AQUARIUS TECHNOLOGIES PTY LTD
WATER QUALITY CONTROL

Quality System

Quality Endorsed Company ISO 9001 Lic. No. 5403

Aquarius Technical Bulletin - No. 38

Notes and experiences with Linear Polarisation Corrosion Monitoring

The origin of Linear Polarisation for Corrosion Measurement goes back to 1957 when M. Stern and A.C... Geary published their paper "Theoretical Analysis of the Shape of Polarisation Curves" in the Journal of the Electrochemical Society.

Whilst the theory of linear polarisation is reasonably complex and usually only fully understood by Ph.D electrochemists, the understanding of a few do's and don'ts should allow the rest of us mortals to use Linear Polarisation instrumentation and to get meaningful results from it, in much the same way we get meaningful results with a pH meter and without being able to explain the Nernst Equation.

An opportunity arose where we could link 5 x KPI units in series, allowing 5 sets of probe tips to be exposed to exactly the same temperature, same flow velocity, and the same water treatment chemistry. Synthetic water was used to simulate 5 concentrations of Brisbane mains water with addition of 300 ppm of a molybdate based scale and corrosion inhibitor. Literature states that the reproducibility of LP corrosion measuring is from about+/- 50 % to+/- 100 %

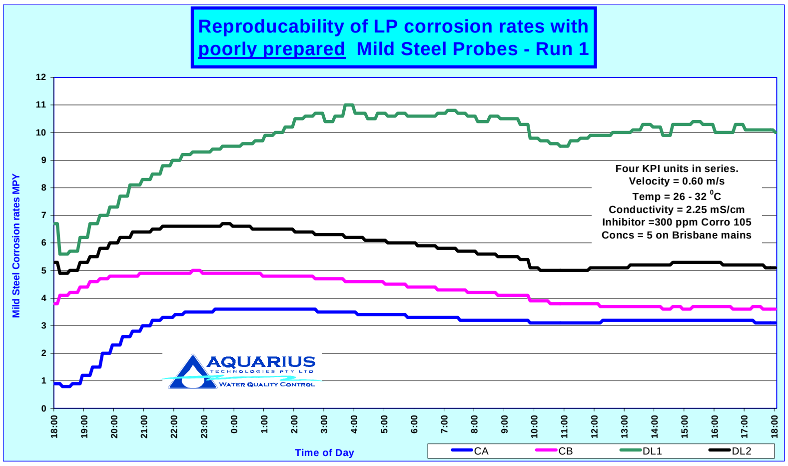
Run no. 1 in the top graph opposite had probe tips which were degreased only, and exposed to air for 8 to 10 hours, prior to installation in the above cooling water solution. As shown by the graph, reproducability is very poor, or non existent and numbers are very high compared to Run 2 and Run 3

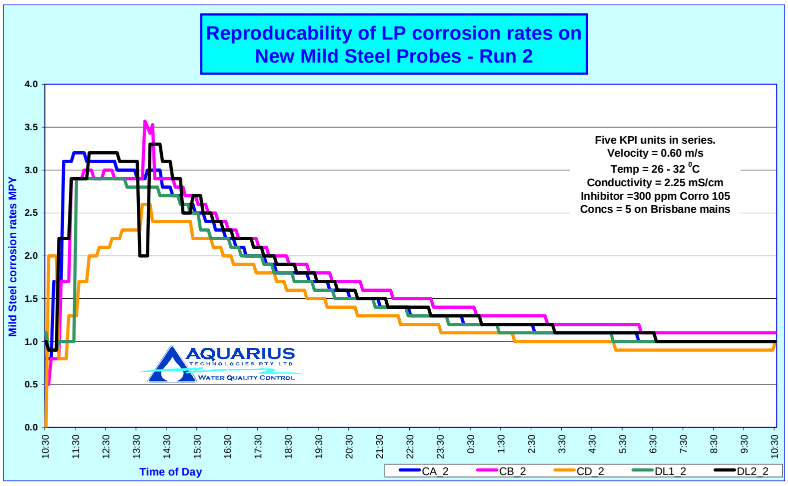
Run no. 2 probe tips were polished with 600 wet and dry paper to a smooth bright finish, degreased with acetone, and thoroughly rinsed with distilled water, and immediately installed in the flowing cooling water system.

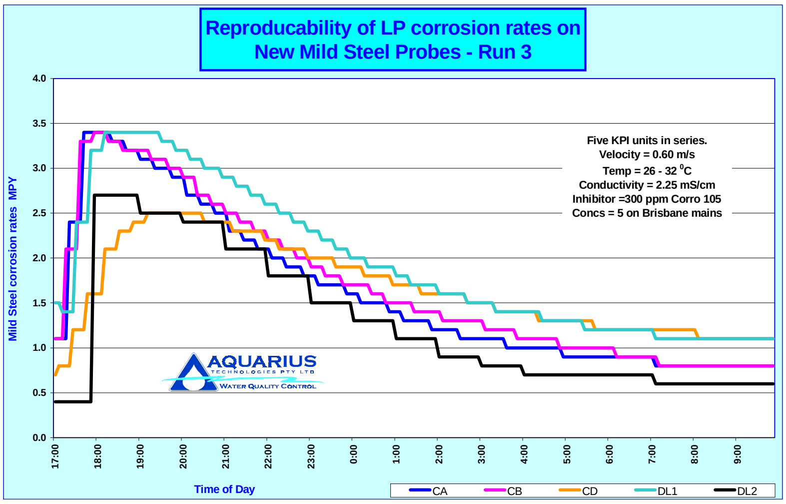
This data log at 5 minute intervals (See graph for Run 2 opposite) shows very good reproducability after first 8 hours.

Run No. 3 is a fresh set of probe tips prepared as in Run No. 2 and again shows good reproducability when the probe tips are thoroughly prepared.

The range of results from Run 2 are 0.9 - 1.1 with an average of 1.0 mpy. Run 3 results are from 0.6 to 1.1 with an average of 0.88 mpy.







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The reproducibility of Pitting Index numbers measured at same time as MPY numbers is graphically illustrated opposite in Run 2 and Run 3 charts.

Only the probe tips on DL2 do not fit the overall pattern. The remainder of probe tips in Run 2 range from 0.3 to 1.3 with an average of 0.7 Pit Index at the end of the run. Run 3 values range from 0.3 to 1.2 with an average of 0.68 Pit Index at the end of the run.

The range of results are probably comparable to results from coupon exposure tests which give an average corrosion value over the entire period.

Both the KPI data logger and Controller systems allow for great flexibility in corrosion monitoring, i.e.

1. Both Mild Steel and Copper specimens can be monitored simultaneously.

2. Two of the same specimens and preparation can be exposed simultaneously to give an average result with improved confidence.

3. A clean bright set of tips can be exposed simultaneously with a "rusty" set to verify both the Water Treatment Program and the ease of passivation of any "rusty" mild steel existing in the cooling system.

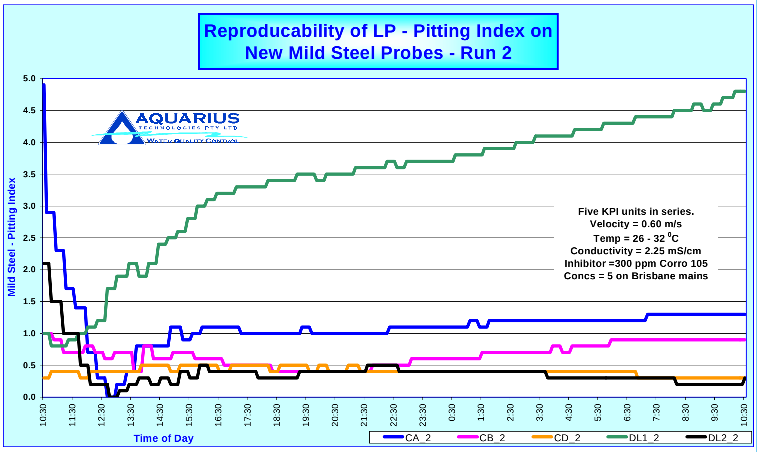
4. The KPI is programmed to take a range of common metals - e.g. S/S, Admiralty Brass, Arsenical Brass, Zinc, Mild Steel and Copper.

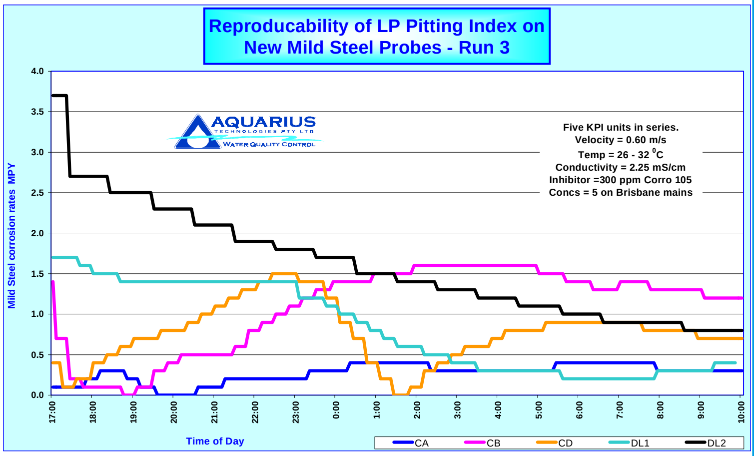
5. Trends in both MPY and Pit Index should be taken very seriously as this indicates a change in corrosion conditions, and allows for rapid remedial action where the corrosion rates have increased.

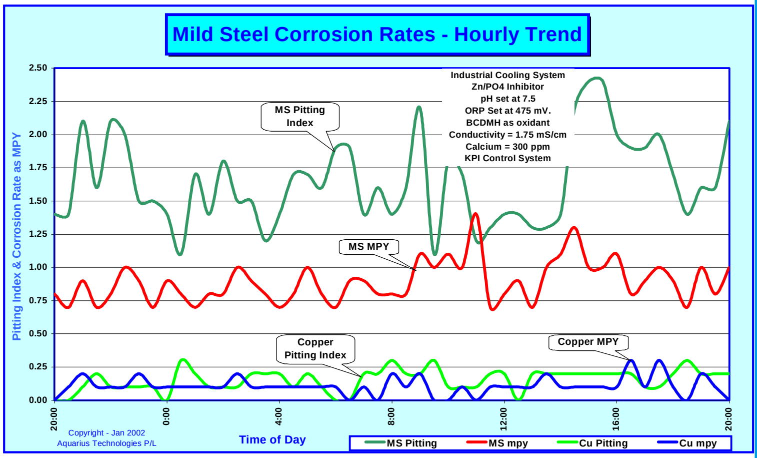
6. The KPI units are supplied with a full set of test probes to allow for verification of the electronics and thus ensure accurate voltage and current measurements = accurate corrosion numbers.

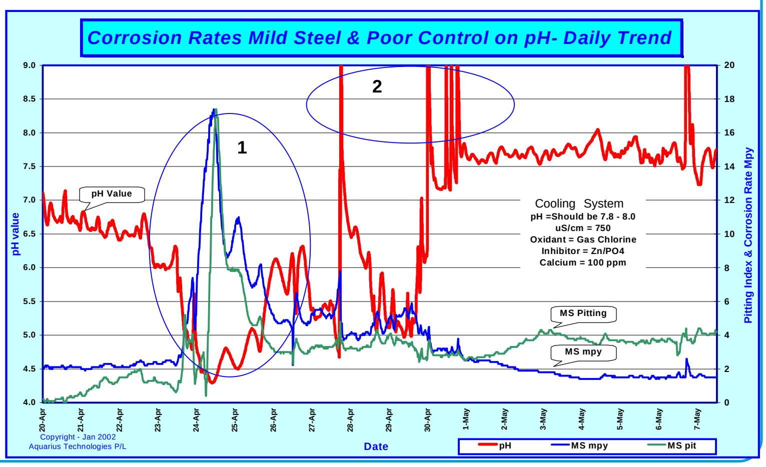
Chart 3 - "Mild Steel Corrosion Rates - Hourly Trend" is from a continuously operating cooling system under good water treatment chemical control and with dosage of BCDMH on demand to maintain a constant 450 mV. ORP value.

Chart 4 - opposite - "Corrosion Rates Mild Steel & Poor Control on pH" - shows the effect of a low pH excursion on both pitting and MPY corrosion rates (circle 1) and then a high pH excursion (circle 2) and that corrosion rates for both pitting and MPY are returned to normal when pH values are brought back under control. The chart also demonstrates that this particular inhibitor program is an effective inhibitor down to a pH of 6.5.









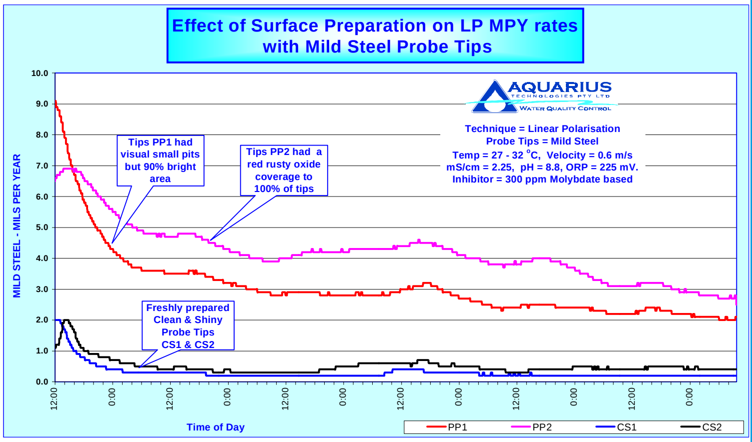
Effect of Surface Preparation on Probe Tips

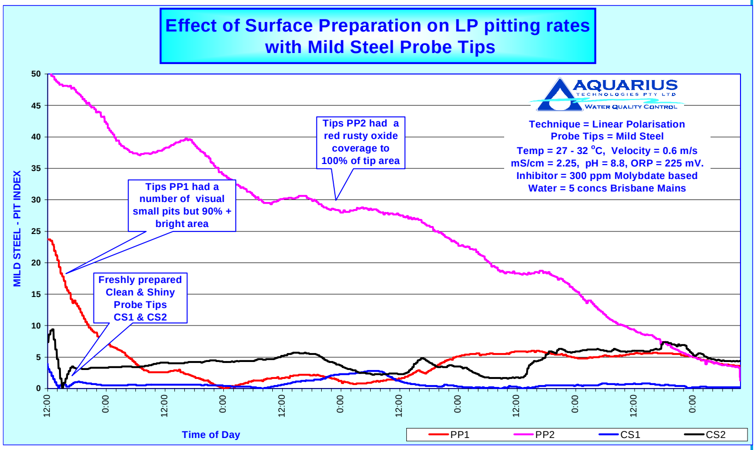
To gauge the effect of surface preparation and the effect on MPY and Pit Index numbers, and also to gauge the effect of passivation on "rusty" or slightly pitted surfaces, probe tips CS1 and CS2 were freshly polished, degreased with acetone, and rinsed in distilled water and immediately placed in the cooling water circuit. Probe tips PP1 were selected as they had a few minor but visible pits but 90% of surfaces were bright mild steel. PP2 probe tips were selected from tips which were some years old, and had a smooth, red rusty oxide coating over 100% of surface.

The top chart opposite shows that both the PP (poorly prepared) probe tips had not been adequately passivated after 6 days exposure, with MPY rates of 2.0 and 2.7 MPY.

The CS probe tips (clean & shiny) showed that good levels of passivation were achieved after only 24 hours exposure with MPY rates were at 0.3 and 0.5 MPY, and these rates remained reasonably constant for the remaining 5 days of this run.

The Pit Index showed that on tips PP1 and both CS tips the Index was under 5 within 24 hours. Probe tip PP2 (red rusty tips) as expected took 5 days to passivate to less that 5 Pit Index value.





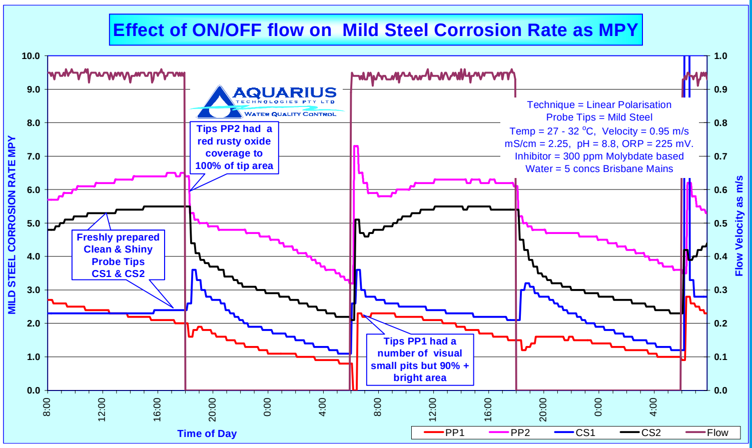
Effect of ON/OFF Flow versus Continuous Flow

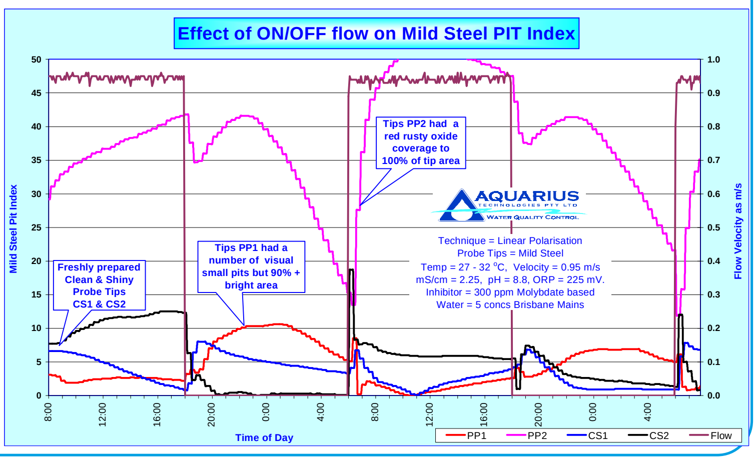
A Time clock was now added to switch the circulating pump - ON for 12 hours, and - OFF for 12 hours, to simulate comfort cooling water system conditions. Monitoring continued on the same probe tips and water chemistry as above.

The chart opposite shows that MPY rates drop when flow stops, and rapidly increase MPY readings on commencement of flow. With Pit Index the numbers appear to increase with flow = ON as would be expected.

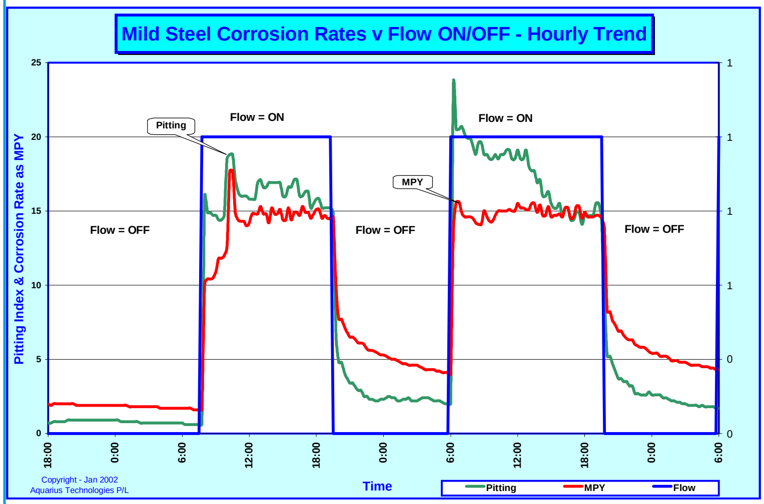
The average corrosion rates over 3.5 days of Continuous flow, versus 3.5 days of ON/OFF flow, show that ***continuous flow allows for lower corrosion rates and better passivation.***

	Cont.	ON/OFF	Cont.	ON/OFF
Tip No.	MPY	MPY	Pit	Pit
CS1	4.0	4.9	0.3	1.7
CS2	0.5	3.0	5.6	3.9
PP1	1.4	3.1	34.7	29.1
PP2	3.6	5.1	10.0	33.0





Effect of ON/OFF Flow continued



This graph was logged on a major CBD building in Sydney, NSW and shows high corrosion rates when condenser flow is on, and dramatically reduced rates when flow is off and the probe tips are stagnant.

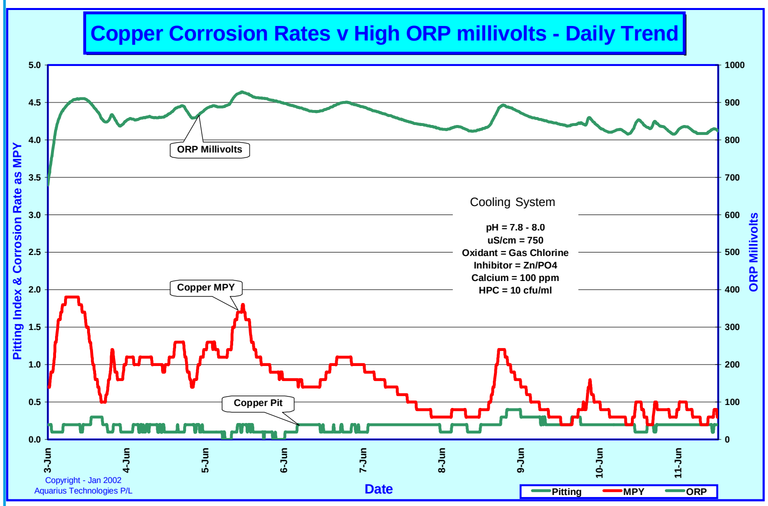
This graph highlights the need to set accurate flow rates and velocity across the probe tips similar to the flow rates in the heat exchangers.

The graph also highlights that dramatic improvements in corrosion rates are required.

Corrosion coupons if installed in an area of low flow can show acceptable rates even with exchanger corrosion as above.

The KPI units are fitted with flow velocity sensors and velocity is displayed in m/s.

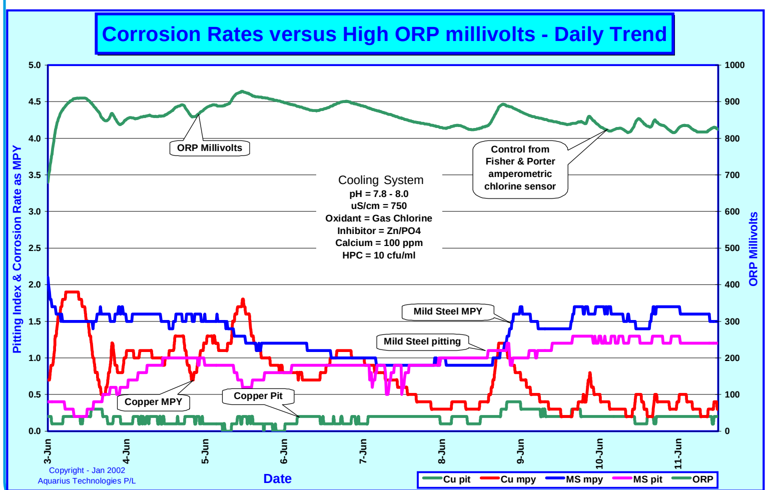
Effect of Oxidising Biocides on LP Corrosion Rates and using oxidant stable corrosion inhibitors.



Many times we are read that oxidants, which are very effective biocides, are a major cause of corrosion, and this may be true in, e.g. hot water systems, where good oxidant stable corrosion inhibitors cannot be employed.

This graph shows that where oxidant stable corrosion inhibitor levels are consistently maintained, very acceptable corrosion rates can be maintained on copper.

The benefits of using a KPI and instantaneous electrochemical corrosion monitoring is that should corrosion rates increase for any reason, the fact is instantly known and rapid remedial action can be immediately taken.

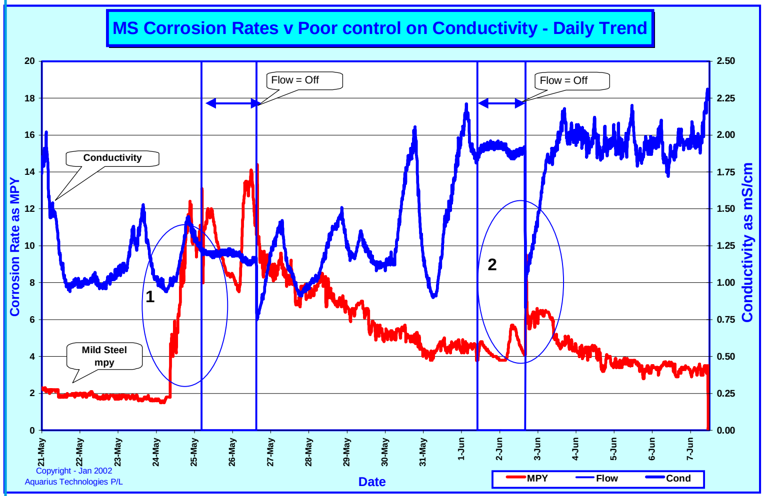


This graph is from the same data as that above and shows very acceptable corrosion rates on mild steel as well as copper even though the ORP millivolt readings are in excess of 800 mV. or about 5.0 ppm as free chlorine.

The control from the Fisher & Porter amperometric chlorine sensor is not as could be achieved with the much cheaper ORP potentiometric sensor when coupled with P.I.D. dosage outputs.

HPC plate counts on this system average about 10 cfu/ml.

More Charts



This graph was from data logged at a milk processing plant where the cooling system duty was blow molding of milk bottles. A history of poor bacterial control and a few minor LDB positive results lead to a legionella risk assessment on the entire plant.

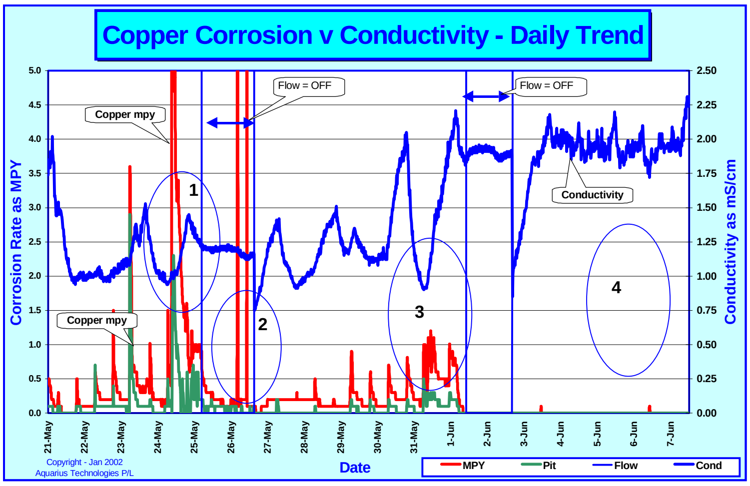
The dosage of Inhibitor was proportional to bleed off rate and this is a very common dosage technique for inhibitor chemical on small cooling systems. This technique assumes that all the water lost from the system is via an activated bleed solenoid, and where this is actually the case maintains excellent control on inhibitor levels.

The chart readily identifies a unreliable bleed off solenoid (not reliably closing on deactivation) is the major cause of the poor control on conductivity, and thus the inhibitor levels

Circle 1. - shows that as excess water is bleed off, which causes inhibitor losses which is then seen as an increase in corrosion rates.

Circle 2. - shows that water is lost prior to start up and again corrosion rates rapidly increase due to loss of inhibitor

Corrosion coupons which only show the average corrosion rate over the exposure period would not highlight this problem.



This chart is also from data logged above and shows the effect on copper corrosion rates - due to poor control on concentrations and inhibitor levels, from the uncontrolled water losses.

Circle 1. - Shows increased copper corrosion rates due to an uncontrolled loss of water and thus also loss of corrosion inhibitor.

Circle 2. As in 1. similar to above

Circle 3. As in 1. similar to above.

Circle 4. Shows the effect of increased conductivity levels, plus no uncontrolled water losses, and thus also an increased calcium level has all resulted in very acceptable copper corrosion rates.

Corrosion coupons would show a corrosion rate of less that 0.5 mpy (the average rate) and would be considered as very satisfactory and again the problem would not be highlighted.

The use of KPI with "instantaneous" corrosion monitoring and data logging facilities can easily highlight problems such as pitting or variation in corrosion rates and lead to remediation of the offending problem.

Current Measurement Cycle

The basic technique of LP in measuring MPY is to, measure a stable rest potential or Ecorr, to superimpose a + and - 20 millivolt potential, and measure the resulting current after polarisation. Due to capacitance within the circuit, the initial current values are high and sufficient time must be allowed for polarisation, to allow the current value to drop to a stable value when the current reading is taken, and calculated as a corrosion rate. For most electrodes in flowing water a 60 -100 second current measurement cycle is normally sufficient time for nearly complete polarisation to be obtained and a valid current reading can be taken.

By pressing **Cal** and **Read** buttons on the KPI units, the complete cycle of voltage and current values can be seen. The default current measurement cycle value set in the KPI units is 2.5 minutes or 150 seconds but longer periods can be set when required for the very rare occasions that this time period does not allow for complete polarisation.

Verification of Corrosion Values

To verify corrosion values from KPI units.

1. The KPI units are supplied with a full set of test probes for simulation of MS, Cu, Temperature and Conductivity values and use of these test probes allow for verification and accuracy of the electronic circuitry. Follow the procedure as set out in the KPI operating instructions.

2. Conductivity values are used in the corrosion calculations to compensate for solution resistivity in the corrosion equations, and thus the conductivity probe should be regularly cleaned and calibrated with the standard conductivity solutions supplied.

3. Ensure that the surface preparation of probe tips installed allows for, in case of mild steel - shiny, bright, clean tips, thoroughly degreased, rinsed with distilled water, attached using either gloves or tissue paper to avoid fingerprints on the tips, and that probes are installed in flowing cooling water without delay.

Ignore the corrosion values for the at least the initial 24 hours, whilst the probe surfaces are being passivated to a similar state as the plant metal.

4. Whilst the corrosion values from a single probe may not always be absolute, due to minor differences in metallurgy, the trend in values is certainly valid, and any increase in values is a definite increase in corrosion rates and would warrant further investigation of the cooling water chemistry

Verification continued

5. Where absolute numbers are required for Corrosion rates, the KPI allows for the two probes to be of the same metallurgy, allowing for data on two probes to be obtained and averaged.

6. As flow rates or velocity across the probe tips have a major bearing on actual corrosion values, it is important to set and maintain flow velocities similar to those in the heat exchangers at the plant.
Typical velocities are about 1 m/sec, but actual plant data on exchanger velocities should be obtained.

The KPI units are unique in that a flow velocity sensor is installed in the manifold, the velocity displayed and velocity values are data logged.

Summary

The KPI data loggers and KPI controllers allow for a high degree of flexibility in corrosion monitoring and data logging, as well as their other chemistry measurements. Like a pH meter where the degree of accuracy is dependant on good probes and frequent calibration, the KPI should be occasionally verified to give a high degree of confidence to the data extracted.

The data extracted on corrosion rates and trends can lead to many major improvements in the water treatment Key Performance Indicators only some of which have been outlined in this article.

Measurement of corrosion trends on an hour by hour basis can save huge sums of money by early intervention on corrosion problems, e.g. a pit about the size of a match head in a heat exchanger tube can lead to a plant shutdown and many days production lost. Early indication of pitting problems could have prevented this shutdown.

Corrosion monitoring can verify the water treatment chemistry and that maximum plant protection is being afforded at all times.

Linear polarisation in producing "instantaneous" corrosion can highlight problem areas which would be unnoticed with corrosion coupons which average the corrosion over the period of exposure.

Like a pH meter in the hands of a skilled operator, the KPI data logger or KPI Controller system in the hands of a skilled water treatment professional can be an invaluable tool and really should be part of the "water treatment test kit" for the new millennium.