EVALUATION OF MAX HT® AT QUEENSLAND ALUMINA LTD

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Abstract

During the Digestion step of the Bayer Process, silica containing minerals within bauxite are dissolved into caustic liquor and re-precipitate as sodalite. As a result, Bayer liquors are supersaturated in Silica at all points within the liquor circuit, which promotes scaling of process equipment with sodalite. This scaling is most problematic in heat exchange equipment responsible for heating spent Bayer liquor to Digester conditions, where high temperatures (>150°C) and high silica supersaturation promote high scaling rates. Cytec Industries have developed a chemical product (MAX HT®) capable of inhibiting sodalite scale formation under spent Bayer liquor conditions[1,2]. This paper outlines the details and results of first generation MAX HT® trials conducted in the spent liquor circuit at the Queensland Alumina Refinery (QAL).

1. Introduction

Silica scale forms at QAL in spent liquor (SL) equipment and pipe work, i.e. anywhere from SL Heat Interchange (HID), through Evaporation and Digestion heaters up to the inlet to the Digesters. Due to the strong temperature effect on desilication kinetics[3], the scaling rate is most pronounced in the high temperature heater trains. Silica scale causes a number of problems:

Silica scale formation on the tube side of spent liquor heaters in Digestion, Evaporation and HID causes a significant increase in the resistance to heat transfer and hence reduces the overall heat transfer coefficient (HTC). Thus spent liquor heat recovery is reduced and leads to higher plant energy requirements.

Due to this reduction in HTC, heater trains are taken off periodically and cleaned with dilute sulphuric acid to restore the heater to its initial condition. Acid is also used to clean pumps, pipework etc.

Increased flow resistance due to scale roughness and reduction in pipe/tube diameter. Often this is a bottleneck to plant flow.

Difficulties in getting isolation on spent liquor equipment, often requiring long periods of valve grinding to achieve positive isolation.

MAX HT® is a chemical additive developed by Cytec Industries, which acts to inhibit silica scale formation in Bayer spent liquor systems[1,2]. It was introduced to the Bayer industry in 2005, and a series of trials have been conducted at QAL since then to evaluate the effectiveness of the additive at inhibiting scale formation. It should be noted that this paper only details the results of trials conducted using first generation MAX HT®.

2. Experimental

2.1 Trial Dosing Equipment and Control

Figure 1 below shows a simplified process flow diagram for the dosing of MAX HT® to Digestion Unit 3. Equipment was obtained from Cytec for dosing of MAX HT®, which allowed:

- The concentration of MAX HT® to be maintained at 5% using process water as a diluent
- Control the MAX HT® dose rate to the SL at the desired level. Dose rates tested ranged from 3 – 70ppm

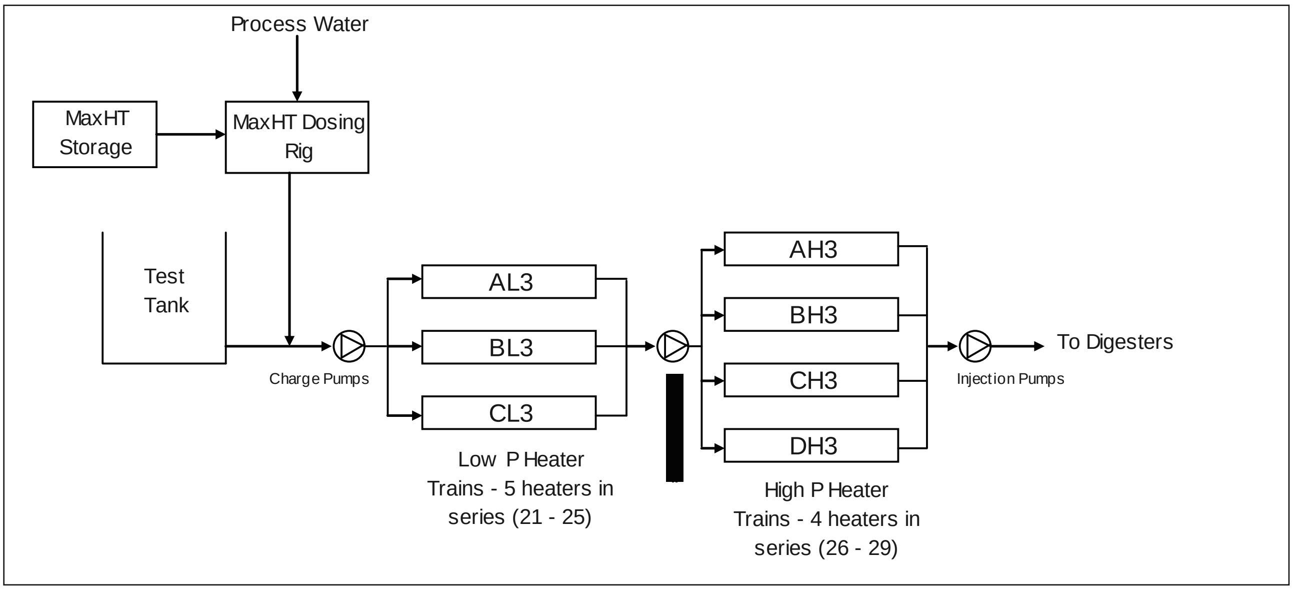

Figure 1: Simplified PFD for Addition of MAX HT® to Unit 3

2.2 29D Heater HTC Calculation

The heater operating at the highest temperature on the DH3 heater train (i.e. 29D Heater) was chosen to evaluate the impact of MAX HT® on HTC as this is the highest scaling position heater. In order to accurately calculate the HTC, 29D heater had the following instrumentation installed:

- Resistive thermal devices (RTD) to measure spent liquor inlet and outlet temperatures more accurately than the existing thermocouples.
- A RTD to measure the steam inlet temperature
- A RTD to measure the condensate temperature leaving the heater
- A pressure measurement for the steam inlet pressure

The instrumentation was connected to a local datataker, which recorded the temperatures and pressure periodically.

Flow through 29D heater is known by ensuring that Charge and Booster pump manifolds are split, such that the flow through one of the online Charge Pumps corresponds to the flow through 29D heater.

The HTC was then calculated using the following methodology and assumptions:

Calculate the rate of heat transfer to the SL using equation 1 below

$$\dot{q} = V_{SL}.\rho.c_p.\left(T_{SL,out} - T_{SL,in}\right) \quad \textbf{Eqn 1}$$

where $\dot{q}$ is the rate of heat transfer (kW) to the SL, VSL is the volumetric flow rate (kL/h) of SL at the Charge Pumps, measured by the existing flow meter; ρ is the liquor density (kg/kL) at charge pump conditions, cp is the liquor heat capacity (kJ/(kg.K)) evaluated at the SL inlet temperature, and TSL,out and TSL,in are the SL outlet and inlet temperatures (K) respectively.

Calculate the log mean temperature difference (ΔTlm (K)) using equation 2

$$\Delta T_{lm} = \frac{\left(T_{sat} - T_{SL,out}\right) - \left(T_{sat} - T_{SL,in}\right)}{\ln\left(\dfrac{T_{sat} - T_{SL,out}}{T_{sat} - T_{SL,in}}\right)} \quad \textbf{Eqn 2}$$

where Tsat is the saturation temperature of the steam (K) at the pressure measured entering the heater. The underlying assumption here is that negligible heat transfer area within the shell and tube heat exchanger is used to de-superheat the steam and cool the condensate below the saturation temperature (i.e. there is only condensing heat transfer occurring within the heater). This assumption was checked by measuring both the steam superheat and condensate temperature.

Calculate the overall HTC using equation 3:

$$U = \frac{\dot{q}}{A.\Delta T_{lm}} \times 1000 \quad \textbf{Eqn 3}$$

where U is the overall heater HTC (W.m-2.K-1)), and A is the heater heat transfer area (m2).

2.3 Scaling Rate Calculated from Acid Consumption Data

Another measure used to evaluate the performance of MAX HT® on the scaling rate was the drop in acid concentration during chemical cleaning of the HP and LP heater trains. This data was converted to a scaling rate (t/d) using equation 4 below:

$$ScalingRate = \frac{V_{shot}.\left([Acid]_{in} - [Acid]_{out}\right).MW_{Sodalite}}{MW_{H_2SO_4}.Ratio_{mole}.DaysOnline} \times 0.01 \quad \textbf{Eqn 4}$$

where Vshot is the volume of the acid shot (kL), [Acid]in and [Acid]out are the sulphuric acid concentrations (% w/v) initially and at the conclusion of cleaning respectively, MWsodalite is the molecular weight of sodalite (approximated to 1066.4 g/mol), MWH2SO4 is the molecular weight of sulphuric acid (98.08 g/mol), Ratiomole is the ratio of moles of H2SO4 consumed per mole of sodalite dissolved (13 mol/mol)4, and DaysOnline is the number of days the heater train was online

2.4 Visual Inspection and Scale Thickness Measurement

At the conclusion of DH3 campaigns the return head was removed prior to being acid cleaned to allow a visual inspection of the heater to be made. The visual inspection involved:

- Inspection of the inside of tubes using a pipe camera
- Measurement of scale thickness on the inside of tubes. This was done by breaking off pieces of scale from within the first 5-10cm of the tube and measuring the thickness using digital callipers. A scaling rate (mm/day) was calculated by dividing the average thickness measured from 16 tubes by the days the heater train was online

2.5 Flow Resistance Calculation

Another parameter used to determine the impact of MAX HT® on scaling rate was the flow resistance across both HP and LP heater trains. Equation 5 is a measure of flow resistance (assuming constant density over time):

$$\text{Flow Resistance} = \frac{\left(P_{in} - P_{out}\right)}{V_{SL}^{2}} \quad \textbf{Eqn 5}$$

where Pin and Pout are the SL pressure (kPa) at the inlet and outlet of the heater train respectively, and VSL is the volumetric flow rate (kL/h) of SL measured at the Charge Pumps.

The rate at which the Flow Resistance increases over the online time of the heater train is related to both the rate of increase in scale roughness and rate of reduction in tube diameter as scale grows. As the diameter reduces and/or the scale roughness increases, the pressure drop increases across the heater train.

Timeline of MAX HT® Trials at QAL

The following is a timeline of the MAX HT® trials conducted at QAL:

- 1st of June 2006. Trial conducted on DH3 at 50ppm for a 12 day cycle
- 19th of June 2006. Trial conducted on DH3 for a 24 day cycle. The dose rate was initially at 70ppm, which was then gradually reduced to 30ppm by the end of the 24 day cycle
- 23rd of August 2007. Trial conducted on DH3 for a 16 day cycle at a dose rate of 20ppm
- 30th of October 2007. Baseline measurements conducted on DH3 for a 5.5 day cycle
- 12th of December 2007. Baseline measurements conducted on DH3 for a 12.5 day cycle
- 8th of January 2008. Full Unit 3 trial commenced at a dose rate of 20ppm. Dose rate reduced over time to 6ppm by 11/02/09. A number of separate cycles were analysed during this time.

3. Results and Discussion

The 29D heater HTC was calculated for a number of cycles at various MAX HT® dose rates. Figure 2 below shows the average (for clarity) HTC over the nine cycles with MAX HT® compared to the two baseline cycles with no MAX HT®. The fact that the HTC declines while MAX HT® is dosed is evidence of scale forming within the heater. However, the rate at which the HTC declines is lower with MAX HT® on, which is evidence that the scale formation rate is reduced.

A better way of representing the HTC data is as resistance to heat transfer (i.e. 1/HTC), as shown in Figure 3 below. The slope of the 1/HTC curve is the rate at which resistance to heat transfer increases over the heater cycle, and is a measure of the scaling rate within the heater. It is clear from Figure 3 that the addition of MAX HT® reduces the scaling rate when compared to the baseline results.

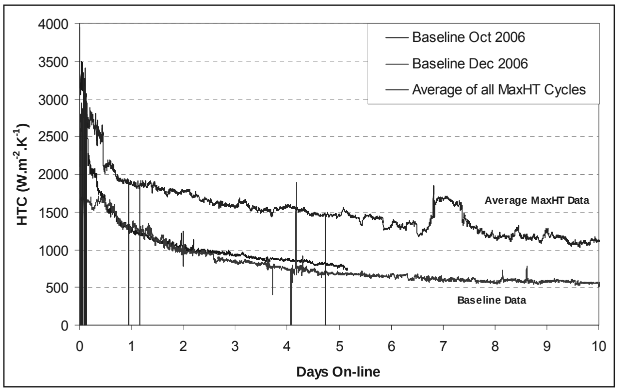

Figure 2: **Heat Transfer Coefficient as a Function of Time**

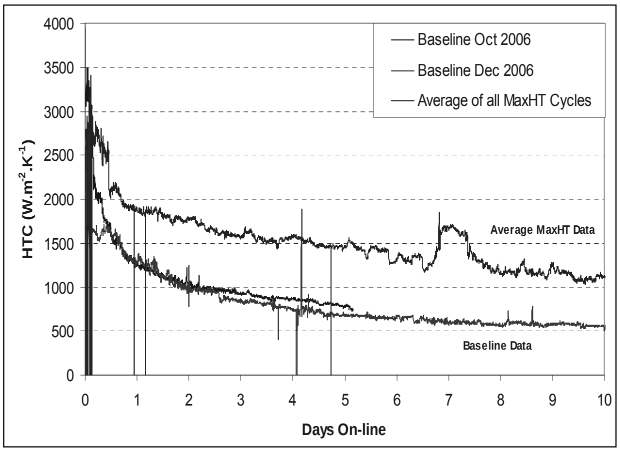

Figure 3: **Resistance to Heat Transfer as a Function of Time**

It was found that there was some variation in the scaling rate (d/dt 1/HTC) between different cycles with MAX HT® addition. Silica supersaturation is expected to impact scaling rate, so this was investigated to see if it could explain the variation observed. Figure 4 below shows that there is a strong relationship between the square of silica supersaturation (evaluated at heater DH3 conditions) and scaling rate with MAX HT® addition, and that this accounts for ~90% (R^2 = 0.9) of the variation observed in d/dt 1/HTC. It is also observed that changes in MAX HT® dose rate have no impact on scaling rate over a range of 70ppm down to 6ppm, and it was only when the dose was reduced to 3ppm that a drop-off in performance was observed.

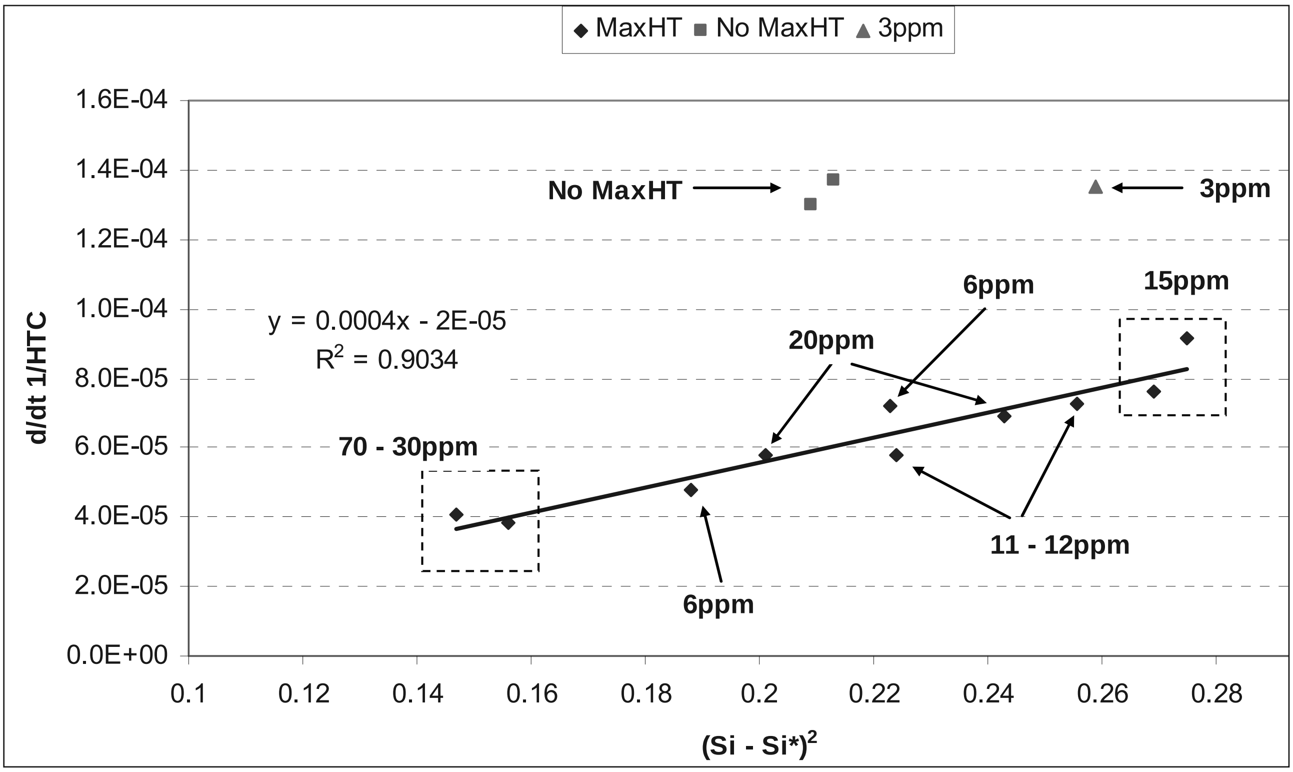

Figure 4: **Scaling Rate as a Function of the Square of Silica Supersaturation**

The results for scaling rate as measured by acid consumption during cleaning are shown in Table 1 below. There is a reduction in scaling rate by a factor of ~4 due to MAX HT® addition as measured by acid consumption.

Table 1: Average Scaling Rate Calculated from Acid Consumption

	Average Scaling Rate (t/d) MAX HT® On	Average Scaling Rate (t/d) MAX HT® Off
HP Heater Trains	0.226	1.063
LP Heater Trains	0.069	0.289

Visual inspections of 29D heater were done prior to acid cleaning for a number of cycles with and without MAX HT® addition. It was noticed that the morphology of the scale formed with MAX HT® addition is different to that observed under normal conditions. There was a significant change in the scale colouration, MAX HT® scale being black whereas normal scale was of a much lighter creamy-brown colour. Scale was much less crystalline in nature with MAX HT® addition, and was much more friable than normal scale. It was easily scratched and removed from the tubes in comparison to the normal scale. This observation is backed up by reductions in time to achieve isolations on heater trains, with the required duration for valve grinding reduced significantly.

Scaling rate as calculated from scale thickness measurements is summarised in Table 2 below. On average there is a reduction in the scaling rate by a factor of ~7 as calculated from scale thickness.

Table 2: Average Scaling Rate Calculated from Scale Thickness Measurements

	MAX HT® On	MAX HT® Off
Scaling Rate (mm/day)	0.05	0.36

The reduction in scaling rate as measured by scale thickness (factor of ~7) is inconsistent with that observed from heat transfer analysis (factor of ~2.25). Consistency between these two measures would be expected if the scale was of the same nature and had the same thermal conductivity. The thermal conductivity was calculated for both the MAX HT® and normal sodalite scales using equation 6:

$$\frac{1}{HTC} = \frac{1}{h_o} + \frac{t_{scale}}{k_{scale}} + \frac{1}{h_i} \qquad \textbf{Eqn 6}$$

where ho is the convective heat transfer coefficient on the outside of the tube wall, tscale is the scale thickness, kscale is the thermal conductivity of the scale, and hi is the convective heat transfer coefficient at the scale/liquor interface on the inside of the heater tube.

Taking the derivative of both sides with respect to time, and assuming that the convective heat transfer coefficients on the inside and outside of the tubes are constant over the online cycle of the heater; equation 6 can be simplified to:

$$\frac{d}{dt} \cdot \left(\frac{1}{HTC} \right) = \frac{1}{k_{scale}} \cdot \frac{d}{dt} \left(t_{scale} \right) \qquad \textbf{Eqn 7}$$

Substituting in the rate of increase in 1/HTC and scale thickness as measured during the trials allows one to solve for kscale. The thermal conductivity of the normal sodalite scale is calculated to be approximately 2.67 W.m-1.K-1, whereas the thermal conductivity of MAX HT® scale is ~0.83 W.m-1.K-1. One reason for this difference in thermal conductivity could be the difference in the morphology of the MAX HT® scale, which was less crystalline than the normal sodalite scale.

Use of a pipe camera also yielded some interesting results. Figure 5 shows photos from within scaled heater tubes, which indicate that the normal sodalite scale is significantly rougher than the MAX HT® scale. This explains much of the difference observed in flow resistance, which is detailed below.

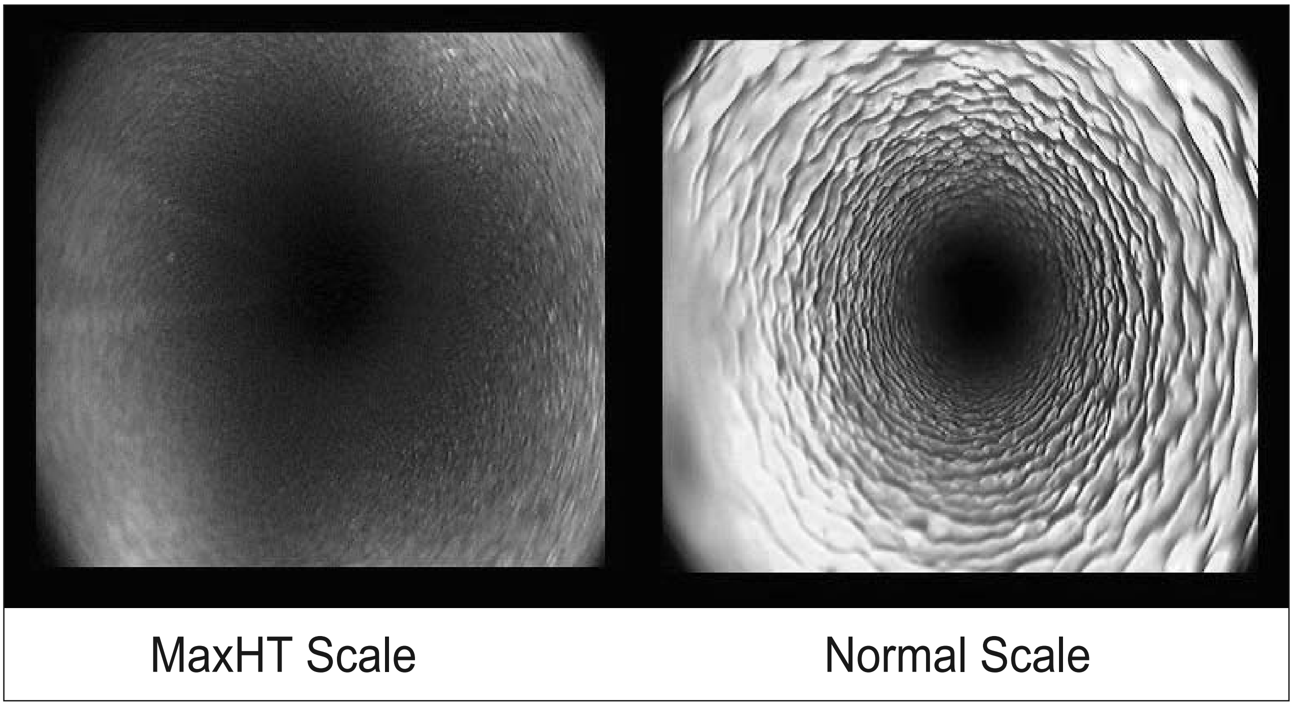

Figure 5: Photos of MAX HT® and Normal Scale within Heater Tubes

Analysis shows that the rate at which flow resistance increases is significantly reduced. Figure 6 shows the data for the LP heater trains, and Figure 7 shows the data for the HP heater trains. The saw tooth pattern prior to MAX HT® addition is due to heater trains coming online and offline; once MAX HT® is added to the system the increases in the flow resistance over heater cycles are removed. Comparison of the individual slopes for flow resistance with and without MAX HT® shows a reduction in the scaling rate much greater than observed from the other measures of scaling rate. This is almost entirely due to the change in scale roughness observed during the visual inspections described above.

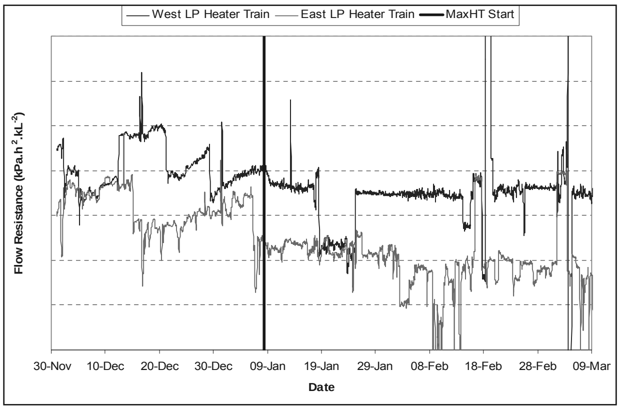

Figure 6: LP Heater Train Flow Resistance

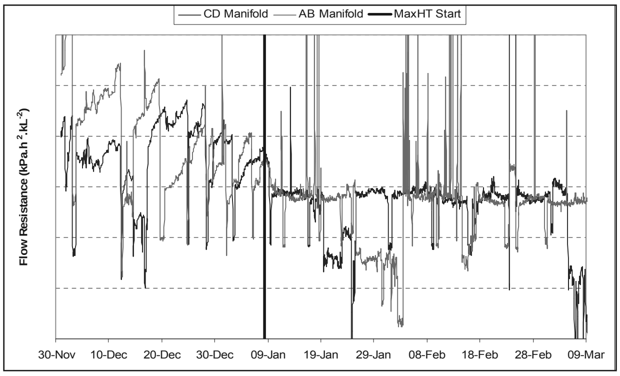

Figure 7: HP Heater Train Flow Resistance

4. Conclusions

The performance of MAX HT®, a chemical additive developed by Cytec for inhibition of sodalite scale, has been evaluated at QAL. The results of the trial have shown that:

- Based on heater HTC, scaling rate was reduced by 55%
- Based on scale thickness measurements, scaling rate was reduced by 85%
- Based on acid consumption, scaling rate was reduced by 75%
- Scale formed with MAX HT® addition has a lower thermal conductivity than normal sodalite scale. It is hypothesised that this is due to differences observed in scale morphology, in particular scale crystallinity.
- Normal sodalite scale is much rougher than scale formed with MAX HT® addition. This has had the effect of removing limitations due to resistance to flow through the SL system.
- Scale formed with MAX HT® addition is more friable than normal sodalite scale, which has made SL system equipment isolations more easily attained.

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