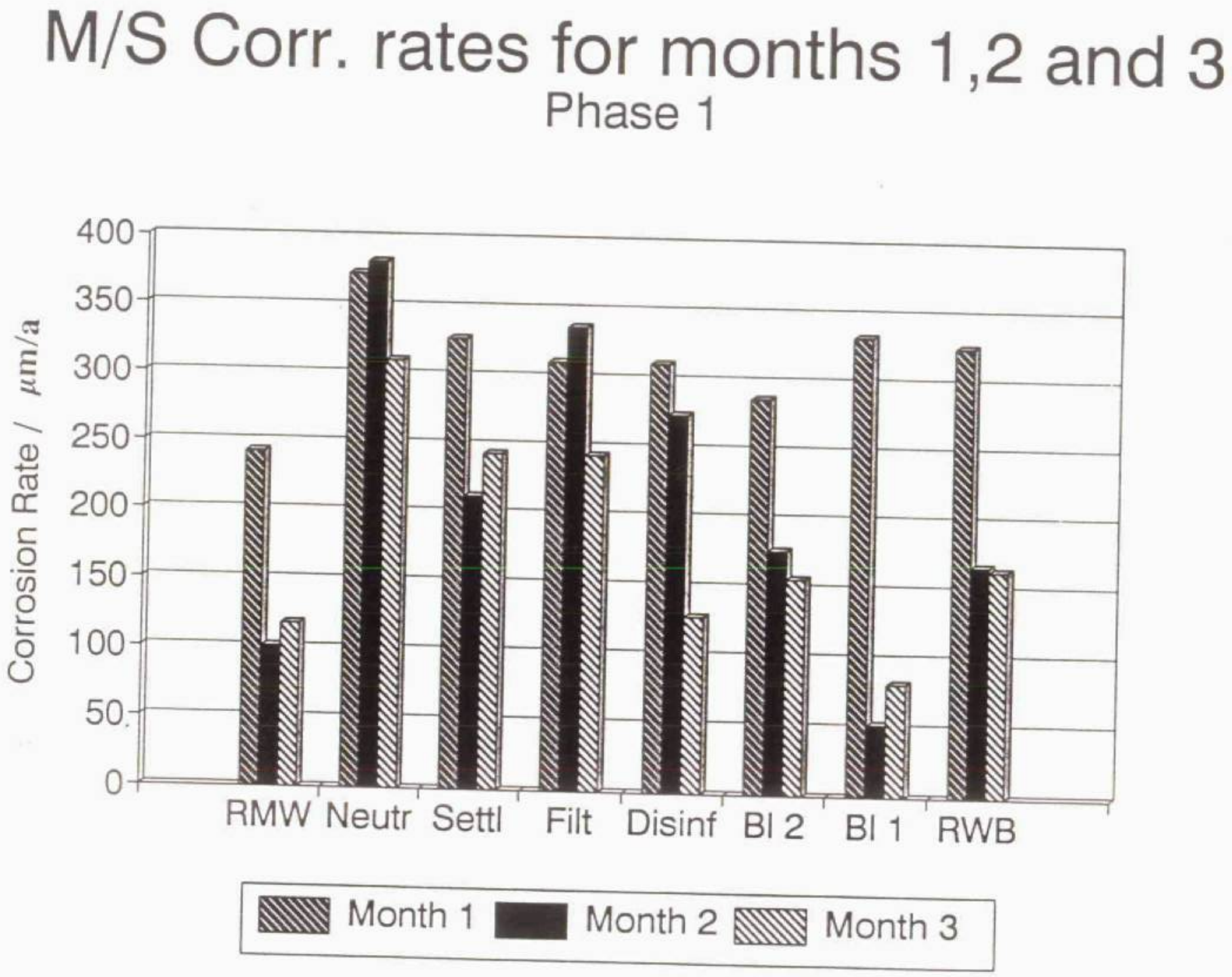

Figure 11: Mild steel corrosion rates for months 1, 2 and 3 (Phase 1).

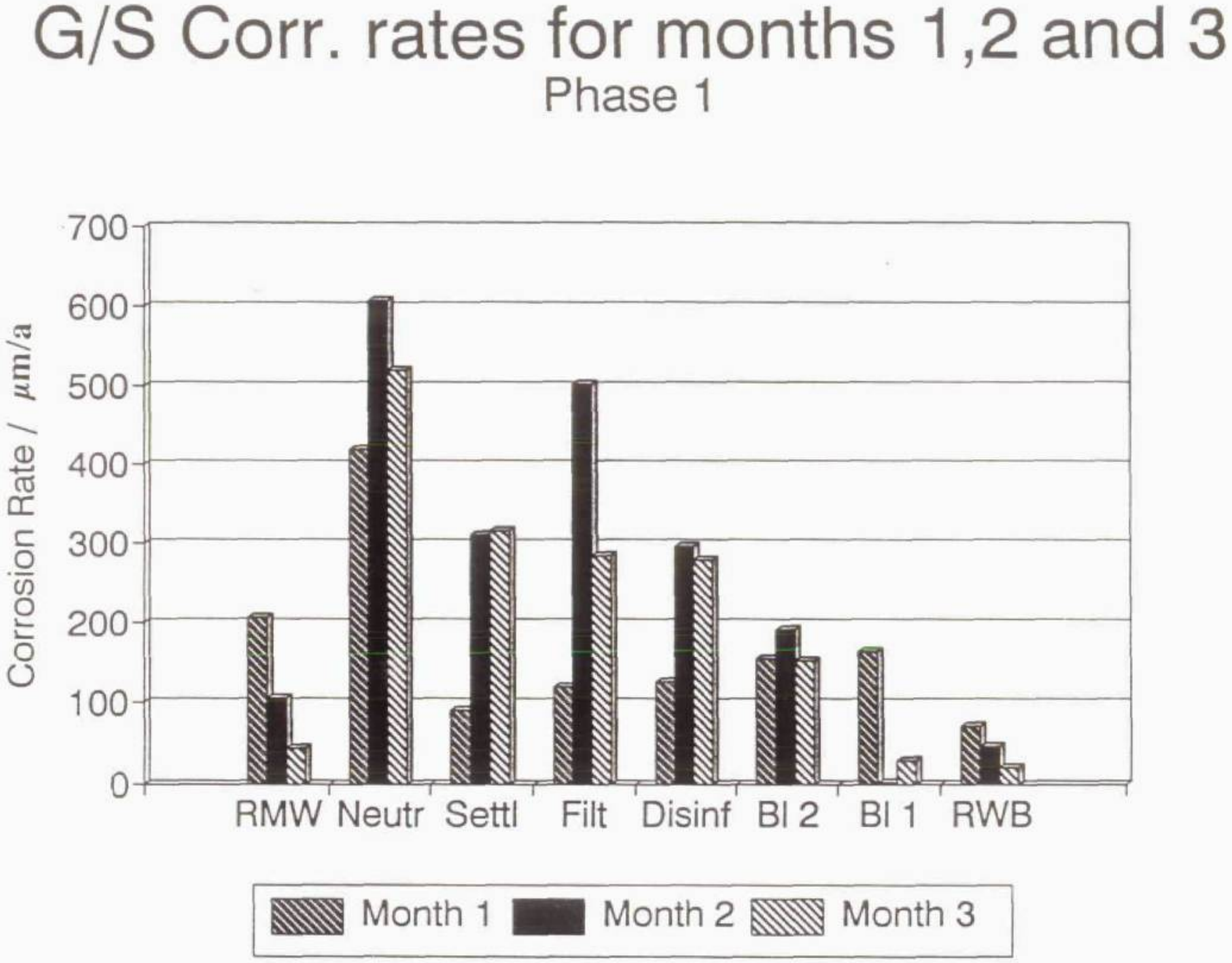

Figure 12: Galvanized steel corrosion rates for months 1, 2 and 3 (Phase 1).

neutralized and filtered water that this trend is not observed. The decrease in corrosion rate with exposure time can be ascribed to high initial corrosion rates on the clean steel surface with a decrease in the rate as protective corrosion product and scale form on the surface of the steel until a stable corrosion rate is achieved. It is evident from Figure 11 that if the corrosion rates are averaged over the 1, 2 and 3 month periods, the neutralized and filtered waters are the most aggressive. The more aggressive the medium, the sooner corrosion rates will stabilize and this could be the explanation for these two waters not exhibiting the same phenomenon as described above.

In Figures 11 and 12, the intuitive trend in corrosion rates is not observed. Contrary to expectations, the treated waters (neutralized, settled, filtered and disinfected) generally have the highest corrosion rates for both materials. The increased corrosivity of these four waters is also clearly illustrated by the galvanized steel coupon evaluations presented in Table 6. It is only in these four waters that red rust was observed on the galvanised steel coupons. In the raw mine water, first and second blends and Rand Water Board water, only staining and general corrosion was observed indicating that the zinc coatings did not fail in these media.

In order to interpret coupon corrosion data, continuous data on corrosive species (eg. pH, TDS, Cl^-, SO_4^{2-}, temp, dissolved oxygen) is required, or a constant water chemistry throughout the programme of testing must be maintained. For Phase 1 the intention was to have a constant water chemistry for each unit process but the data shows that neutralization was ineffective and in fact that excess NaOH and H_2SO_4 was sometimes dosed into the system. A constant water chemistry was therefore not achieved.

The increased corrosivity of the neutralized, settled, filtered and disinfected waters can be ascribed to the incorrect functioning of the neutralization system. It is well known that corrosion of mild steel and galvanized steel is dependant on pH and that corrosion is accelerated significantly at low and high pH's.

The dissolved oxygen content of the various waters was mainly dependent on temperature, which varied with the ambient temperature. The nett result, as shown by the average values in Table 3, was that temperature and dissolved oxygen contents of the various waters were similar for all the unit processes. The slightly higher temperature of the raw mine water and the neutralized water is not sufficient to influence the corrosion results significantly.

The anions (SO_4^{2-}, Cl^- and NO_3^-) analyzed in the laboratory (Table 4) are presented graphically in Figure 13. The total dissolved solids results are also included in this figure. The decrease in anion concentration after blending the disinfected water with Rand Water Board water is clearly evident. Sulphate is the anion present at the highest concentration and a close correlation between sulphate ion concentration and total dissolved solids is evident. The average pH values reported in Table 4 do not reflect the variation in pH illustrated in Figures 2 and 3 (on line measurement).

Average corrosion rates calculated from the 1, 2 and 3 month data for mild steel and galvanised steel are plotted against total dissolved solids contents in Figures 14 and 15 respectively. A general increase in corrosion rate with increasing TDS is evident.

A surprising result in Phase 1 is that mild steel has a higher corrosion rate in RWB water than in raw mine water, even though its TDS is significantly lower. No explanation for this phenomenon could be found in the available data. A possible explanation would be that the mine water contained some inhibiting specie not analyzed for (eg. nitrite).

No satisfactory correlation between corrosion rate and Langelier Index or corrosivity index could be found.

The copper and the Cu-Ni coupons all had low corrosion rates as shown by the data in Table 5. The average corrosion rates calculated from 1, 2 and 3 month data are presented in Figure 16 for Cu and Cu-Ni. The highest corrosion rate is once again exhibited in the neutralized water. The low corrosion rate of the first blend could not be explained. With the exception of the neutralized water and blend 1, the corrosion rates are all between 10 and 20 μm per year.

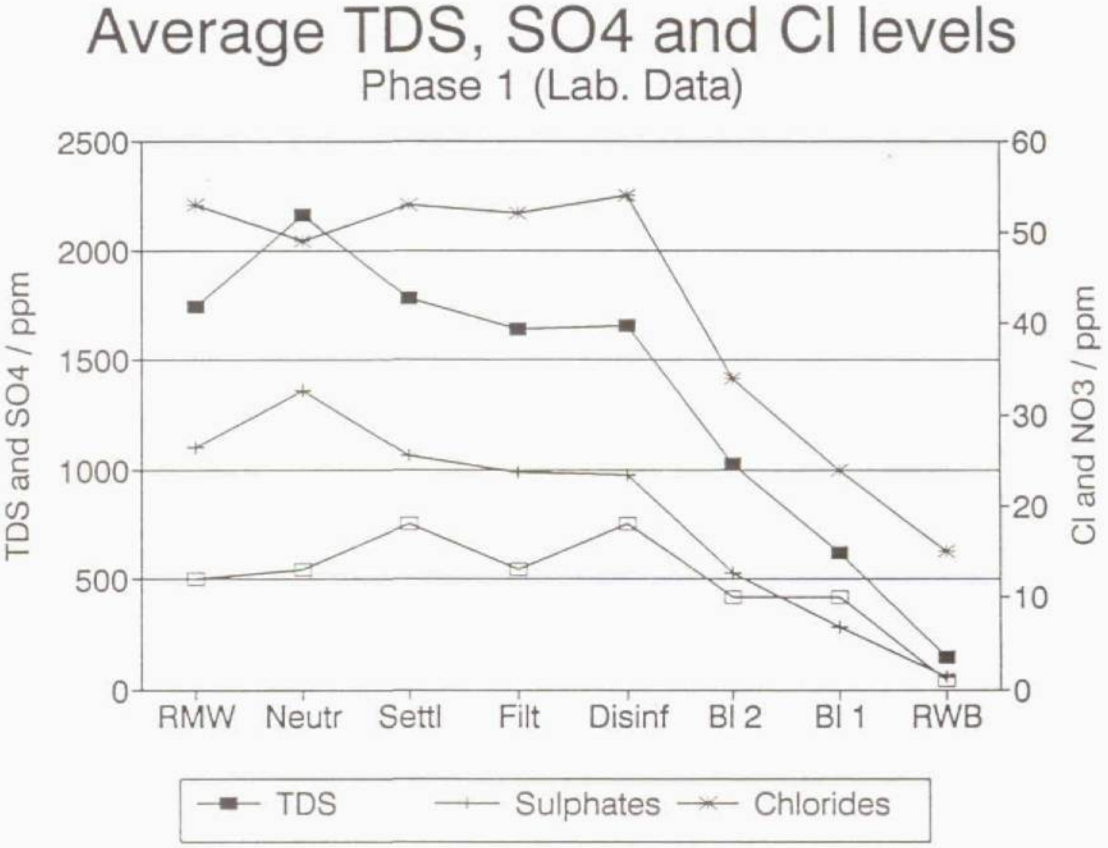

Figure 13: Sulphate, chloride, nitrate and total dissolved solids contents of the various waters tested during Phase 1.

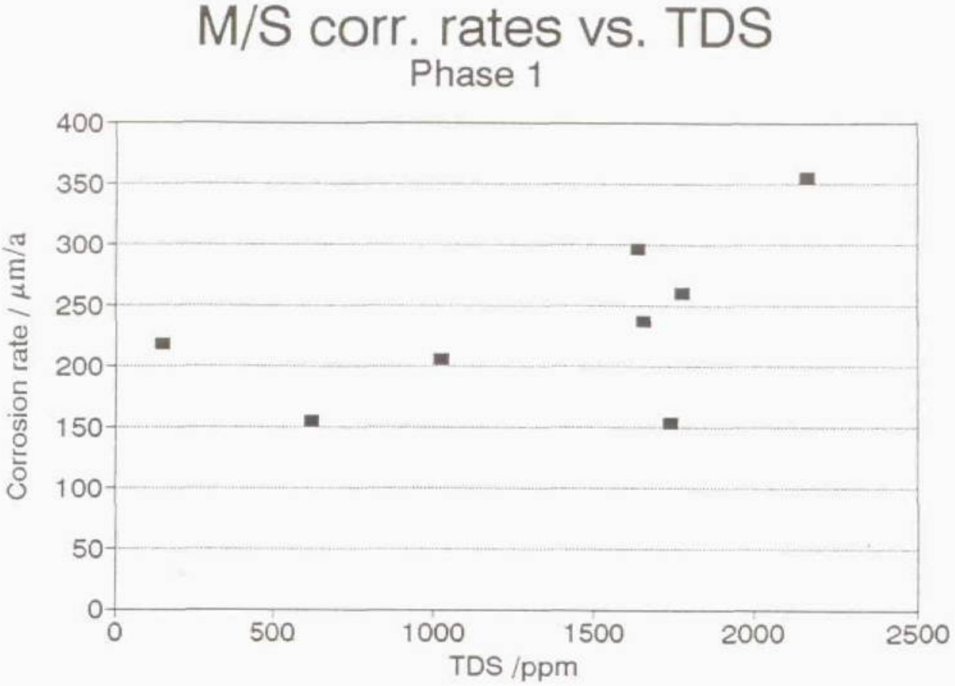

Figure 14: Average mild steel corrosion rates as a function of total dissolved solids (Phase 1).

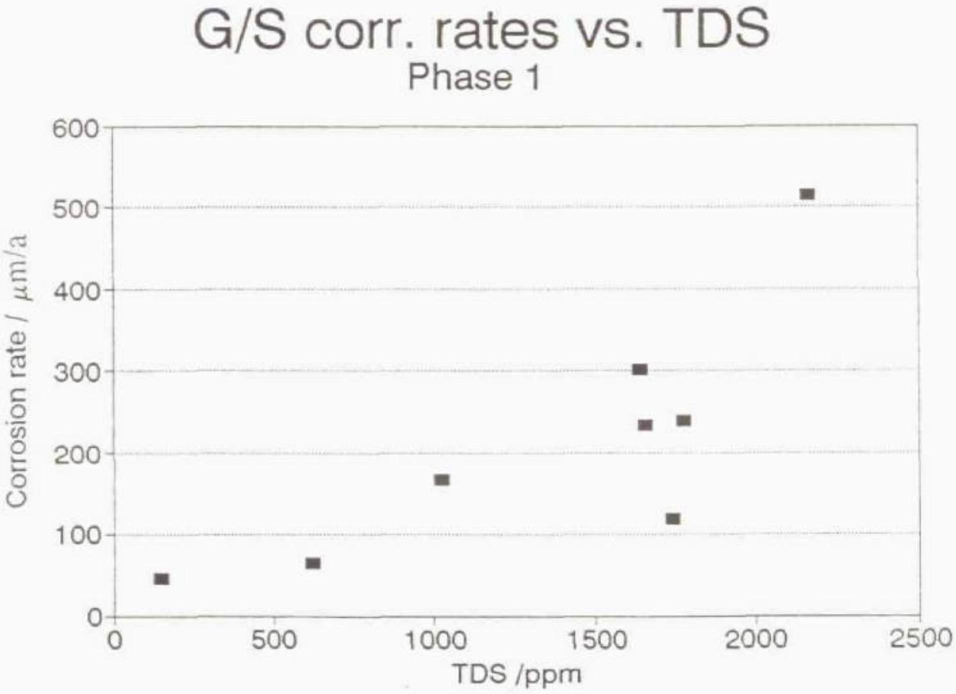

Figure 15: Average galvanized steel corrosion rates as a function of TDS (Phase 1).

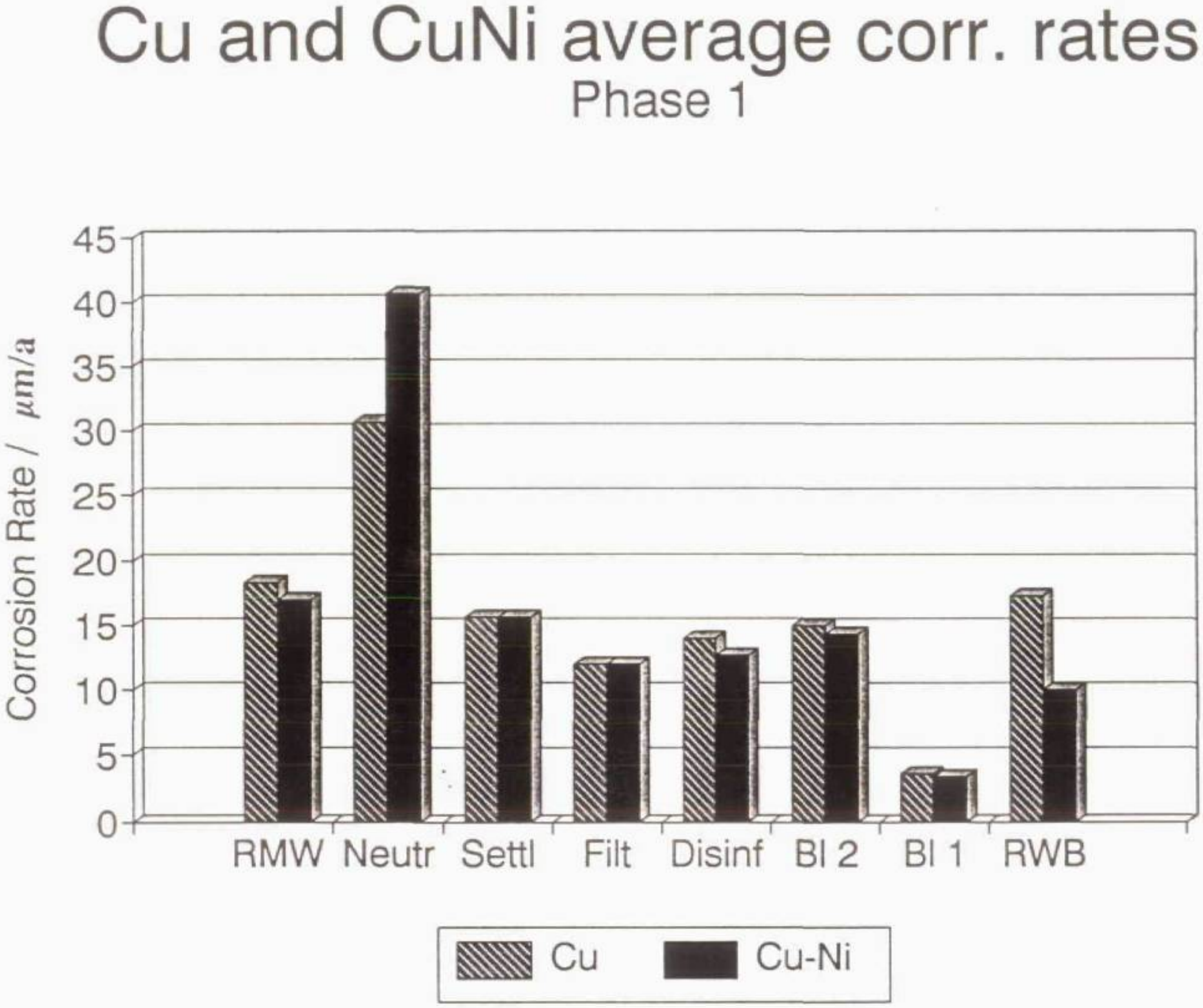

Figure 16: Average copper and copper-nickel corrosion rates measured in the various waters during Phase 1.

The 316 coupons did not exhibit any signs of corrosion while staining and edge attack only was observed on some of the 3CR12 coupons. Edge attack was only observed in the treated waters, confirming previous observations that these were the most aggressive waters tested. The data indicates that a three month exposure period is not sufficient to generate data for stainless alloys.

4. RESULTS - PHASE 2

4.1 Water Reclamation Plant Details

During Phase 2, ERPM mine service water was dosed with chemicals to simulate a Klerksdorp water. This water (designated raw mine water, RMW) was then treated in the water reclamation test plant in order to fill the various storage tanks. As in Phase 1, desalinated water from the SPARRO plant was substituted with Rand Water Board water.

The water in each tank was recirculated through a monitoring loop for a period of ninety days. Evaporative losses were compensated for by topping up the storage tanks. Water samples from each line were analysed in the laboratory on a weekly basis.

Although flow data was lost, it was reported that the flow rate varied between 1,6 m/s and 2 m/s.

4.2 Water Quality Data - Phase 2

Recirculation of water ensured a much more constant water chemistry than during Phase 1. Conductivity data for each unit process measured on-line is shown in Figures 17 to 23. From these graphs it is clear that the conductivity curve of the various waters remained fairly smooth over this time period. Typical pH data recorded during Phase 2 can be seen in Figure 24 (pH of the neutralised water). Clearly the large pH fluctuations observed in Phase 1 is absent here.

The conductivity data presented in Figures 17 to 23 illustrate the effect of evaporation and subsequent make-up with either RWB water or raw mine water. Although the curves remain quite smooth (i.e. no sudden changes are observed), a steady increase in conductivity throughout the period of testing is apparent for all the tanks except raw mine water. It is therefore apparent that although the water chemistry was constant over short time periods, there was a gradual increase in the level of total dissolved solids

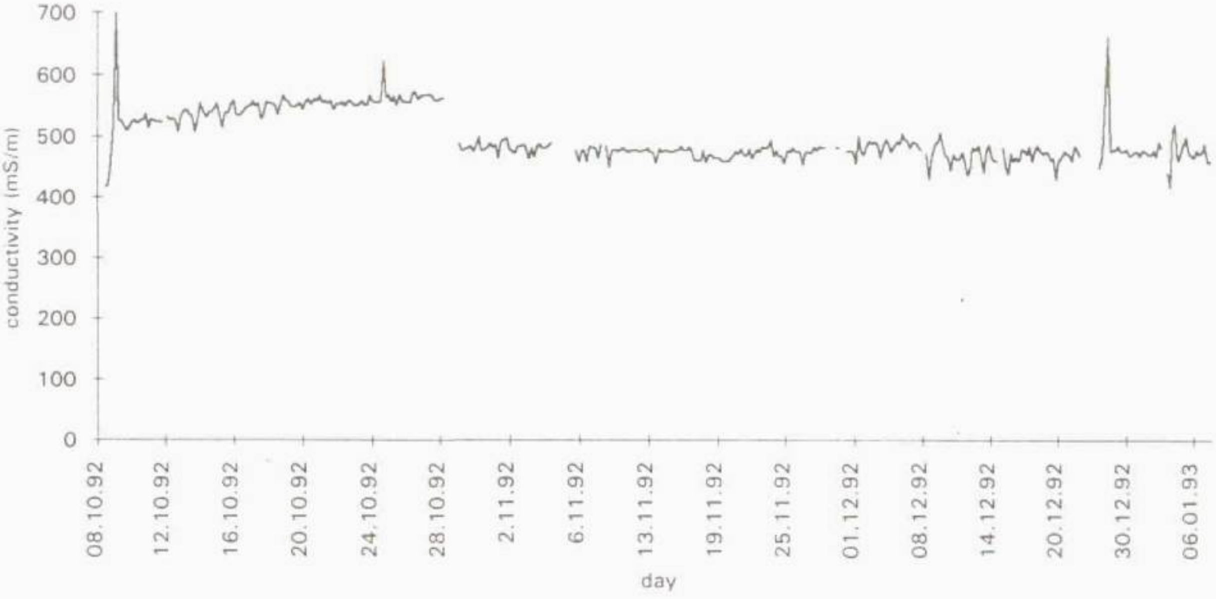

Figure 17: The conductivity of raw mine water during Phase 2.

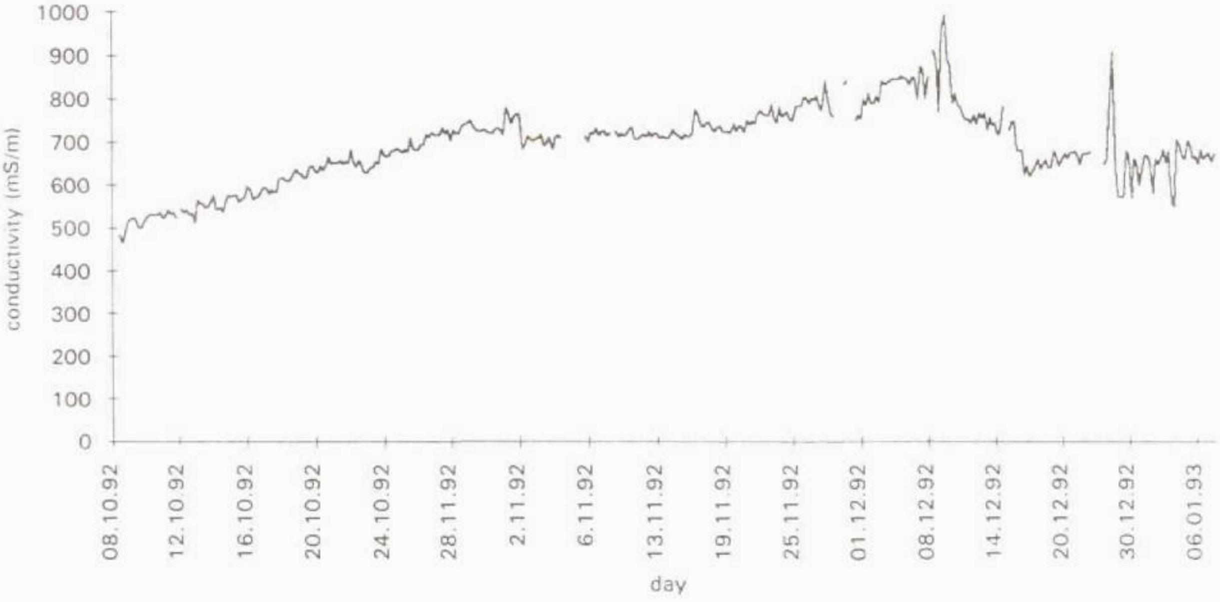

Figure 18: The conductivity of neutralized water during Phase 2.

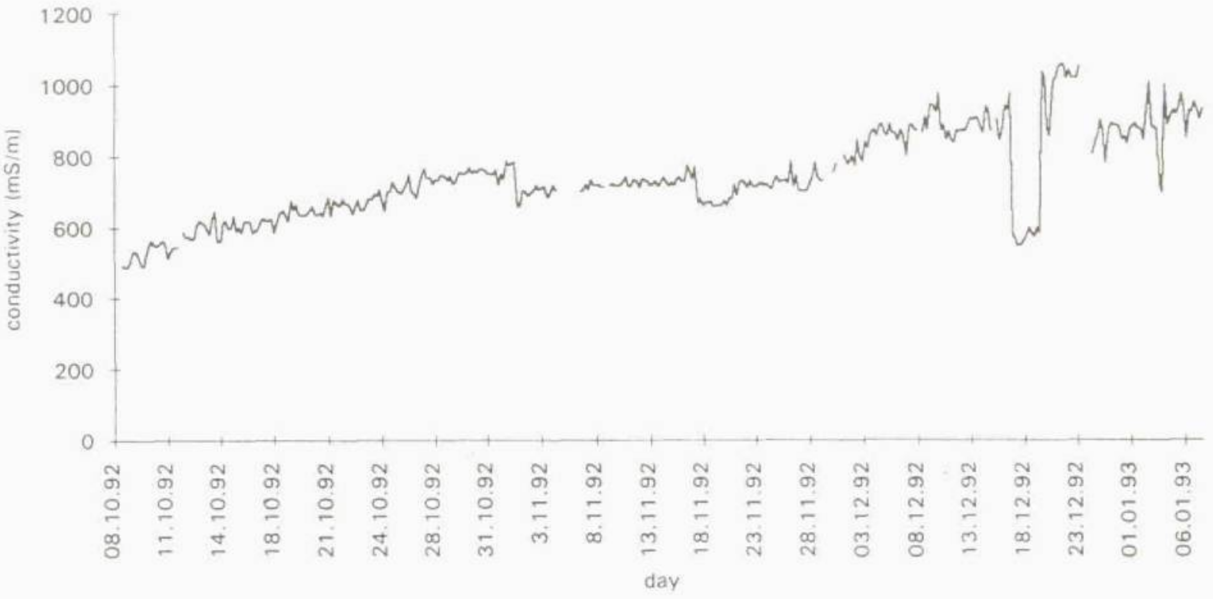

Figure 19: The conductivity of settled water during Phase 2.

Figure 20: The conductivity of disinfected water during Phase 2.

Figure 21: The conductivity of Rand Water Board water during Phase 2.

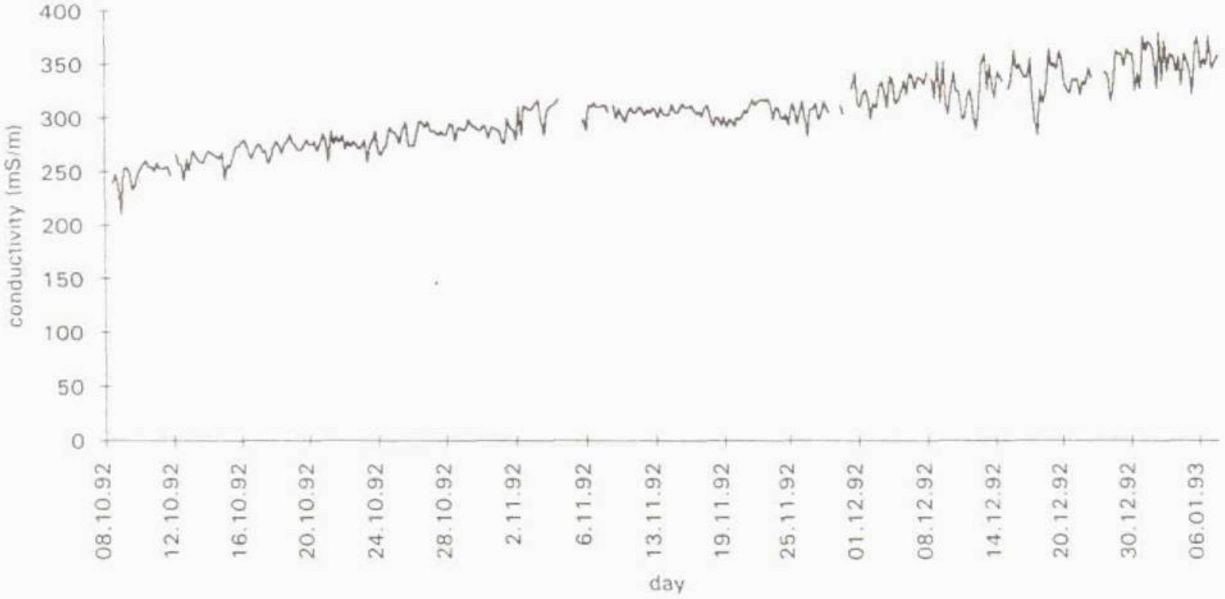

Figure 22: The conductivity of first blend water during Phase 2.

Figure 23: The conductivity of second blend water during Phase 2.

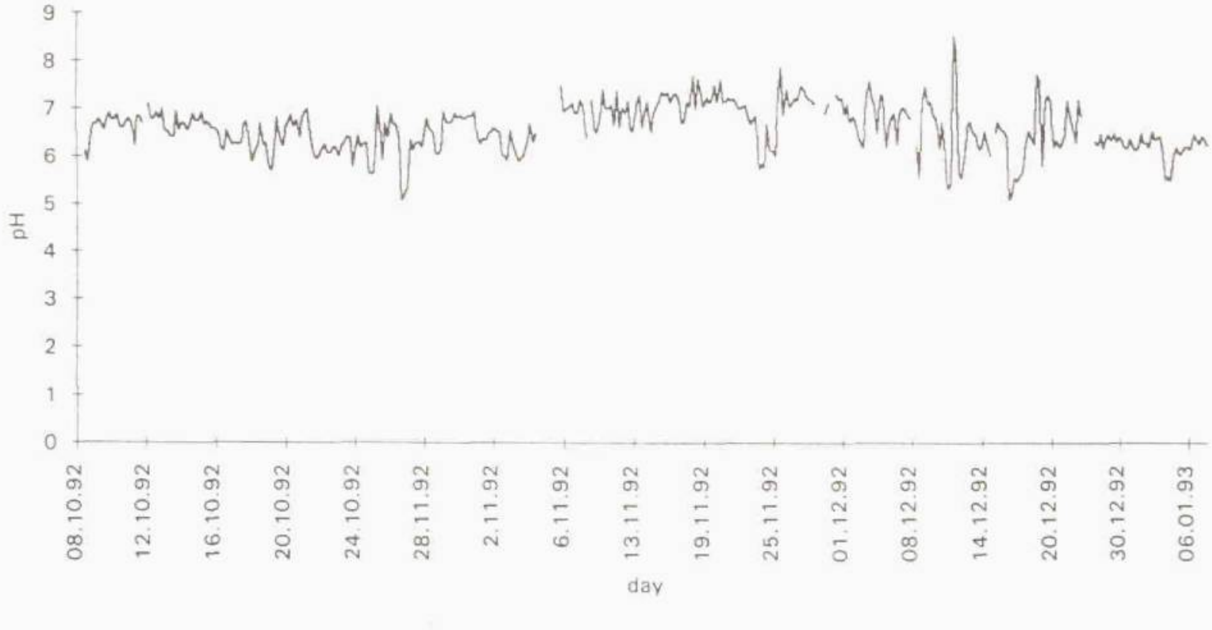

Figure 24: The pH of neutralised water during Phase 2.

over the three month period. The absence of this effect in the raw mine water can be ascribed to the much larger volume of this tank (20 m^3 compared to approximately 1,5 m^3 for the other tanks). The effect of evaporation in this large volume of water was therefore much less than in the smaller tanks.

The build-up of corrosion products in the recirculating water caused the turbidity to increase during the period of testing. Figure 25 shows the turbidity of the settled storage line and increasing turbidity over the first month with values staying fairly constant after that, as can be seen.

The correlation between dissolved oxygen and temperature described in Phase 1 was again found for Phase 2. The recirculating pumps caused the temperature of the various waters to be increased above ambient and the average temperatures were found to vary between 25,6°C (RMW) to 32,6°C (settled storage). Figure 26 is a plot of dissolved oxygen versus temperature for the various tanks and a decreasing oxygen content with increasing temperature is evident.

Table 7 is a summary of various water quality parameters measured during Phase 2. Averages of all measurements taken over the three month period are reported.

4.3 Corrosion Results - Phase 2

4.3.1 Mild Steel Results

The weight loss results (calculated as in Phase 1) and visual appearance of mild steel coupons from Phase 2 are summarized in Tables 8 and 9, respectively. The same abbreviations as in Table 6 are used.

The increasing total dissolved solids content, high turbidity and the temperature variation between the various tanks make it impossible to treat the corrosion data as was initially intended i.e. to investigate the effect of each unit water treatment process on corrosion. Due to the water being

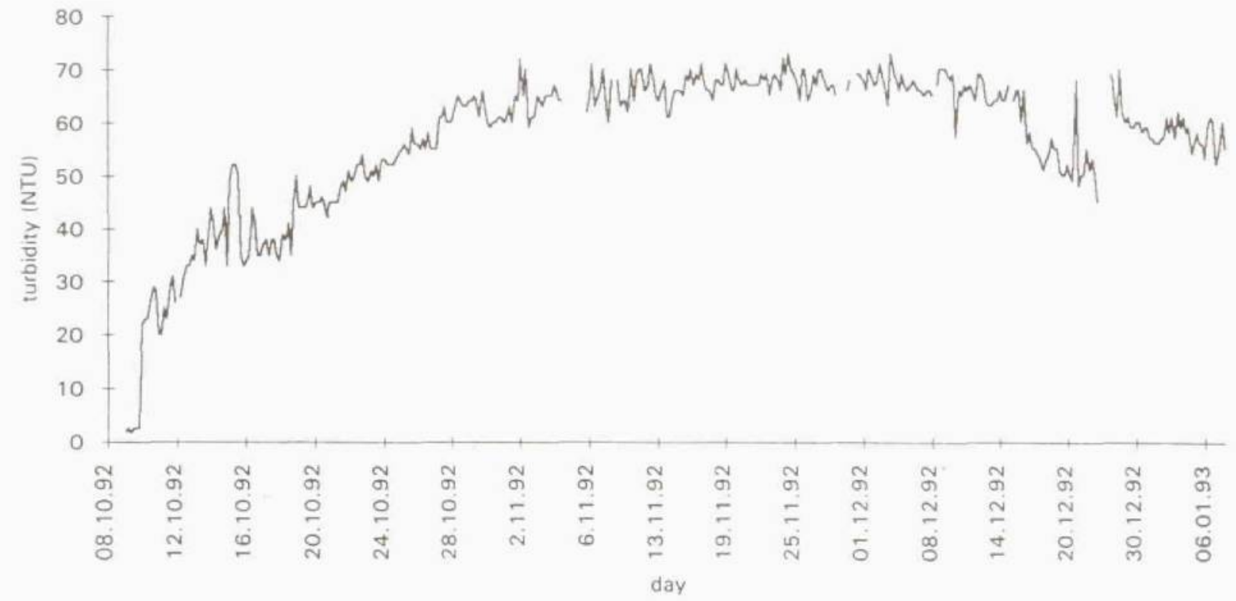

Figure 25: The turbidity of the settled storage tank during Phase 2.

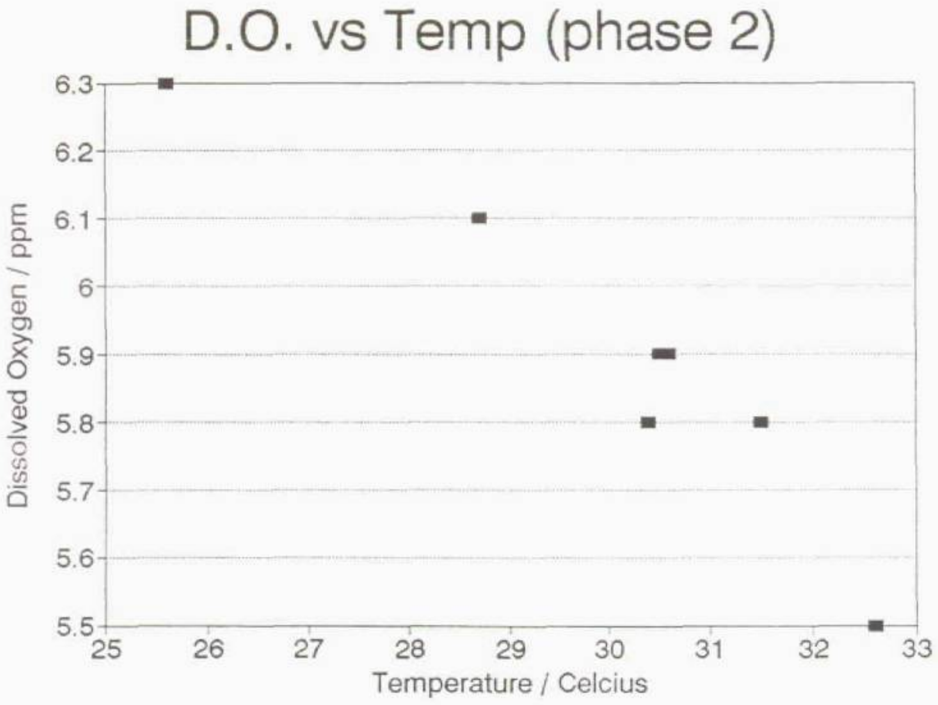

Figure 26: Dissolved oxygen content as a function of temperature for the various waters in Phase 2.

TABLE 7: Water quality parameters measured during Phase 2. All values in mg/ℓ unless otherwise stated.

PARAMETER	RMW	NEUTRALIZED	SETTLED STORAGE	FILTERED & DISINFECTED	RWB	1ST BLEND	2ND BLEND
pH	5,3	6,6	6,8	7,0	7,3	7,2	7,3
Conductivity (mS/m)	497	690	740	552	75	303	184
TDS	4173	5714	6297	4416	438	2260	1237
Alkalinity	30	26	22	19	62	36	48
Total Hardness	1318	1631	1820	1366	158	636	393
Calcium	393	527	590	459	49	204	125
Magnesium	82	82	94	59	10	33	22
Turbidity (NTU)	13	56	57	56	37	57	48
Temperature (°C)	25,6	28,7	32,6	30,4	31,5	30,6	30,5
Chlorides	552	706	948	641	154	358	236
Sulphates	2315	2694	2843	2143	50	945	503
Nitrates	463	637	694	446	9	208	95
Ammonia	37	30	27	17	0,4	3,2	1,0

TABLE 8: Corrosion rate based on mild steel coupon mass losses - Phase 2 (MS1 = removed after one month, MS2 = after two months etc).

	R.M.W. Corrosion Rate (μm/a)	Neutralized Water Corrosion Rate (μm/a)	Settled Storage Corrosion Rate (μm/a)	Disinfected Storage Corrosion Rate (μm/a)	R.W.B. Water Corrosion Rate (μm/a)	First Blend Corrosion Rate (μm/a)	Second Blend Corrosion Rate (μm/a)
MS1	575,11	1996,24	1811,24	1795,89	777,18	1380,68	951,45
MS2	470,15	1537,05	2375,19	1645,76	481,36	1141,26	754,16
MS3	343,38	550,59	689,50	758,79	301,95	713,00	424,72

TABLE 9: The appearance of mild steel coupons - Phase 2 (Duplicate coupons removed)

	R.M.W.	Neutralized Water	Settled Storage	Disinfected Storage	R.W.B. Water	First Blend	Second Blend
MS1	Gen; Edge (1)	Edge (3); C/C(1) Loc(0,56); Gen	Edge (3); C/C (1) Gen; Loc (0,45)	Edge (3); Gen; Loc(0,63); Pit(0,43)	Gen; Edge (1)	Edge(2); Gen Loc(0,70);	Gen; Edge(2); Loc(0,46); C/C(1)
	Gen; Edge (1)	Gen; Edge(3); Loc(0,5); Pit(0,61)	Edge(3); Gen; Loc (0,91)	Edge(3); C/C(3); Gen Loc(1,20) "Severe Loc"	Gen; Edge (1)	Gen; Edge(2); Loc (0,56)	Edge(1); C/C(1); Pit(0,42); Loc(0,33); Gen
MS2	Gen; Loc(0,46); Edge(2)	Gen; Edge(3); Loc (0,74)	Gen; C/C(3); Edge(3); Loc(1,56)	Loc(Perforated); Edge(3); Pit(1,70);Gen	Gen; Edge (3)	Edge(3); C/C(2); Loc(1,10); Gen	Loc(0,69); Gen Edge (3)
	Gen; Edge(1); Loc (0,25)	Edge(3); C/C(2); Gen; Loc(1,43)	Severe Loc(2,18) Edge(3); Gen	Very Severe; Loc(1,70) C/C(3); Edge(3); Gen	Gen; Edge (2)	Edge(3); C/C(2); Loc(1,53); Gen	C/C(2); Edge(3) Loc(1,05); Gen
MS3	Gen	Edge(2); Gen; Loc (0,72)	Edge(3); Loc(0,41); Gen	Gen; Edge(1) Loc (0,45)	Edge(2); Gen; Loc (0,22)	Gen; C/C(1); Edge(3); Loc(0,35)	Edge (3); Gen
	Gen; Edge (1)	C/C(3); Edge(3); Gen; Loc (0,91)	Edge(3); Loc(0,36); Pit (0,40)	C/C(2); Edge(3); Gen; Loc(0,71)	Gen; Edge(1); Loc(0,46)	Edge(3); C/C(2); Loc(0,51); Gen	Gen; Edge(2); Loc (0,24)

recirculated, the water chemistry for each tank changed to such an extent that it was decided to interpret the corrosion data purely in terms of water quality.

Figure 27 is a plot of the mild steel corrosion rates for the 1 month, 2 month and 3 month exposures. The seven different waters used are arranged in order of decreasing total dissolved solids (from left to right). The general decrease in corrosion rate with exposure time is clearly evident.

The mild steel corrosion rates were plotted against various parameters i.e. pH, total dissolved solids, chlorides, nitrates, sulphates, ammonia, turbidity, temperature, Langelier Index and corrosivity index. The one, two and three month data were plotted individually as well as average values calculated from all the data. The only plots which showed a degree of correlation were those of corrosion rate versus the dissolved solids. Plots obtained for the chloride, nitrate, sulphate and total dissolved solids contents are shown in Figures 28 and 29. Average corrosion rate values were used here but the individual one, two and three month data showed similar trends.

The largest variation from the trend of increasing corrosion rate with increasing TDS was exhibited by the raw mine water. Even though this water had a total dissolved solids content of over 4000 ppm, it exhibited the lowest mild steel corrosion rate of all the waters tested. The raw mine water also had the highest oxygen content at 6.3 ppm (Figure 26) which should increase the corrosion rate in this water.

The lower temperature and turbidity of the raw mine water (due to a larger volume of water being recirculated) could make it less corrosive. However, the corrosion rate in the raw mine water is approximately three times less than that of the filtered and disinfected water even though both these waters have similar total dissolved solids contents.

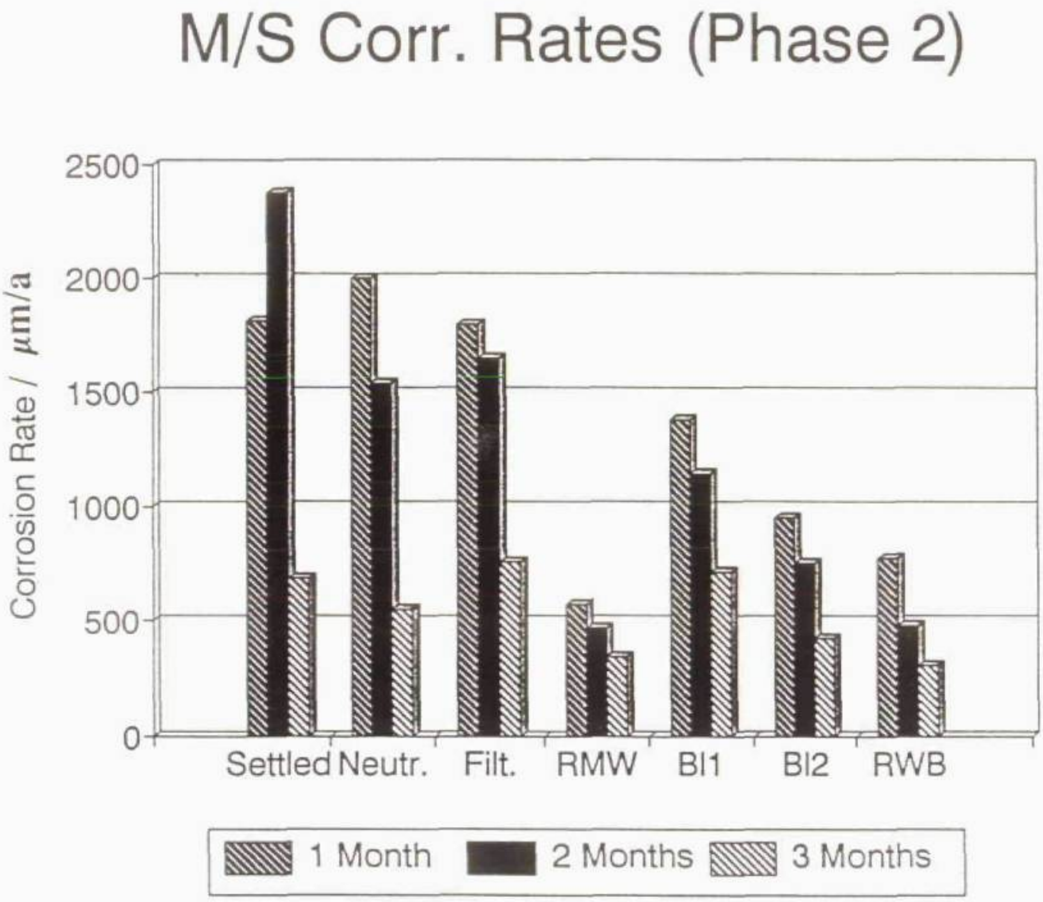

Figure 27: Mild steel corrosion rates after 1, 2 and 3 months (Phase 2).

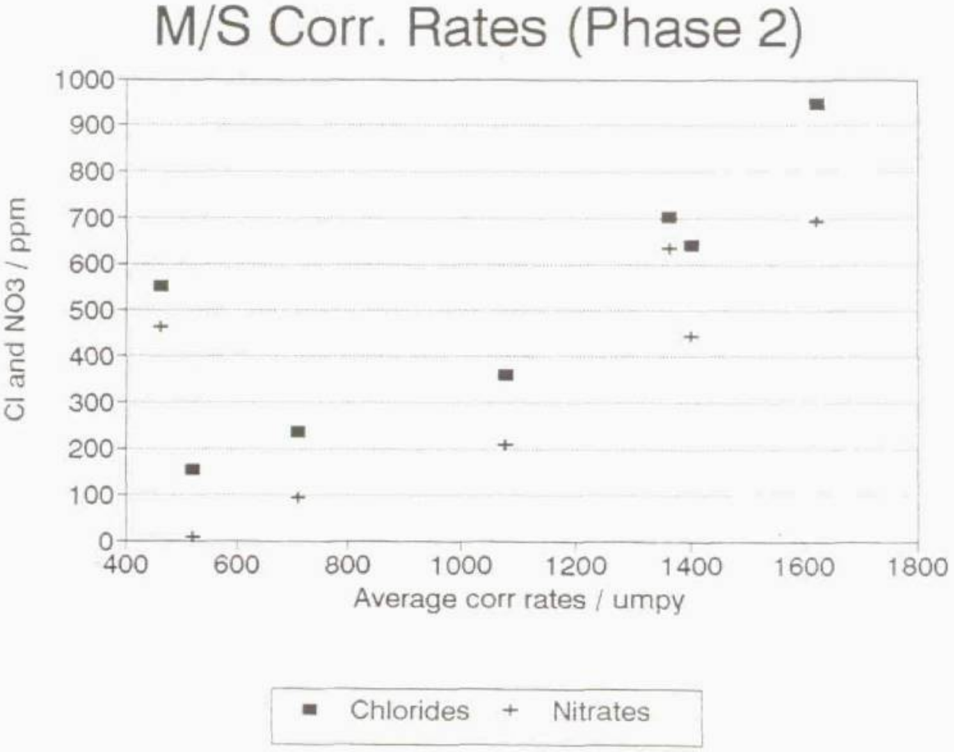

Figure 28: The effect of chloride and nitrate contents on corrosion rate of mild steel (Phase 2).

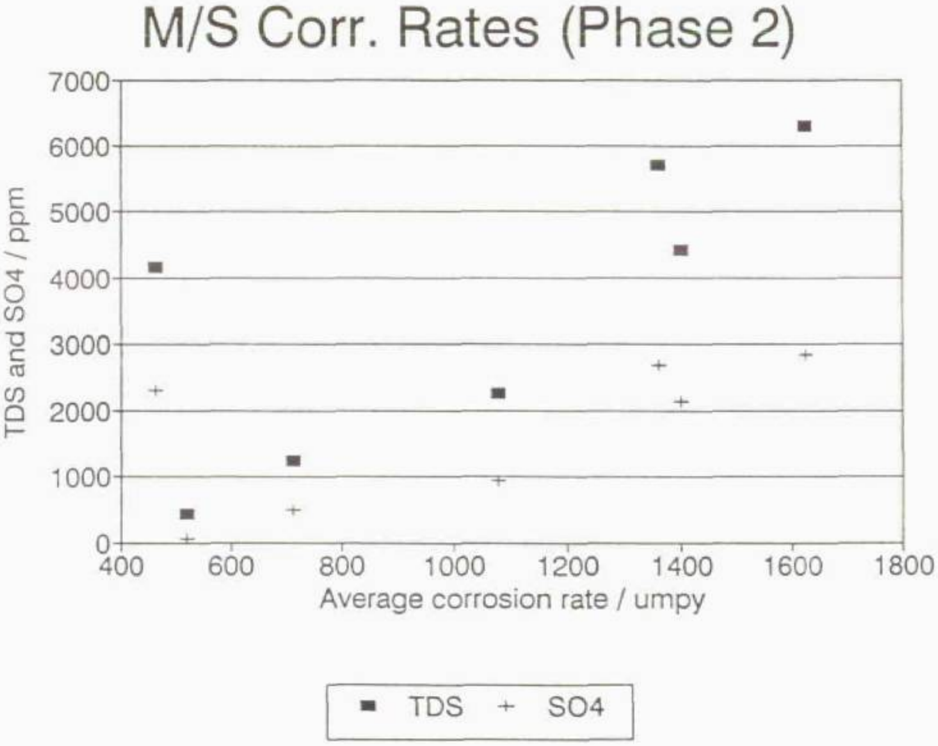

Figure 29: The effect of sulphates and total dissolved solids on corrosion rate of mild steel (Phase 2).

During Phase 2, Linear Polarization Resistance (LPR) probes were also used to continuously monitor the corrosion of mild steel in the various lines. This is an electrochemical technique which provides an instantaneous measurement of the polarization resistance, Rp. By assuming values for the anodic and cathodic Tafel constants for mild steel, it is possible to express the polarization resistance as a corrosion current density which in turn can be converted to a corrosion rate (expressed as metal loss) by using Faraday's law. As with all electrochemical techniques, corrosion rates obtained using LPR probes must not be seen as absolute corrosion rates but more emphasis should be placed on trends as conditions change. It should also be kept in mind that the polarization resistance technique generates an average corrosion rate and no distinction is made between localised processes (e.g. pitting, crevice corrosion, microbial influenced corrosion) and general corrosion.

The instrumentation used gives a direct read-out of corrosion rate in terms of %-full scale on a specific scale setting. The actual scale settings used were not available and the data is therefore presented as percentage change over a time period. Although it is therefore not possible to read off actual penetration rates (in μm/a), variations in corrosion rate with time can certainly be evaluated from the data.

Reliable LPR data was recorded between 23 October 1992 and 15 December 1992. Plots of corrosion rate (expressed as %-full scale) as a function of time measured during this period are shown in Figures 30 to 36. No LPR data was recorded during the period 5 November 1992 to 11 November 1992, giving rise to the discontinuity in the curves.

It is clear from Figures 30 to 36 that the corrosion rates remained fairly stable throughout the measurement time. Daily maxima and minima, related to the temperature fluctuations of the water, are evident.

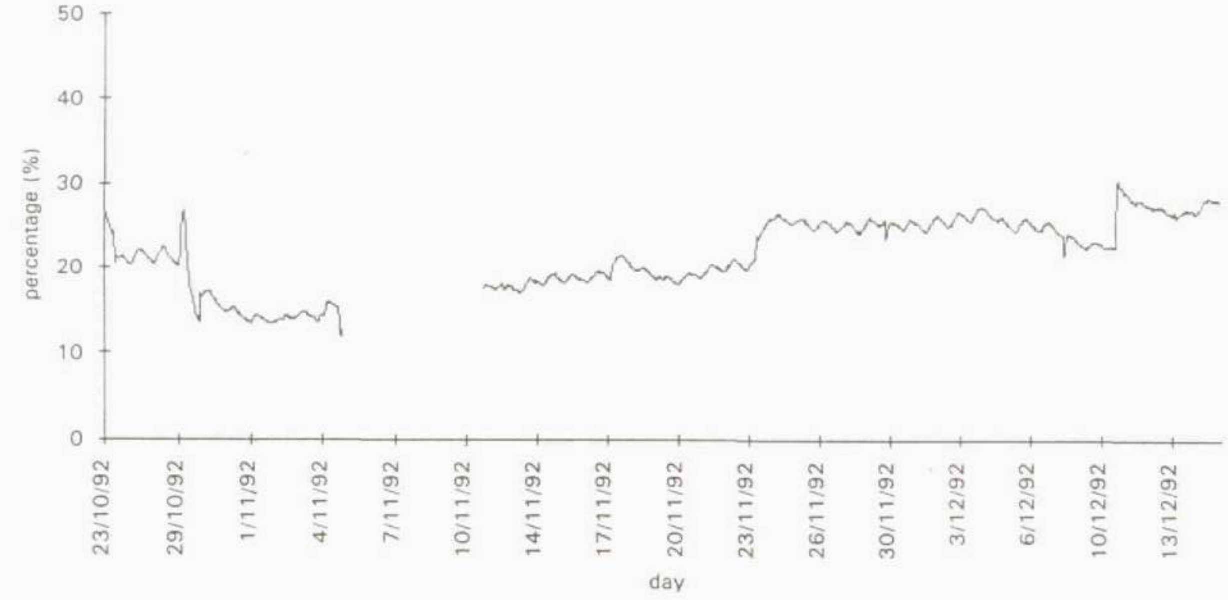

Figure 30: LPR data of raw mine water (Phase 2).

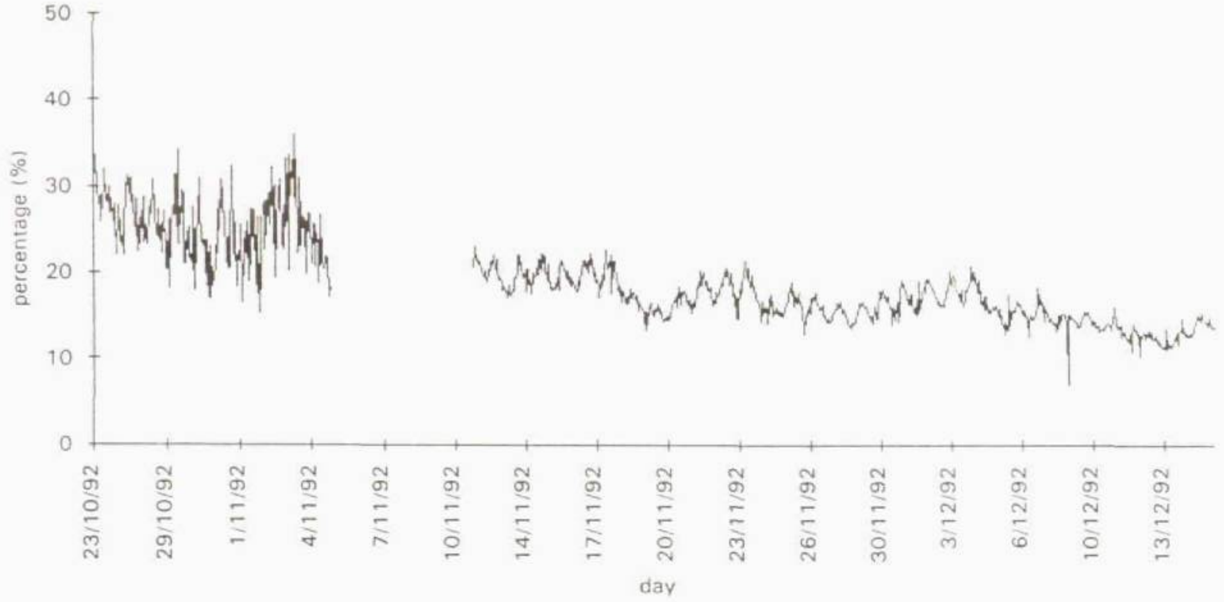

Figure 31: LPR data of neutralized water (Phase 2).

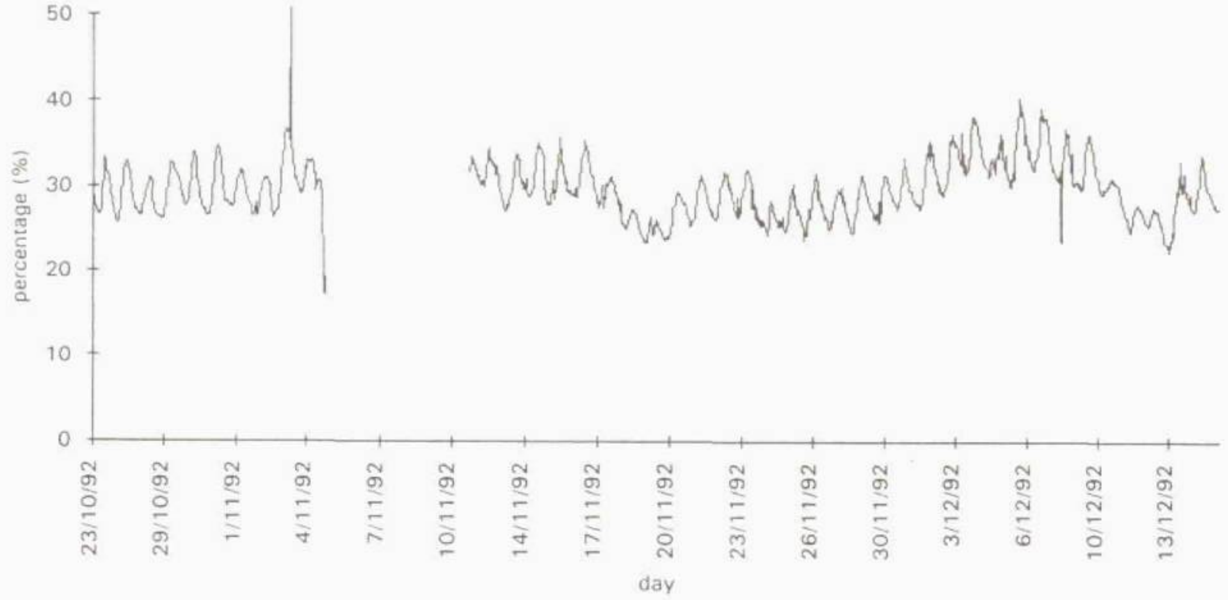

Figure 32: LPR data of settled water (Phase 2).

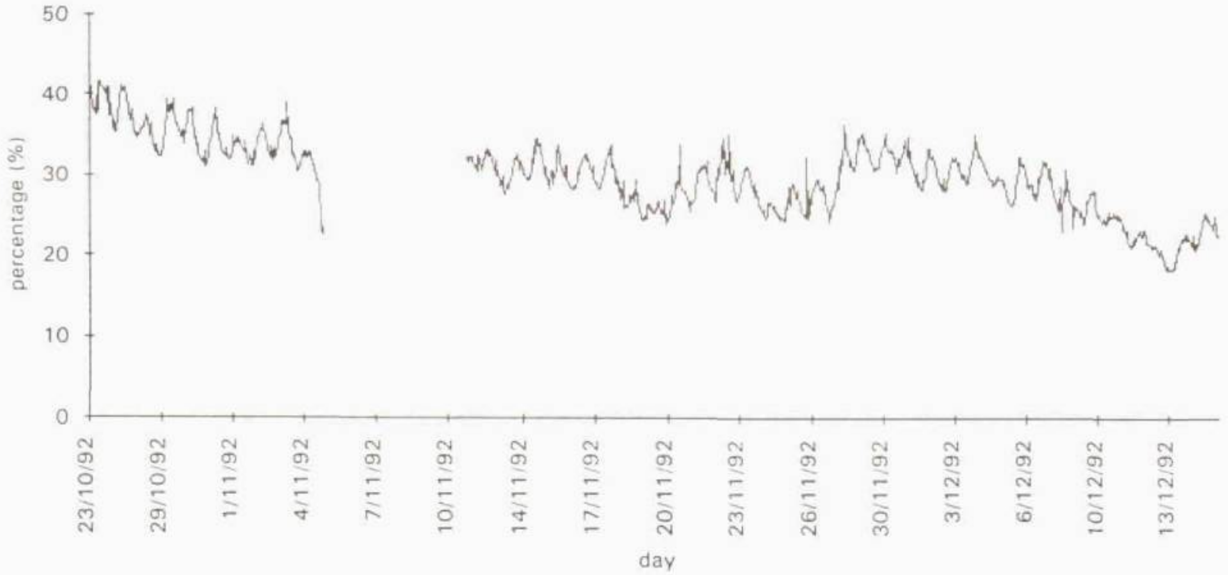

Figure 33: LPR data of disinfected water (Phase 2).

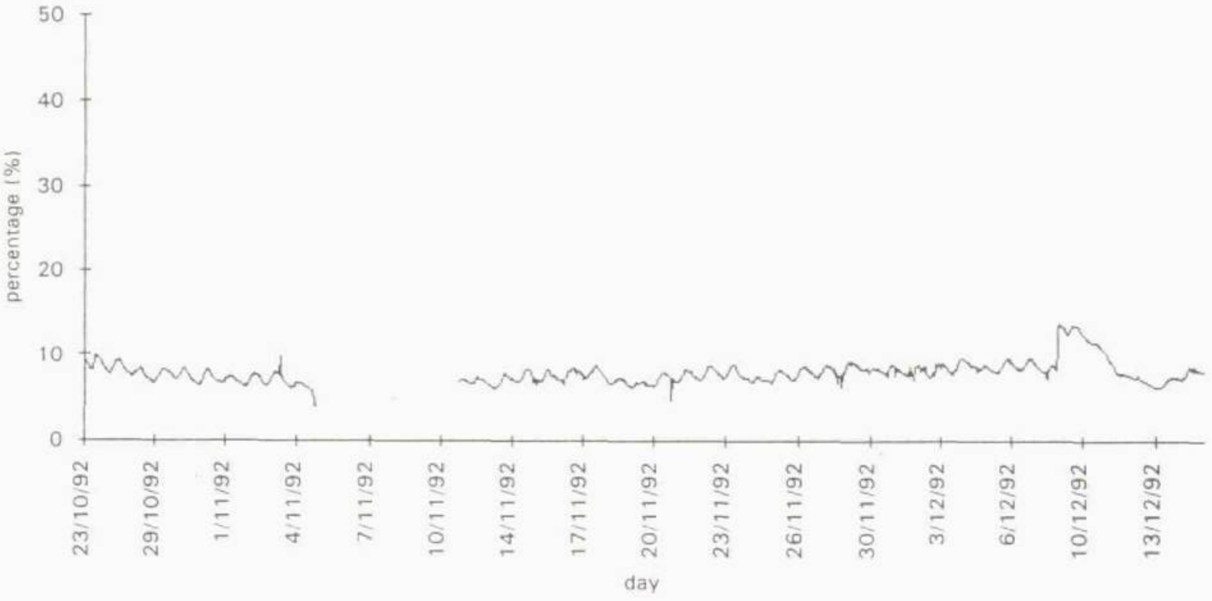

Figure 34: LPR data of Rand Water Board water (Phase 2).

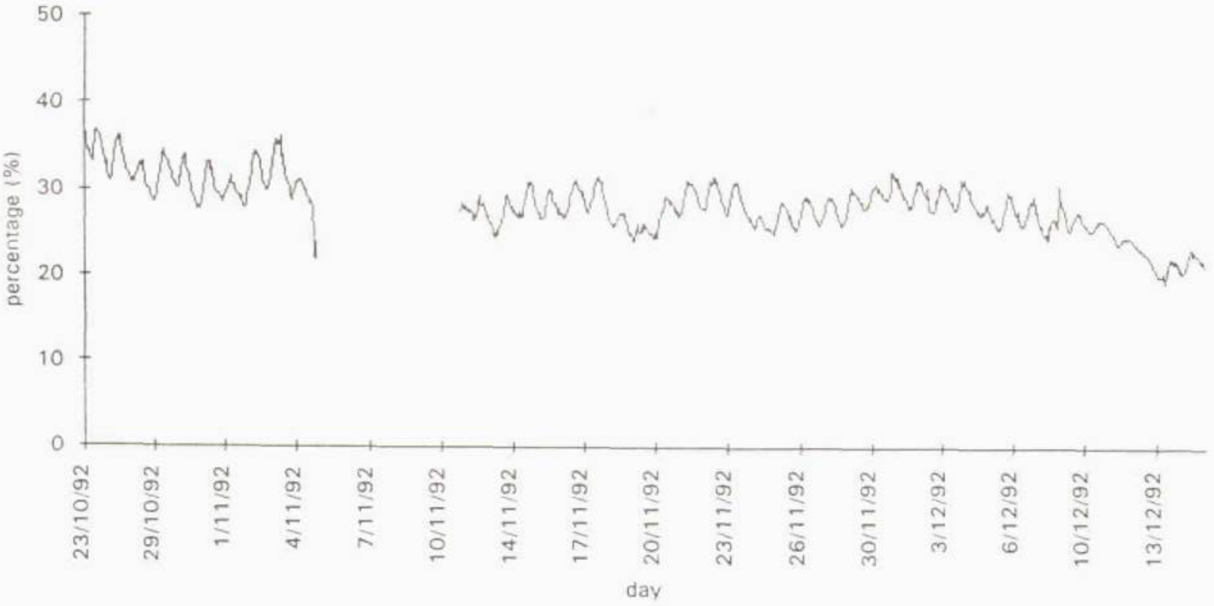

Figure 35: LPR data of first blend water (Phase 2).

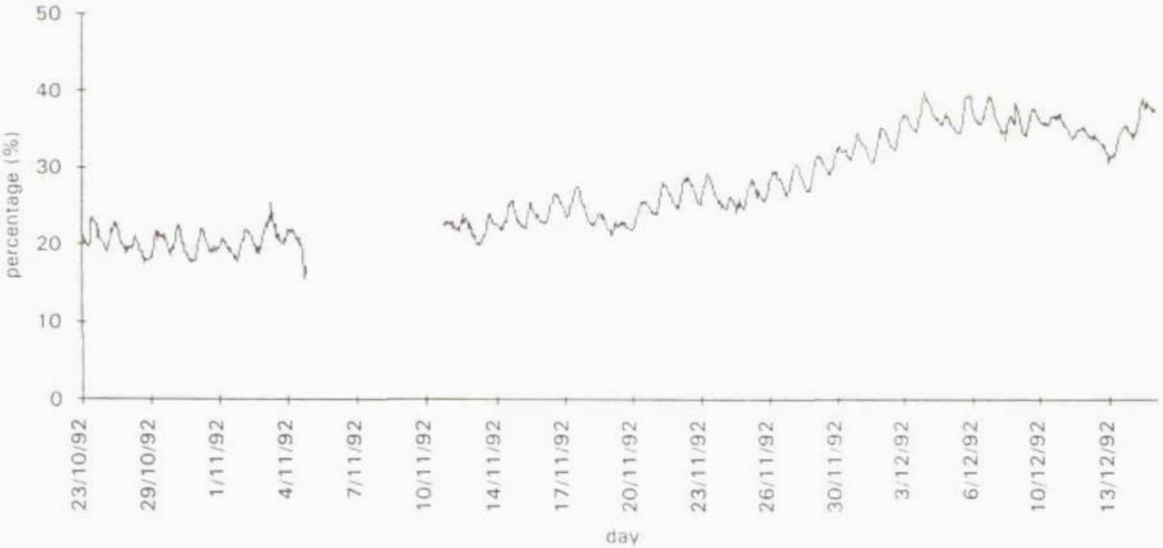

Figure 36: LPR data of second blend water (Phase 2).

For a constant water chemistry, one would expect the corrosion rates to show a gradual decrease with exposure time as corrosion products build-up and stabilize. However, as discussed in the previous section, the conductivity and turbidity of all the tanks increased with exposure time and the LPR data therefore reflects the combined effect of this changing water chemistry and exposure time. The nett result was that the corrosion rates in the settled storage, RWB and first blend lines stayed constant while a slight decrease in corrosion rate with time is evident for the disinfected storage and neutralized water lines. In the second blend and RMW lines, the corrosion rate increased with time.

Results of visual examination of the mild steel coupons in Table 9 indicate that the corrosion rates calculated from weight losses must be treated with caution. Most of the coupons exhibited localised forms of attack (crevice, pitting, edge and localised general corrosion) and in at least one case perforation of the 3 mm thick coupon actually occurred. If only the general corrosion rate in this particular water is considered (1,65 mm per year), a loss in wall thickness of 0,41 mm over the three month period would be predicted whereas severe pitting (with a local penetration rate of at least 12 mm per year) could have actually led to a failure.

4.3.2 Galvanized Steel Results

The results of weight loss determinations and visual inspection of the galvanized steel coupons from Phase 2 are presented in Tables 10 and 11. The corrosion rates for the 1, 2 and 3 month exposures are presented graphically in Figure 37. The waters have been arranged in order of decreasing TDS. The same trend in corrosion rate as was observed for mild steel (i.e. decreasing corrosion rate with increasing exposure time) is not

TABLE 10: Corrosion rates based on galvanised steel coupon mass losses -Phase 2

	R.M.W. Corrosion Rate (µm/a)	Neutralized Water Corrosion Rate (µm/a)	Settled Storage Corrosion Rate (µm/a)	Disinfected Storage Corrosion Rate (µm/a)	R.W.B. Water Corrosion Rate (µm/a)	First Blend Corrosion Rate (µm/a)	Second Blend Corrosion Rate (µm/a)
GS1	412,48	870,70	232,71	249,04	20,07	142,01	87,20
GS2	978,19	896,79	604,99	316,74	118,10	178,72	115,49
GS3	504,73	123,86	394,99	200,52	87,50	127,01	50,40

TABLE 11: The appearance of galvanised steel coupons - Phase 2

	R.M.W.	Neutralized Water	Settled Storage	Disinfected Storage	R.W.B. Water	First Blend	Second Blend
GS1	St; Gen	R/R(100%); Gen	St; R/R(5%); Gen	St; RR(5%); Gen	St; Gen	St; Gen	St; RR(25%); Gen
	St; Gen; R/R(50%)		St; Gen	St; Gen; RR(20%)	St; Gen	St; Gen; RR(10%)	St; Gen
GS2	St; Gen	Edge(2); C/C(1); Gen; Loc(0,45)	C/C(2); Edge(3); Pit(0,54); Loc(0,85) (Severe)	St; Gen	St; Gen	Gen	St; RR(5%); Gen
	St; Gen; Edge(1)	C/C(2); Edge(1); Gen; Loc (0,28)	C/C(2); Edge(2); Pit(0,40); Gen	St; Gen	St; Gen	Gen	St; Gen
GS3	Edge(1); St; Gen	RR(5%); Gen	Edge(2); C/C(1); Gen; Loc(0,37); Pit(0,32)	RR(10%); Gen	St; Gen	St; Gen	St; Gen
	RR(5%); Gen	RR(5%); Gen	Pit(0,65); C/C(1); Edge(1); Gen; RR(5%)	St; Gen	St; Gen	St; Gen	St; Gen

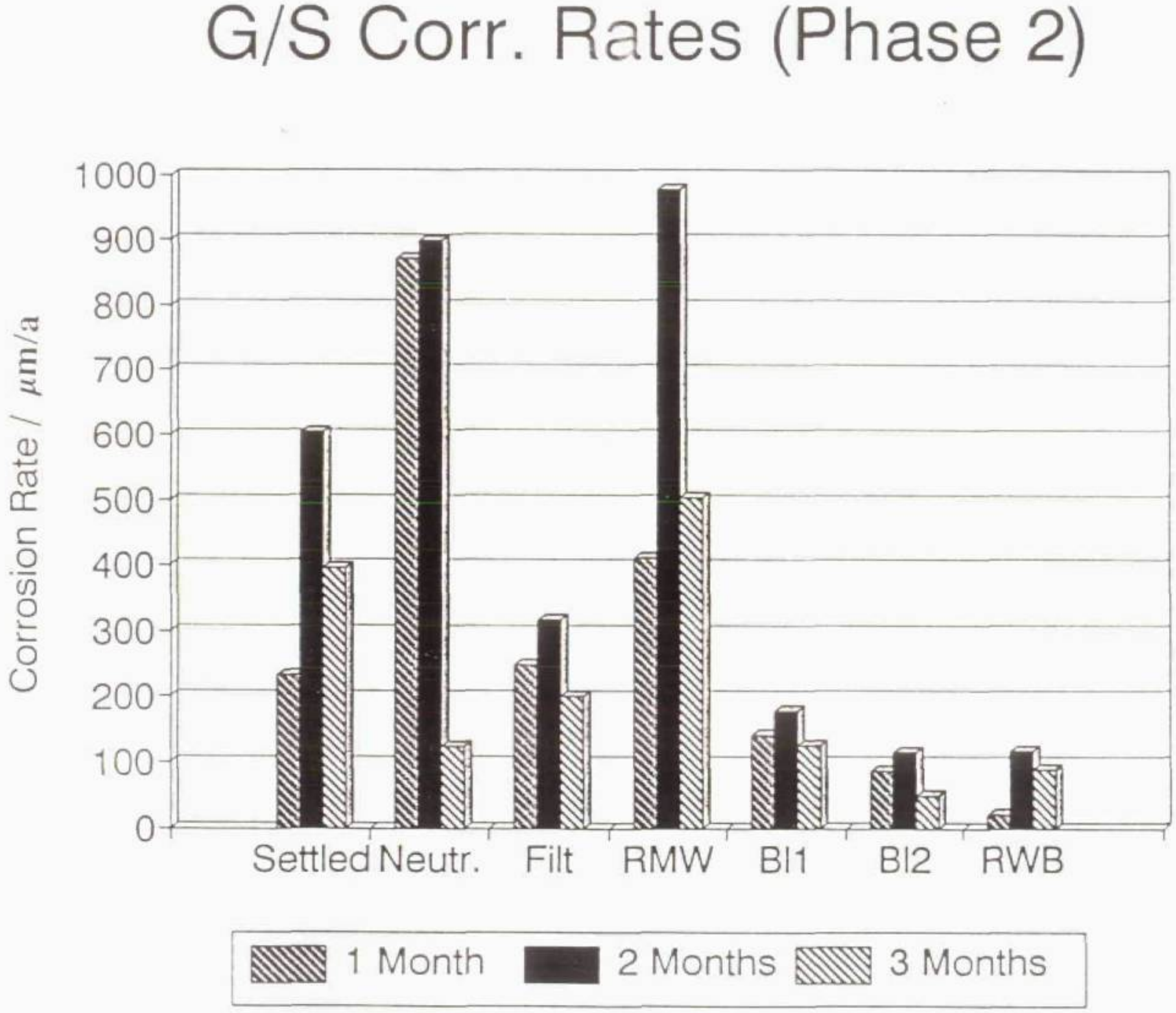

Figure 37: Galvanized steel corrosion rates after 1, 2 and 3 months (Phase 2).

exhibited in any of the waters. It is also apparent that the raw mine water is one of the most corrosive waters for galvanized steel while it was the least corrosive to mild steel.

Figures 38 and 39 are plots of TDS, sulphate, chloride and nitrate content versus corrosion rate (average values for all the galvanized coupons used). A trend of increasing corrosion rate with an increase in total dissolved solids or anion concentration is evident for five of the waters while the neutralized and the raw mine water do not follow this trend. The raw mine water in particular has a very high corrosion rate for a TDS of 4100 ppm. The data in Table 7 indicates that the pH of the raw mine water was 5,3 while all the other waters were closer to pH=7. This factor probably accounts for the increased corrosiveness of raw mine water towards galvanized steel.

4.3.3 Copper and Copper-Nickel Results

The corrosion rates and visual inspection results of the Cu and Cu-Ni coupons are presented in Tables 12 and 13. The 1, 2 and 3 month corrosion rate data is presented graphically in Figures 40 and 41. No obvious trend of corrosion rate with time is evident. Figures 42 and 43 are plots of the TDS and sulphate contents versus corrosion rate (average corrosion rates) for the Cu and Cu-Ni coupons. The data has a large degree of scatter in both these plots. No correlation between corrosion rates on Cu and Cu-Ni and any of the other water parameters could be found.

An interesting feature of the copper and cupro-nickel corrosion data is the corrosivity of the RWB water. Visual inspection of the coupons confirmed it (Table 13) because severe localized corrosion occurred in this water.

4.3.4 Stainless Steel Results

Evaluation of the 316 coupons indicated that no corrosion occurred on this material over the 3 month period in any of the waters tested.

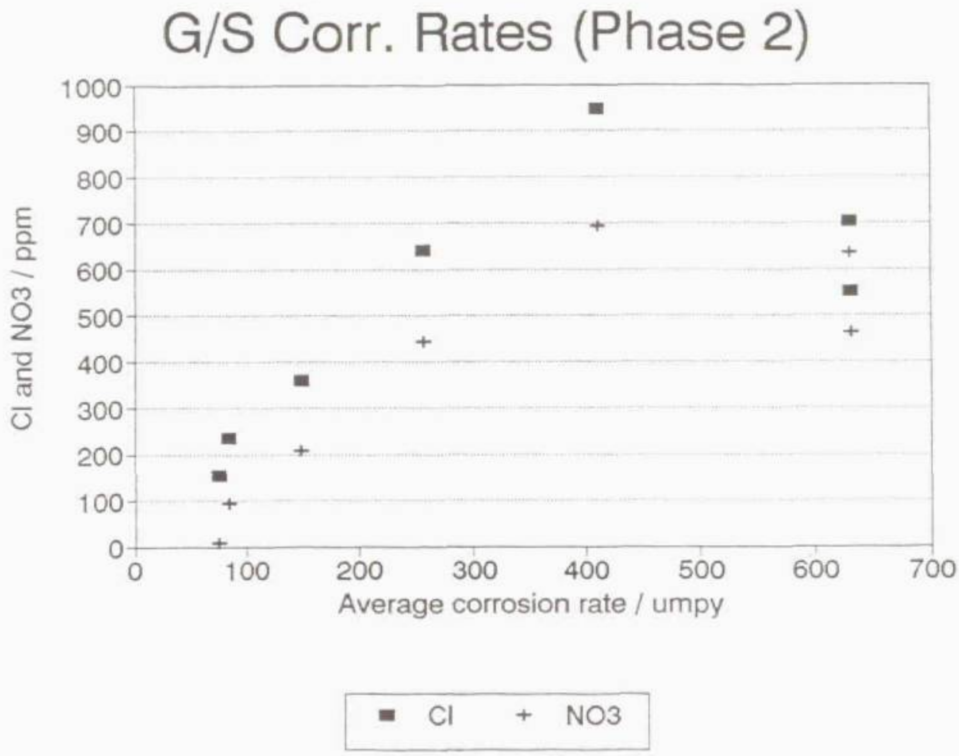

Figure 38: The effect of chloride and nitrate content on the corrosion rate of galvanized steel (Phase 2).

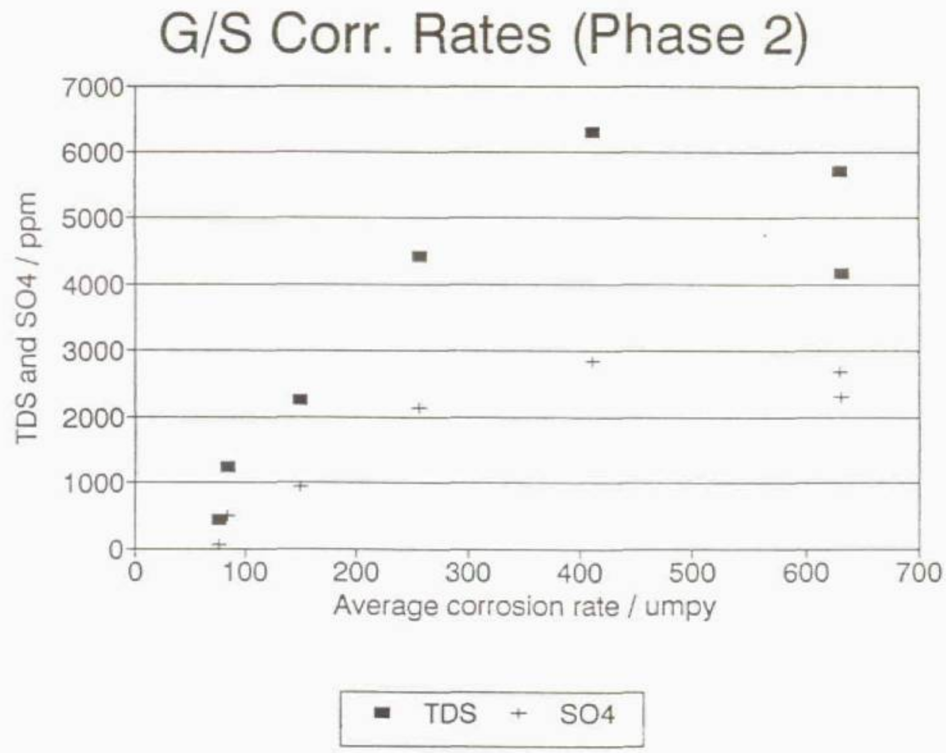

Figure 39: The effect of sulphates and total dissolved solids on the corrosion rate of galvanized steel (Phase 2).

TABLE 12: Corrosion rates based on Cu and Cu-Ni steel coupon mass losses - Phase 2

	R.M.W. Corrosion Rate (μm/a)	Neutralized Water Corrosion Rate (μm/a)	Settled Storage Corrosion Rate (μm/a)	Disinfected Storage Corrosion Rate (μm/a)	R.W.B. Water Corrosion Rate (μm/a)	First Blend Corrosion Rate (μm/a)	Second Blend Corrosion Rate (μm/a)
CU1	61,65	100,00	35,85	112,64	43,97	67,41	18,98
CU2	109,62	162,83	58,90	12,49	282,67	30,48	72,80
CU3	49,01	67,15	102,44	9,18	160,29	10,31	43,95
CUNI1	129,80	90,10	46,05	47,82	77,97	49,80	40,84
CUNI2	208,19	59,13	9,32	12,50	66,21	40,53	54,71
CUNI3	100,94	26,41	27,78	12,81	68,02	30,46	35,78

TABLE 13: The appearance of Cu and Cu-Ni steel coupons - Phase 2

	R.M.W.	Neutralized Water	Settled Storage	Disinfected Storage	R.W.B. Water	First Blend	Second Blend
CU1	St	St	St	St	St; Gen	St	St
CU2	St	St	St; Edge(1)	St	St; Pit(0,35); Loc(0,08); Edge (1)	St; Edge(1); C/C(1)	St; Gen
	St	St; Edge(1)	St	St	St; Loc(0,32); Pit(0,06); Edge(1)	St; C/C(2); Pit(0,01)	St; Gen
CU3	St	St; Gen	St	St	Edge(1); Loc(0,15); St	St; C/C(1)	St; Gen
	St	St	St	St; Edge(1)	St; Loc(0,36); Pit(0,43); Edge(1)	St	St
CUNI1	St	St	St	St; Pit(0,43)	St; Pit(0,12)	St	St
	St; Pit(0,19)	St	St	St	St; Pit(0,17)	St	St; Edge(1)
CUNI2	St; C/C(1); Gen	St; Gen	St; Edge(1); Pit(0,16)	St; C/C(1)	St; Edge(2); Pit(0,49); Loc(0,05)	St; Gen; Edge(1); Loc(0,05)	St; Gen; C/C(1); Edge(1); Loc(0,10)
	St; C/C(1); Gen	St; Gen	St; C/C(1); Gen	St; Gen; Pit(0,33); Edge(1)	St; Edge(2); Pit(0,18); Loc(0,30); C/C(1)	St; Gen	St; Edge(2); Gen
CUNI3	St; C/C(1)	St; Gen	C/C(1); St; Edge(1)	St; C/C(1)	St; Edge(1); C/C(3); Loc(0,44)	St; Gen	St; C/C(1); Gen
	C/C(1); St	St; Loc(0,17)	C/C(1); Edge(1); St; Loc(0,10)	St; Gen; Loc(0,01)	St; Edge(1); C/C(3); Loc(0,13)	St; Gen	St; Gen; Loc(0,06)

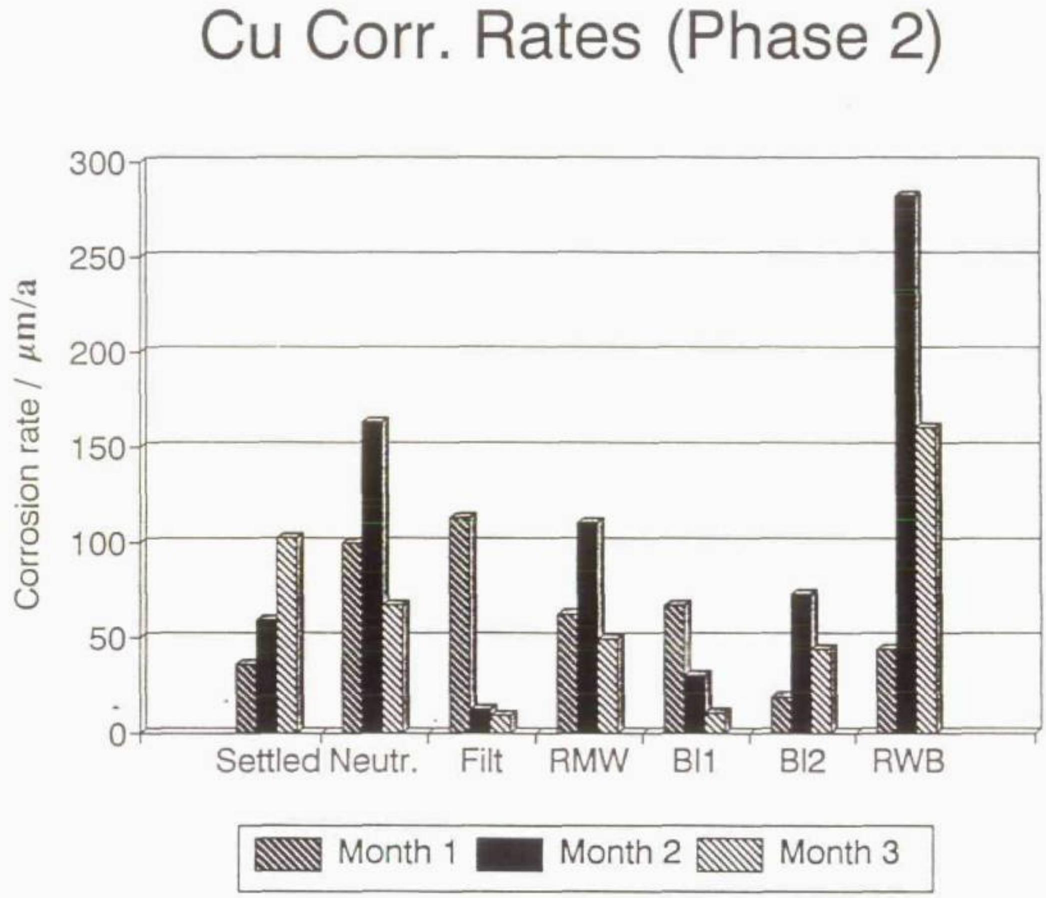

Figure 40: Cu corrosion rates after 1, 2 and 3 months (Phase 2).

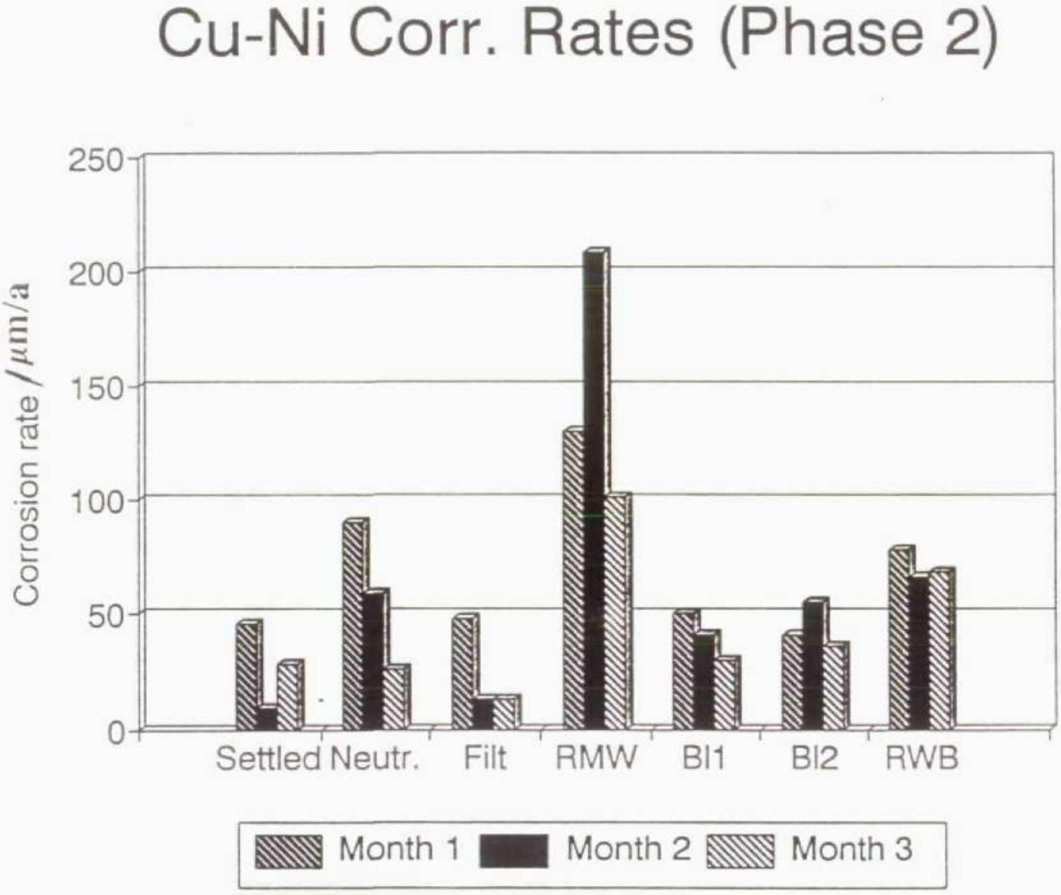

Figure 41: Copper-nickel corrosion rates after 1, 2 and 3 months (Phase 2).

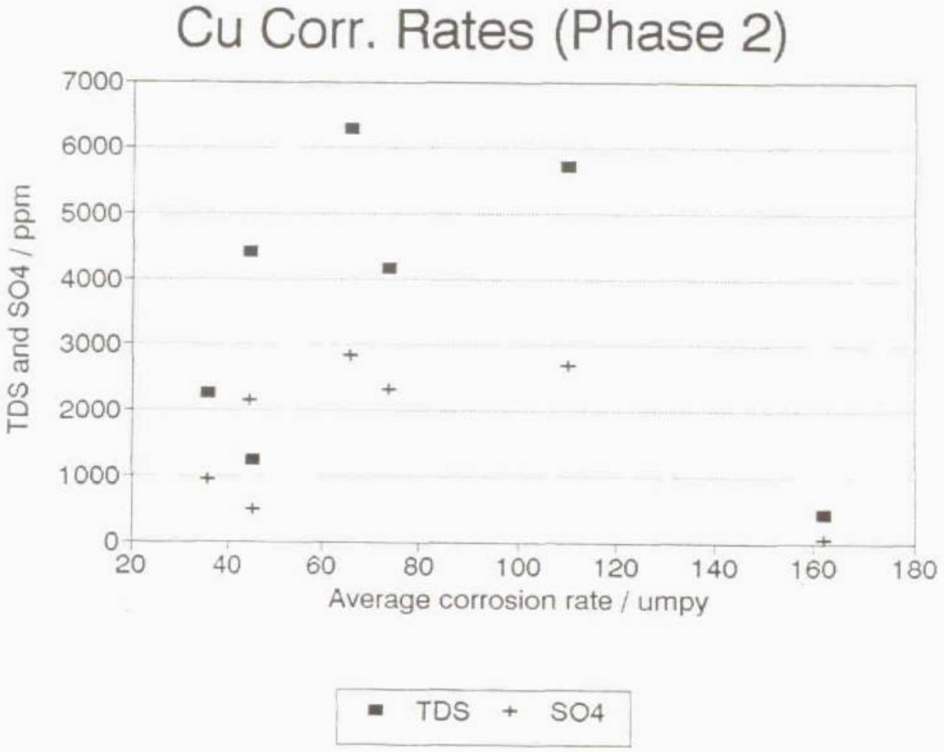

Figure 42: The effect of sulphates and total dissolved solids on the corrosion rate of copper (Phase 2).

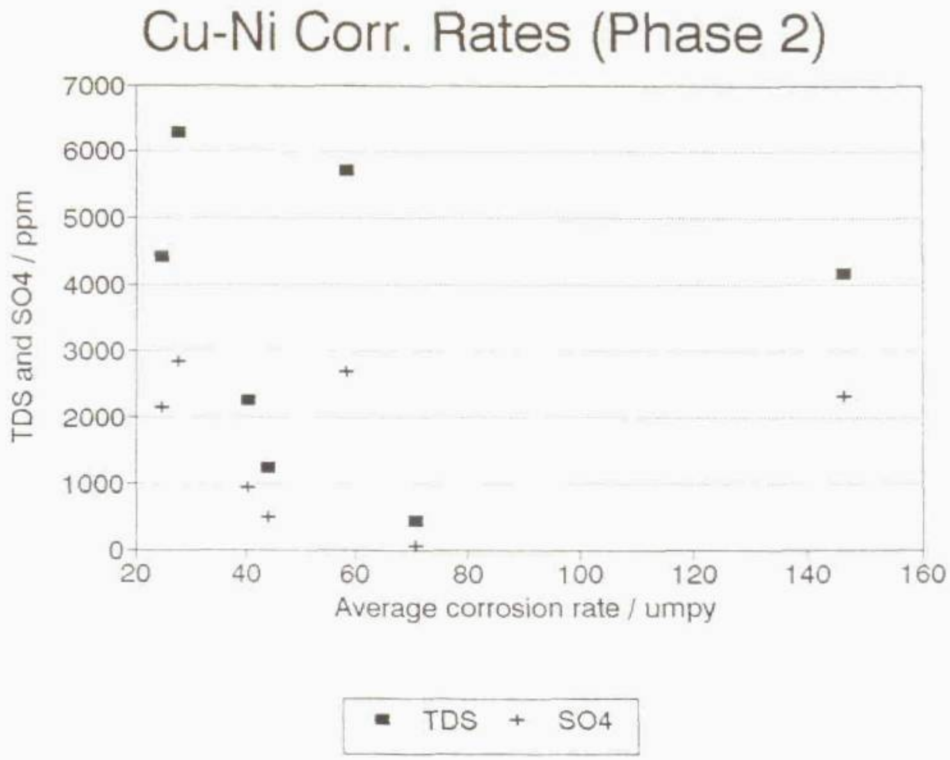

Figure 43: The effect of sulphates and total dissolved solids on the corrosion rate of copper-nickel (Phase 2).

Corrosion rates and the visual appearance of 3CR12 coupons are summarized in Tables 14 and 15. The corrosion rates are presented graphically in Figure 44. The high TDS waters (settled, neutralized, disinfected and RMW) have very low corrosion rates (less than 10 μm/a). This is confirmed by the visual inspection results which indicate that the coupons removed from these waters exhibited very little signs of corrosion. In the RWB, 1st and 2nd blend waters a significant amount of localized attack was evident and this is also reflected by the weight loss data.

TABLE 14: Corrosion rates based on 3CR12 steel coupon mass losses - Phase 2

	R.M.W. Corrosion Rate (μm/a)	Neutralized Water Corrosion Rate (μm/a)	Settled Storage Corrosion Rate (μm/a)	Disinfected Storage Corrosion Rate (μm/a)	R.W.B. Water Corrosion Rate (μm/a)	First Blend Corrosion Rate (μm/a)	Second Blend Corrosion Rate (μm/a)
3CR12 1	1,37	5,46	5,52	8,45	5,93	9,01	7,79
3CR12 2	0,17	0,44	7,41	0,79	61,05	13,39	13,34
3CR12 3	1,02	0,54	1,17	0,80	52,45	19,06	34,13

TABLE 15: The appearance of 3CR12 steel coupons - Phase 2

	R.M.W.	**Neutralized Water**	**Settled Storage**	**Disinfected Storage**	**R.W.B. Water**	**First Blend**	**Second Blend**
3CR12 1	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected
	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected
3CR12 2	St	St	St; Edge(1)	St	Edge(3); St; Pit(0,93)	St; Pit(0,65)	St; Pit(1,42)
	St	St	St	St	Edge(3); St	St; Pit(0,78)	St; Edge(1)
3CR12 3	St	St; Edge(1)	St	St; Edge(1)	St; Edge(3); C/C(1)	St; Edge(2); Pit(0,72); C/C(1)	St; Edge(3)
	St	St	St; Edge(1)	St; Edge(1)	St; Edge(3); Pit(0,56); C/C(2)	St; Edge(1); C/C(1)	St; Edge(2); C/C(2)

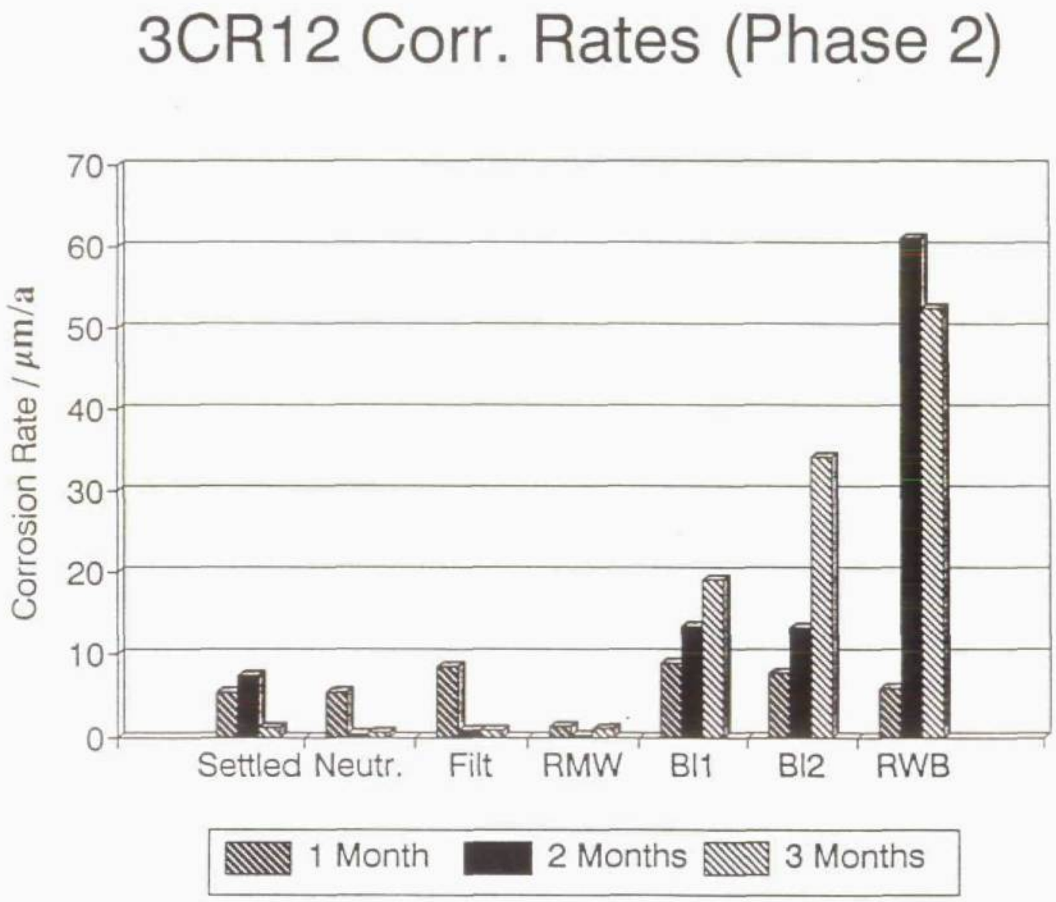

Figure 44: 3CR12 corrosion rates after 1, 2 and 3 months (Phase 2).

5. RESULTS - STATIC IMMERSION TESTS

During ongoing research into the corrosivity of mine waters at COMRO, static immersion tests on various materials were conducted in mine service water collected from several mines. These results have not been published previously and therefore relevant results from these studies will be included in this report.

The corrosion resistance of various materials were evaluated in eleven different mine service waters and also in Rand Water Board water. Triplicate specimens of each material were immersed in beakers containing the various waters and weight losses were recorded over a period of 4 weeks. Corrosion rates were determined by measuring weight losses. Data collected on mild steel and zinc coupons is most relevant to this study and will be reported here.

The pH, TDS, sulphate and chloride contents of the waters tested are presented in Table 16. A significant variation in the composition of these waters is evident (e.g. TDS varies from 412 ppm to 10870 ppm). Possible correlations between corrosion rates of the materials and various water quality parameters (pH, TDS, anion concentration, Langelier index and corrosivity index) were investigated.

Figures 45 and 46 are plots of mild steel corrosion rate vs pH and TDS respectively. Although a general trend of increasing corrosion rate with decreasing pH and increasing total dissolved solids is evident, a large degree of scatter exists. Figures 47 and 48 are plots of chloride and sulphate content vs corrosion rate. These graphs indicate that chloride has the strongest effect on the corrosion rate of mild steel.

The Langelier index and the corrosivity index of the waters tested also did not yield a correlation with corrosion rate. Figure 49 is a plot of corrosion rate vs Langelier Index.

TABLE 16: Chemical composition of waters used for static immersion tests (ppm)

WATER USED	pH	TDS	SULPHATE	CHLORIDE
Rand Water Board	7,5	412	134	44
West Rand Cons.	6,9	2824	1586	36
Randfontein	6,5	2184	829	39
Western Areas	7,6	1820	677	103
Doornfontein	6,5	1130	425	172
Vaal Reefs	6,3	4180	901	1220
Saaiplaas	5,8	3835	106	1880
FS Geduld No. 1 Shaft	6	3502	711	1037
FS Geduld No. 9 Shaft	6,5	3038	265	1203
St Helena	6,3	4975	821	1812
Unisel	5,8	10870	2008	2766
Western Holdings	6,5	6756	2176	1564

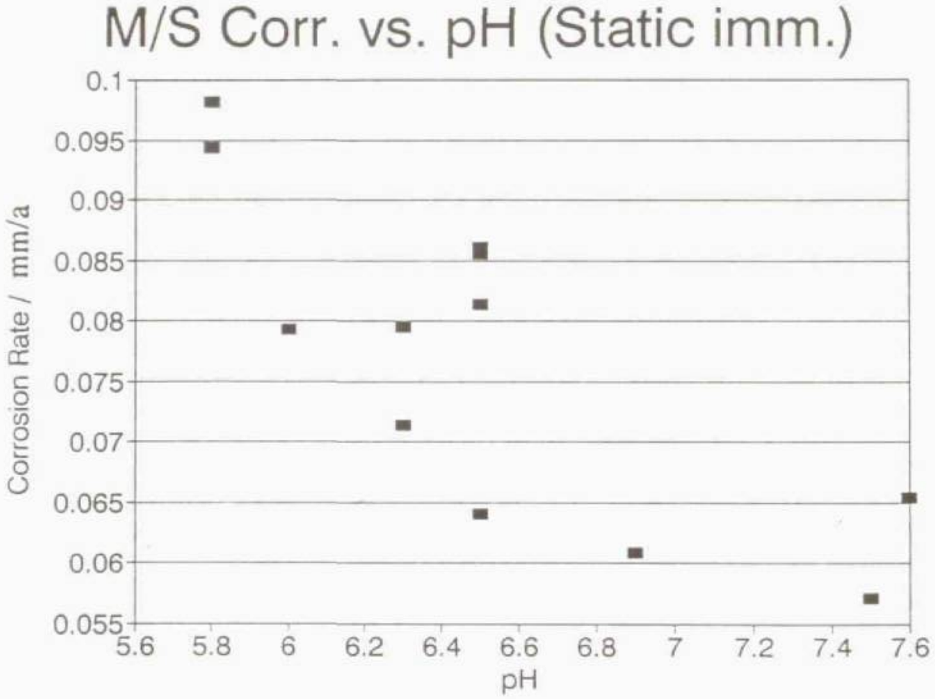

Figure 45: Mild steel corrosion rate as a function of pH (static immersion tests).

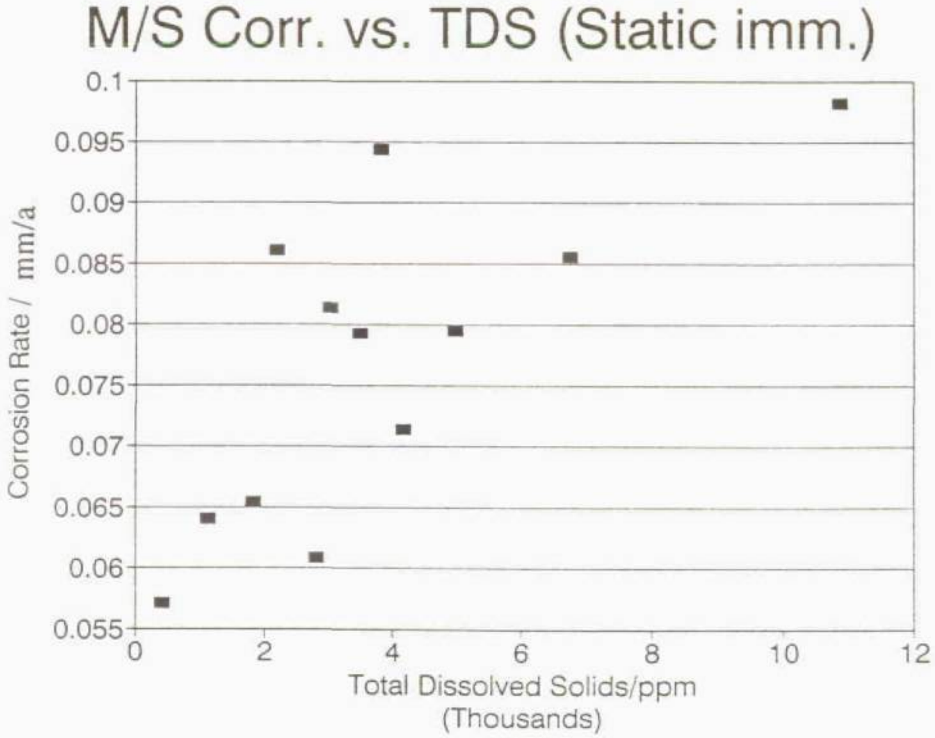

Figure 46: Mild steel corrosion rate as a function of TDS (static immersion tests).

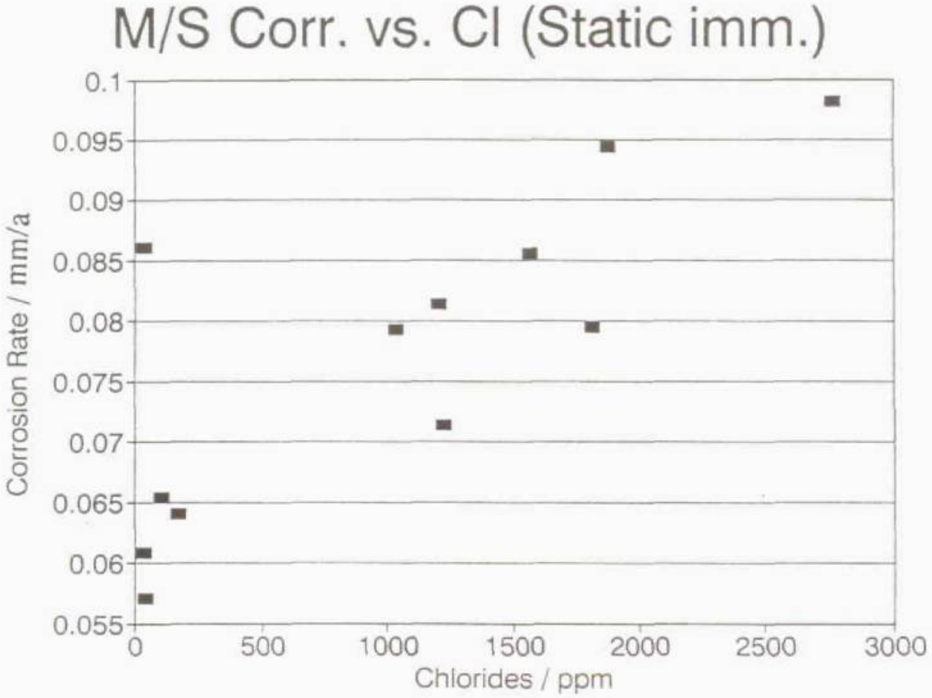

Figure 47: Mild steel corrosion rate as a function of chlorides (static immersion tests).

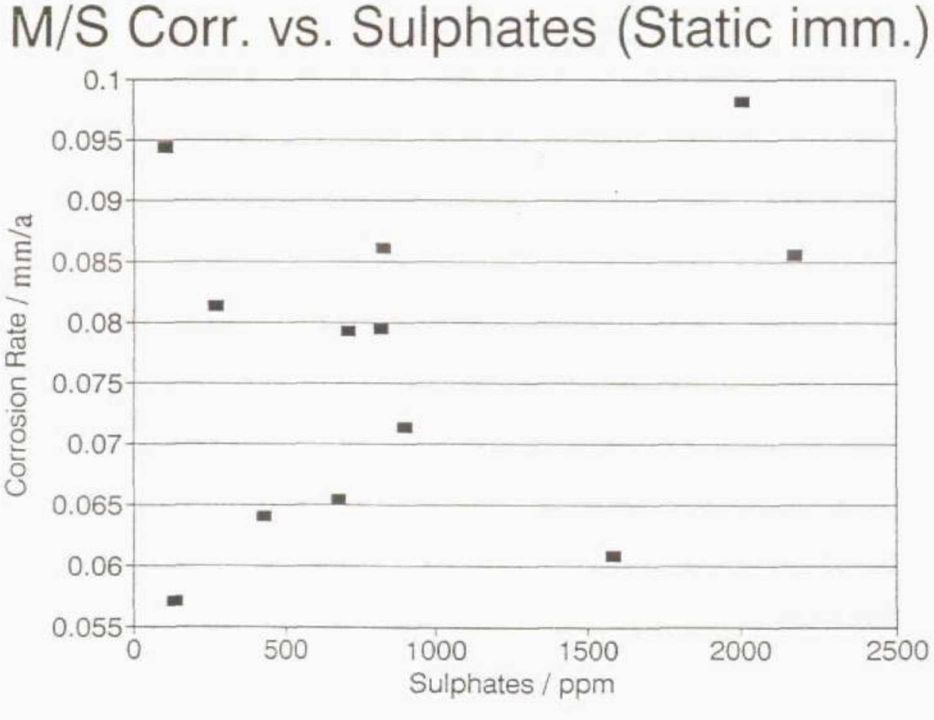

Figure 48: Mild steel corrosion rate as a function of sulphates (static immersion tests).

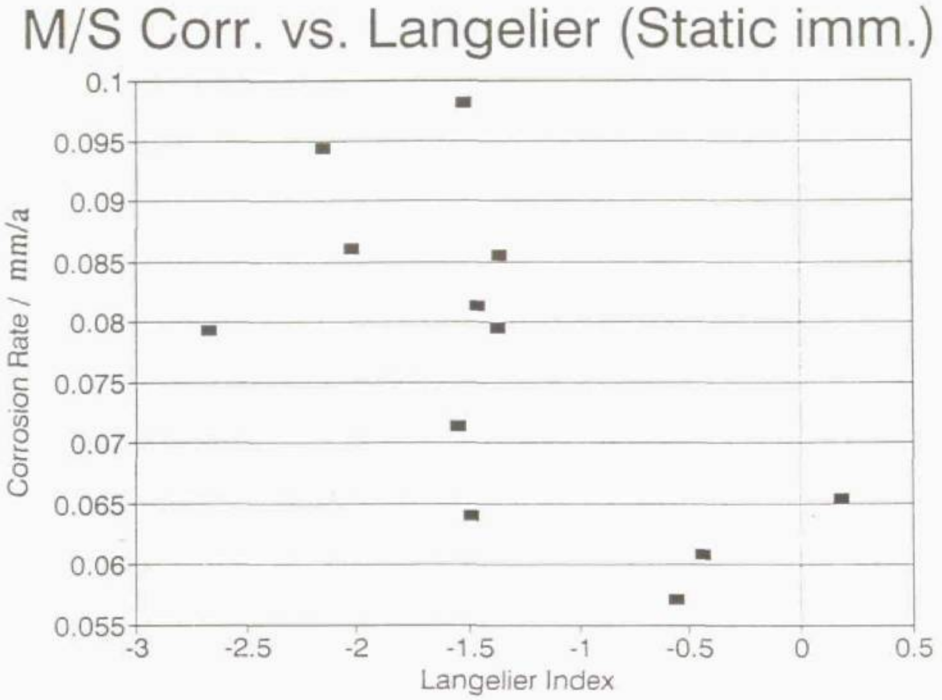

Figure 49: Mild steel corrosion rate vs Langelier index (static immersion tests).

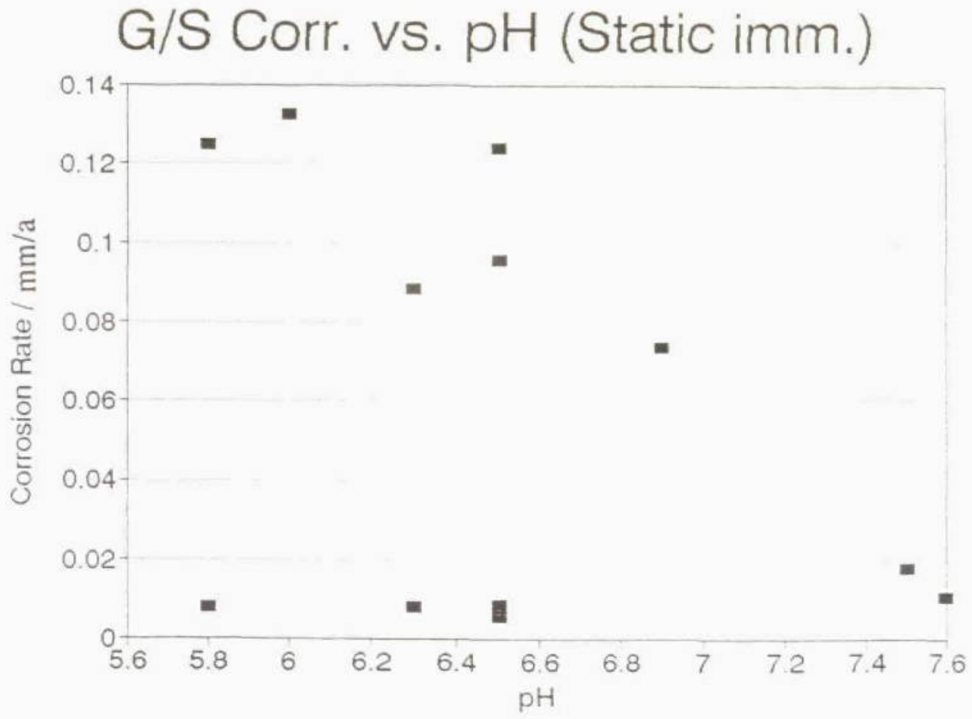

Figure 50: Galvanized steel corrosion rate vs pH (static immersion tests).

The best correlation for galvanized steel was corrosion rate vs pH (Figure 50). However, some of the waters did not follow this trend at all and the lowest corrosion rates were observed in the lower pH waters.

6. DISCUSSION

The primary aim of this project was to assess the influence of individual water treatment process on the corrosion of various metals. From this data the most cost effective solution to minimize corrosion in mine waters of varying quality (i.e. water treatment or material selection) would then be proposed. Severe technical problems were experienced during the course of this project. In particular, the water reclamation plant failed to operate as designed leading to changing water quality parameters for individual processes (e.g. pH) during Phase 1. During Phase 2, the water plant was not used to continuously treat the water and it was recirculated. Build-up of corrosion products and a general trend of increasing TDS with time (due to evaporation losses) occurred during Phase 2. It was therefore not sensible to interpret the corrosion data by comparing the corrosion rates of the various materials as each unit process changed the water chemistry. Doing this would have led to erroneous conclusions regarding the effect of water treatment on corrosion.

The effect that each water treatment process should have on water quality and the effect this may have on corrosion is summarized in Table 17. From this table it can be seen that pH control, disinfection and desalination and blending potentially have the greatest influence on corrosion. No sulphate reducing bacteria were detected during the microbial investigation for any of the monitoring lines throughout this study. In terms of parameters varied during the study, only pH and dissolved solids is therefore expected to affect corrosion rates.

TABLE 17: The effect of water treatment on quality and corrosion

	EFFECT ON WATER QUALITY	EFFECT ON CORROSION
Neutralization	Control pH	Minimize corrosion at neutral pH
Settling	Decrease suspended solids	Decrease fouling which may minimize under deposit /microbial corrosion
Filtering	Decrease suspended solids further	Decrease fouling which may minimize under deposit /microbial corrosion
Disinfection	Eliminate or decrease microbial activity	Minimize microbial induced corrosion
Desalination and Blending	Decrease level of total dissolved solids	Generally lower corrosion rates

TABLE 18: Critical chloride levels (evaluated from a nomogram[9]) and actual chloride levels for Phase 2

WATER	$[\mathrm{Cl}^-]_{crit}$	$[\mathrm{Cl}^-]_{actual}$
RMW	950	552
Neutralized	1300	706
Settled Storage	1400	948
Filt. and Disinf.	950	641
RWB	100	154
1st Blend	420	358
2nd Blend	250	236

6.1 The Effect of Neutralization

The effect of pH on the corrosion of mild steel is well documented in the literature[1,2]. Below pH = 4, reduction of hydrogen ions is the prevalent cathodic reaction and a decrease in pH below this level leads to increasing corrosion rates. Above pH = 4, oxygen reduction becomes the dominant cathodic reaction and between pH = 4 and 9,5 the corrosion rate of mild steel remains fairly constant. A further increase in pH to 12 leads to corrosion rates decreasing further and at pH values greater than 12 the corrosion rate starts to increase again.

The influence of varying pH on the corrosion of mild steel in synthetic mine water has been quantified[3] (Figure 51). The small influence of pH variations between the range of 4 to 9 on corrosion rate, both in aerated and de-aerated mine water, is clearly evident.

During Phase 1, the pH of the raw mine water varied considerably but neutralization was not effective and the influence of pH control on corrosion rate for this particular study could therefore not be evaluated. (In fact, the "neutralized" water had a higher corrosion rate than the raw mine water). During Phase 2, the average pH values of the various waters varied between 5,3 and 7,3 and no effect of this pH variation on corrosion rate could be observed.

Despite the lack of data on the effect of pH on corrosion rate from this study, sufficient data exists in the literature to determine the requirements for pH control in mine waters. The control of pH also has a large influence on scale formation and the Langelier Index is used to predict the tendency of a water to precipitate or dissolve calcium carbonate. This index is often used to predict the corrosivity of waters and waters tending to precipitate calcium carbonate (positive index) is generally considered less corrosive. During this study, no correlation between corrosion rate of mild steel and Langelier Index could be found. This is in agreement with other studies where no correlation could be found in mine waters[4] or in potable waters[5].

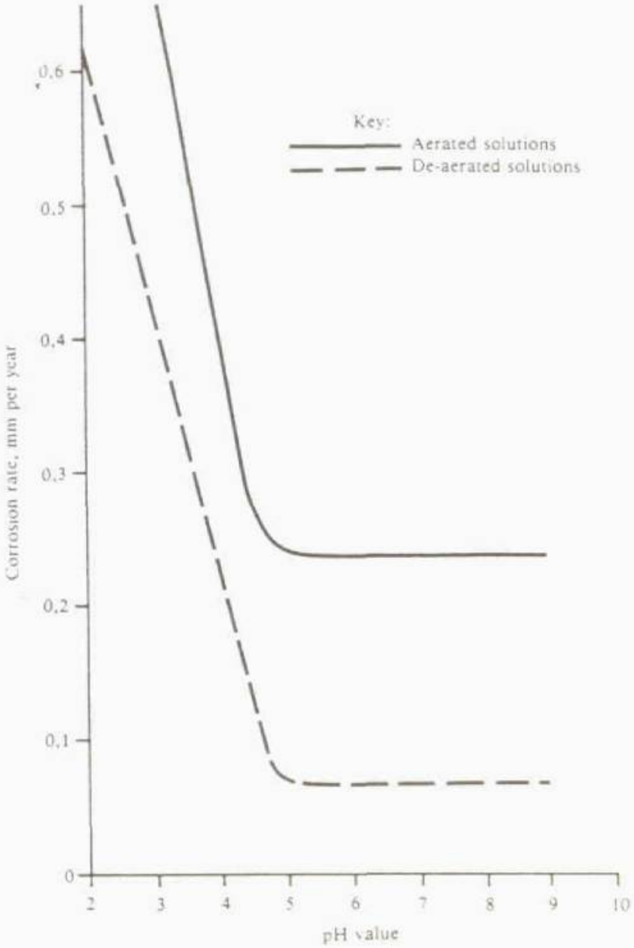

Figure 51: Corrosion rate versus pH for mild steel in mine water.

Galvanised steel relies on the formation of a protective hydrate film on its surface. In the pH range 6 to 12,5 a stable film is formed and low corrosion rates are obtained. At pH values less than 6 the corrosion rate of the zinc coating increases dramatically[8]. This effect was observed in Phase 2 where the highest corrosion rate of galvanized steel was observed in raw mine water (pH = 5,3) even though mild steel had the lowest corrosion rate in this water. All the other waters in Phase 2 had average pH values above 6. The results of static immersion tests also showed a general tendency of decreasing corrosion rates with increasing pH (Figure 51). However, some waters did not follow this trend and one water with a pH of 5,8 exhibited a very low corrosion rate while another of the same pH value had the second highest corrosion rate. Although this phenomenon could not be explained, it does indicate that factors other than pH can have a significant influence on the corrosion of galvanized steel.

No correlation between pH and the corrosion of copper or cupro-nickel could be found. Previous investigations[7,8] found that the corrosion rate of cupro-nickel in mine water increases significantly when the pH decreases below a value of 6.

Stainless steels will be in a passive state in most mine waters and active corrosion will only occur on the less alloyed 3CR12 at very low pH values. As expected, the stainless steels in this investigation were not affected by the pH variations observed.

6.2 The Effect of Dissolved Solids

It is generally accepted that increasing anion concentration increases the corrosion rate of mild steel in waters. Bockris[7] classified various anions in order of acceleration of dissolution:

$$NO_3^- < CH_3COO^- < Cl^- < SO_4^{2-} < IO_4^-$$

Higginson[3] found that increasing chloride, sulphate or nitrate levels of a synthetic mine water had no effect on the corrosion rate of mild steel. In fact, increasing the chloride level of pH = 6,5 mine water to 3 g/ℓ caused a slight decrease in corrosion rate. This decrease was ascribed to a small decrease in the amount of dissolved oxygen at high concentrations of total dissolved solids.

Even though a fair amount of scatter was evident, the results in this report indicate that the corrosion rate of mild steel increases as the total dissolved solids increase (Figures 14, 29 and 47). A notable exception was the raw mine water in Phases 1 and 2 which exhibited the lowest corrosion rate of all the waters tested. Although this phenomenon could not be explained with the available data, it certainly emphasizes the danger of predicting corrosion rates using such simplified indices.

The sulphate, chloride and nitrate levels of the various waters showed a strong correlation with the total dissolved solid levels. It was therefore impossible to separate the effect of each individual anion on corrosion. It has been reported that the corrosion rate of zinc also increases with increasing anion concentration[8]. This was confirmed by the results from Phases 1 and 2 (Figures 15 and 40).

No satisfactory correlation between water quality parameters and corrosion rate could be found for copper or cupro-nickel. Generally these alloys have a good corrosion resistance to water of varying quality i.e. from potable water to sea water. In Phase 1, the average corrosion rates of copper and copper-nickel were mostly less than 20 μm/a while corrosion rates greater than 50 μm/a were often measured in Phase 2. In practice, these alloys will often fail by localized corrosion rather than by general corrosion. The results of visual inspection of the coupons (Table 13) confirm that the most prevalent corrosion damage on these coupons was localized processes. Corrosion rates expressed in terms of μm/a must therefore be treated with extreme caution for these alloys.

In Phase 1, negligible corrosion occurred on the stainless steels (316 and 3CR12). However, crevice corrosion and pitting corrosion may take longer than 3 months to manifest itself and this result should be treated with caution. In Phase 2, no corrosion was observed on the 316 material but some localized corrosion occurred on the 3CR12 coupons.

Stainless steels rely on the formation of a stable, protective passive film for corrosion protection. Chloride ions can cause localized breakdown of this passive film which could lead to pitting or crevice corrosion. A guide on the use of 3CR12 in waters has recently been published[9] and there the relationship between the potential for corrosion and anion concentrations and temperature is summarized for this alloy. Although chloride may cause pitting corrosion, sulphates and nitrates have an inhibiting effect. A nomogram was developed with which the critical chloride content to cause corrosion can be predicted for specific sulphate and nitrate contents.

The results in Phase 2 indicated that 3CR12 suffered the most severe corrosion in Rand Water Board water, followed by the two blends. However, these three waters had the lowest chloride levels. This apparent anomaly is due to the higher chloride containing waters having a more favourable ratio of chlorides to sulphates and nitrates, thereby inhibiting pitting corrosion. In Table 18, the critical chloride contents evaluated from the nomogram[9] are given for each of the waters in Phase 2 (Table 7). Here it can be seen that the waters which did not cause pitting corrosion of 3CR12 have chloride contents well below the critical chloride content (i.e. RMW, neutralized, settled storage and filtered and disinfected). The chloride contents of the three waters that caused pitting corrosion of 3CR12 (RWB, 1st blend and 2nd bled) are greater than or at least close to the critical chloride contents evaluated from the nomogram.

6.3 The Effect of Suspended Solids

The most damaging effect of suspended solids in mine waters is most certainly that of erosion and fouling. Neither of these effects were studied in this investigation. In terms of corrosion, fouling can lead to underdeposit corrosion and more specifically, this could be the initiation site of microbial corrosion. However, no microbial induced corrosion was detected in this study. It is therefore not possible to elaborate on the effect of suspended solids on corrosion in mine waters from the results of this study.

7. CONCLUSIONS AND RECOMMENDATIONS

Although many of the results in this study were inconclusive, it was considered important to report the results as objectively as possible for future reference. It has to be concluded that the study did not meet the primary objective. This was to quantify the effect of various water treatment processes typically used on the corrosion behaviour of a number of metals. The primary reason for this was that technical difficulties experienced during the programme made it impossible to control the water chemistries of the different monitoring lines within design limits.

Although the design of the water reclamation plant did not allow effective control of individual water chemistries, the hardware installed (e.g. water quality monitoring rig, pumps, flowmeters, storage tanks and corrosion and microbiological monitoring lines) can now be used as a powerful research tool to study the effect of systematic variations in water chemistries. It is therefore recommended that serious consideration be given to the use of the hardware to investigate more directed specific projects. In this way the influence of varying one parameter while keeping all other parameters constant can be studied.

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