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Closed Cooling Loop Corrosion – A Laboratory Based Investigation of Possible Causes

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ABSTRACT

Closed loop cooling circuits operate with good quality, low dissolved solids, make up water. Treatment packages are used to control corrosion and bacteria within the medium. Problems with this type of system can arise from a number of causes such as excessive make-up medium, lack of treatment chemical, bacterial degradation of treatment chemical, excessive ingress of oxygen, and poor water quality.

The work presented was initiated to investigate a nitrite / molybdate corrosion inhibitor due to ongoing integrity concerns in the closed loop system. There is not clear published guidance on application of this type of inhibitor package and testing was conducted to evaluate sensitivities around its application to close loop systems.

A thorough technical review of design and previous corrosion issues was conducted to identify likely causes and key contributing factors. A laboratory test programme was conducted to determine the magnitude to which the identified parameters influence corrosion.

The work highlighted in the background review and the laboratory test programme provides clear conclusions as to appropriate dose rate of inhibitor and factors associated with corrosion risks. The laboratory data highlights that of the factors investigated, the salinity of the make-up water had a significant effect on the inhibitor performance and corrosion risk. Such work provides a basis for generating operating key performance indicators (KPI) to monitor and ensure efficient operation of closed loop systems and limit failures in the future.

Key words: Closed loop cooling, nitrite, molybdate, root-cause analysis.

INTRODUCTION

This project was undertaken to investigate the integrity concerns for a closed cooling loop. Following a background review of the data provided, and typical routes for failure in this type of system a series of laboratory tests were carried out to present evidence of the likely causes of corrosion.

Closed system cooling circuits are designed to operate with good quality, low dissolved solids, make up water. Treatment packages are used to control corrosion and bacteria within the medium. Problems with this type of system tend to be related to excessive make-up medium, lack of treatment chemical, bacterial degradation of treatment chemical, excessive ingress of oxygen, operating outside the water chemistry envelope suitable for the treatment type and dose. The closed loop cooling system was protected through the use of a mixed sodium molybdate and sodium nitrite inhibitor package. What is unknown is the magnitude of these parameters which may lead to failure of the carbon steel. The tests performed and described here are designed to determine the performance of the incumbent inhibitor within the operating envelope of the cooling system. Corrosion in the shell side of the heat exchanger has been observed after 18 months of operation. The cooling medium is on the shell side of the heat exchanger. In addition to corrosion a significant amount of deposit (mainly iron oxides) was observed on inspection of the heat exchanger. The cooling medium water chemistry is that shown in Table 1 below. Other system parameters included:

- Temperature: 32°C at inlet, and ranging between 60 – 126°C
- Pressure: 4 - 6 barg
- Gas at inlet is: 127°C, peaking at 136°C
- Cooling medium is treated seawater that then goes through the reverse osmosis (RO) plant
- Nitrite concentration: 300-500 ppm
- Molybdate concentration: ~15 ppm

Table 1
Cooling Medium Water Chemistry

Analyte	Concentration (mg/l)	Analyte	Concentration (mg/l)
Sodium	1290	Boron	55
Potassium	5.8	Silicon	0.6
Calcium	2.1	Phosphorus	<0.3
Magnesium	16	Lithium	<0.1
Barium	<0.5	Chloride	235
Strontium	<0.5	Sulphate	120
Iron	0.81	TSS	14

There is quite a bit of conjecture on detailed mechanism on nitrite/ molybdate inhibition, but some degree of synergy between nitrite and molybdate and has been discussed in the literature.¹ However there are a number of factors that can affect this type of inhibitor performance including:

- Temperature
- Salinity
- Inhibitor Concentration
- Pitting
- Oxygen
- Carbon Dioxide
- Turbulence

To examine these factors a range of monitoring data were reviewed to assess any likely root causes. The data shows good control of parameters, with the exception of chloride. Previous field data (2013-2014, Figure 1) on chloride levels had shown some large increases which are attributed to poor feed water quality. Nitrite and molybdate showed rapid changes which indicate non-makeup of inhibitor or losses due to leaks or use of system water externally. The correlation between molybdate and nitrite is poor (Figures 3, 4, & 5), but indicates a ratio of approximately 1 mg/l MoO_4 : 15 mg/l NO_2 . For a fixed ratio product the scatter of data indicates preferential loss of one component; either by precipitation or other mechanism such as bacterial degradation. The plot of iron concentration, Figure 6, in the system shows high values indicating significant corrosion (given the feed water is RO (reverse osmosis) sourced). These are conservative levels as they do not include precipitated corrosion products.

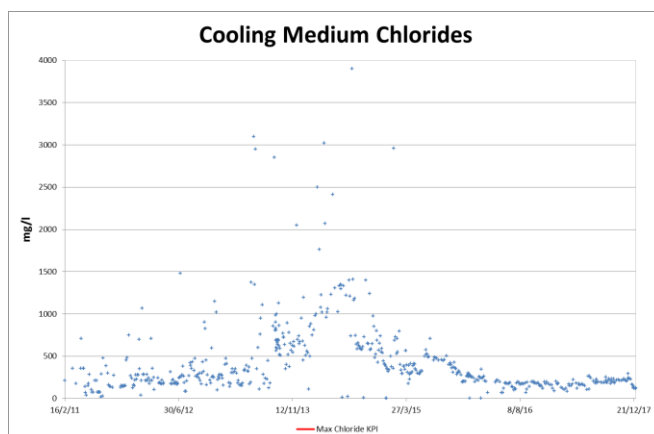


Figure 1: Cooling medium chlorides concentration

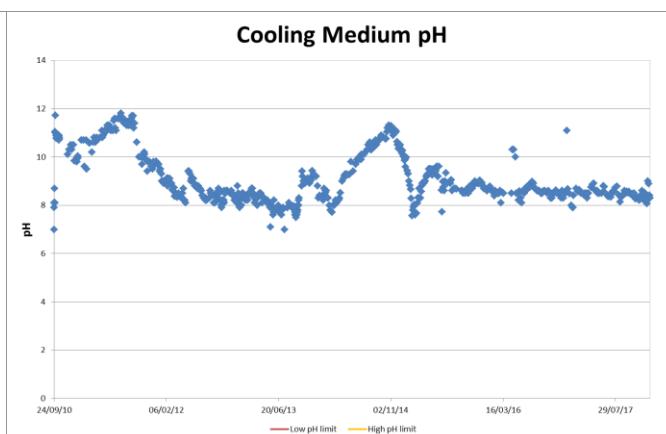


Figure 2: Cooling medium pH

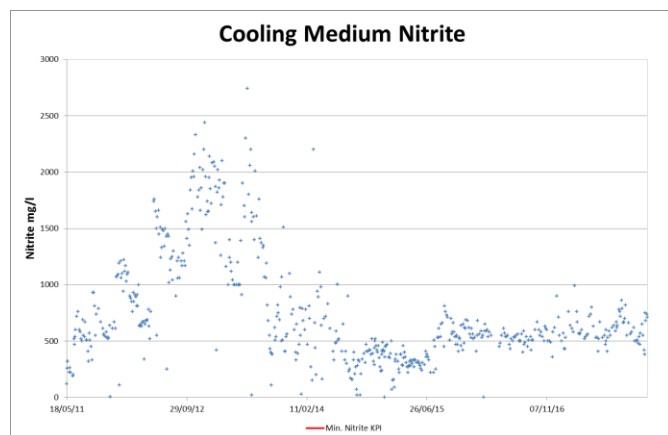


Figure 3: Cooling medium nitrite concentration

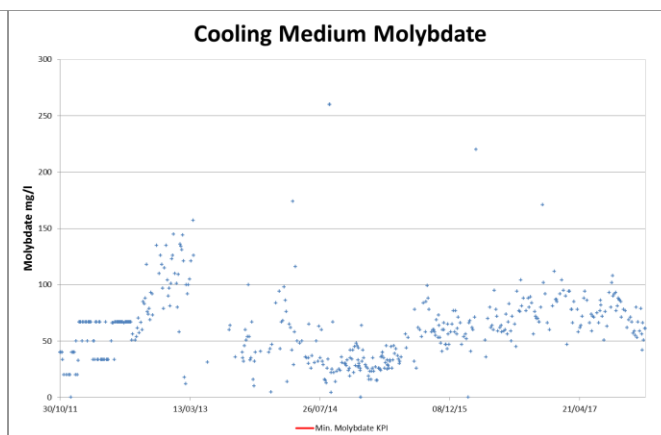


Figure 4: Cooling medium molybdate concentration

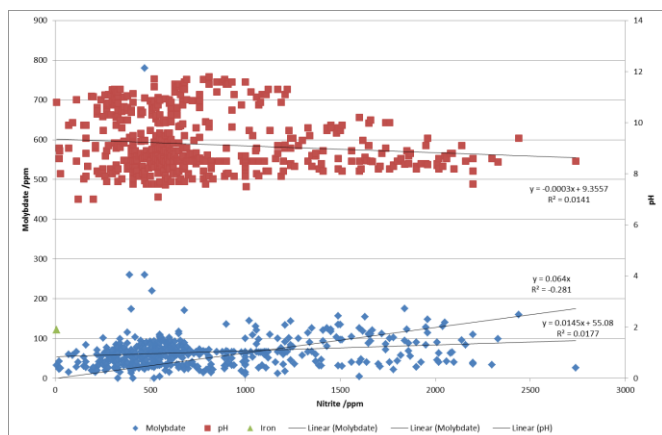


Figure 5: Molybdate concentration & pH vs. nitrite

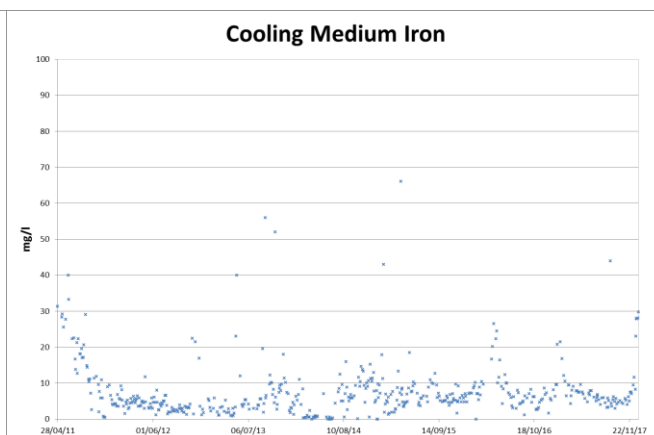


Figure 6: Cooling medium iron concentration

In addition laboratory tests were conducted to validate the dose of the corrosion inhibitor under Jubilee water chemistry conditions, and to assess the performance with a range of variables. The key parameters considered for investigating the envelope of operation of the Jubilee closed loop system in experimental tests are: dose of corrosion inhibitor, temperature, water chemistry, air ingress, pre-corrosion, pH effects, shear stress, pitting

EXPERIMENTAL PROCEDURE

In all tests the metallurgy used was carbon steel (UNS G10180), the duration was 18 hours unless otherwise stated and the pass criterion was ≤ 0.1 mm/y.

Four different brine chemistries were investigated during this study based on the historical field data provided. The “Base” salinity brine is representative of the anticipated water chemistry in the system, with the remaining salinities representative of the excursions discussed in the introduction (Figure 2). Note that in some plots salinity has been shortened to “sal” for brevity.

Table 2
Brine Chemistries Used For All Testing Works

Ion	Base Salinity (mg/l)	Mid Salinity (mg/l)	High Salinity (mg/l)	Ultra-High Salinity (mg/l)
Sodium	174	634	1303	2643
Calcium	2.1	2.1	2.1	2.1
Magnesium	16	16	16	16
Potassium	5.8	5.8	5.8	5.8
Chloride	235	751	1500	3000
Sulphate	120	383	766	1532

Ambient Pressure LPR Bubble Testing

A test matrix for the initial laboratory tests are shown in Table 3, below.

Table 3
Ambient Pressure Corrosion Test Matrix

Oxygen	Temperature (°C)	Nitrite (ppmv)	Water Chemistry
1 ppm	32	0	High and based salinity
		300	
		500	
	60	0	High and based salinity
		300	
		500	
	90	0	High and based salinity
		300	
		500	

In these low shear 100% brine LPR bubble tests, corrosion inhibitor (CI) is added to the brine phase and linear polarisation resistance (LPR) corrosion rate measurements are made to determine the relative rate of corrosion rate reduction and the final corrosion rate achieved. Final corrosion rates are compared to a blank test with no corrosion inhibitor present. The inhibitor dose rate was determined from data available on field residual nitrite, with dose representative of different periods of operation. The conditions used are shown below:

CI:	300 and 500 ppmv (based on the nitrate active component)
Brine:	Base and High salinity (see Table 2)
Temperature:	32, 60 and 90°C
Oxygen:	1 ppm
Sparge gas:	Air/nitrogen mix
Duration:	18 hours
Metallurgy:	Carbon steel (UNS G10180)
Pass Criterion:	Corrosion rate < 0.1 mm/y

Additional Ambient LPR testing- Impact of Environmental Changes

For the additional ambient LPR tests to assess the impact of environmental changes, the standard bubble cell set up is to be used as described above with the following adjustments:

O₂ Ingress

Tests were carried out as above at 90°C with both the base and high salinity brine, but rather than sparging with mixed gas to achieve 1 ppm O₂ the tests were initially sparged to < 5 ppb O₂ with oxygen free nitrogen (OFN). The oxygen concentration was measured in the liquid phase using colorimetric test kits. The tests were started with OFN sparging for the first 3 hours of the test, the gas was changed to compressed air to mimic oxygen ingress for 3 hours then changed back to OFN for the remainder of the test. The conditions used are as follows:

CI:	300 and 500 ppmv active
Brine:	Base and high salinity (see Table 2)
Temperature:	90°C
Sparge gas:	N ₂ for 3 hour, compressed air for 3 hours, then N ₂ for the remaining duration
Duration:	18 hours
Metallurgy:	Carbon steel (UNS G10180)
Pass Criterion:	Corrosion rate < 0.1 mm/y
CI:	300 and 500 ppmv active