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Scale controlling chemical additives for phosphoric acid production plants

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Abstract

During the past two years, Cytec Industries has successfully developed and demonstrated an antiscalant technology that substantially reduces the fouling issue that remains a perennial problem in wet-process phosphoric acid production plants. The technology has offered significant benefits at various points in the process including a 90% reduction of scale mass in process piping, reducing the number of tubes plugged in a heat exchanger by 85% with concomitant decrease in cleanout time of 85%, and increasing the operational cycle of a heat exchanger by almost 100%. To cap all these benefits, there are no downstream effects and product grade acid was produced throughout all of the trials. The technology is easily implemented at existing plants with no requirement for significant capital investment.

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Keywords: antiscalant, fouling, heat exchanger, phosphoric acid

1. Introduction

Accumulation of scale is a perennial problem in phosphoric acid production processes. The large quantities of dissolved and un-dissolved species present during the digestion and concentration process lead to the formation of scale deposits on the filters, pipelines carrying the acid, evaporators, heat exchangers and coolers [1-2]. The scale deposits can cause a number of operational problems such as plugging of equipment, inefficient feed rate to the evaporators, increased utility costs, lost production due to downtime, and downgraded products from lower concentration due to poor heat transfer. The concentrated phosphoric acid solution is supersaturated with respect to calcium sulfate resulting in its deposition on the material of contact [3]. Since the thermal conductivity of these scales is low, even a thin layer of scale can reduce the overall heat transfer coefficient significantly [4]. Further, gypsum scale can host the growth of fluorosilicate and fluoroaluminate deposits on the acid lines to the clarifier tanks and the evaporators, reducing the diameter of the pipelines leading to reduced throughput. In spite of extensive efforts and research into antiscalants for phosphoric acid type scale, no commercially viable solution has been found [5-7].

A rough calculation of potential production gain from extending the operating cycle of a heat exchanger is illustrated in Table 1 assuming 50 weeks/year operation with a capacity of 300 T P_2O_5/day (i.e. 105 000 T/year or 12.5 T/h) with a shutdown frequency of every 2 weeks and a shutdown duration of 20 hours.

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Table 1: Production gain by extending cycle

New shut down frequency (from 2 weeks to)	Production time saved (hrs/year)	Merchant grade acid production increase (T/year)	(%)
4 weeks	=[(50/2) – (50/4)]*20 = 250 hrs	3125	3.0
5 weeks	=[(50/2) – (50/5)]*20 = 300 hrs	3750	3.6
6 weeks	=[(50/2) – (50/6)]*20 = 333 hrs	4167	4.0

Cytec has developed a novel family of antiscalants, PHOSFLOW™, to maximize flow in phosphoric acid plants. This new range of products reduces the fluorosilicate, calcium sulfate and aluminate scale formation in phosphoric acid operations allowing for longer cycle times, increased production, and reduced maintenance time. The efficacy of the technology has been demonstrated via three commercial scale plant trials at two distinct points in the phosphoric acid production process. There were no negative downstream effects and product grade acid was made during the trials. The antiscalant is easily applied to the process through a piston pump requiring minimal capital investment. This paper will summarize the results of the application of this technology on scale buildup in filtrate lines and present more detailed results of the application to the mitigation of scale buildup in a commercial phosphoric acid heat exchanger and feed line.

2. Summary of initial trial of PHOSFLOW™ technology in phosphoric acid plant filtrate process piping

The first commercial plant level trial was conducted on a pipeline carrying 28% P_2O_5 acid from a belt filter after digestion to a clarifier. Typically, the line would operate for 72 hours before requiring a shutdown to clean out accumulated scale that had reduced the flow rate to the clarifier as well as placing an increased current load on the filtrate pump. The line was cleaned with hot condensate and was typically down for a period of 8 hours. The filtrate line also had two spool pieces that could be removed and weighed as a measure of the amount of scale that formed in the pipe.

The composition of the scale and acid was studied using x-ray diffraction (XRD) and inductively coupled plasma atomic emission spectrometry (ICP-AES) respectively. The scale is mainly composed of fluorosilicate and gypsum type scale as shown in figure 1. The composition of the acid is shown in table 2. Fluorine and chlorine could not be quantified by ICP-AES.

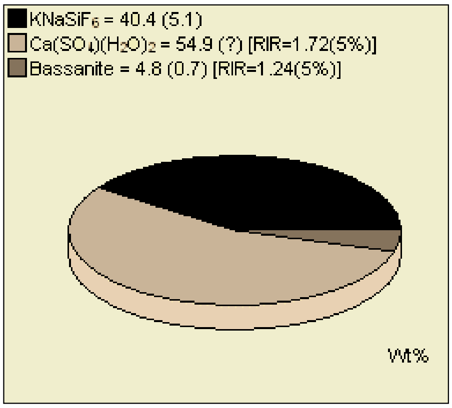


Figure 1. XRD analysis of a typical plant scale sample

Table 2. Elemental analysis results of typical 28% P_2O_5 acid sample. Concentrations are reported in ppm (mg/L).

Al	Ca	Cd	Cr	Fe	K	Mg	Mn	Na	S	Si	Sr	Zn
5300	860	85	300	3700	270	2300	130	370	3900	3200	52	970

It was proposed that Cytec's antiscalant could provide a benefit by reducing the amount of accumulated scale allowing for higher flow rates, decreased clean out times, and an extension of the cycle.

PHOSFLOW™ was dosed into the acid line at 100 g/T P_2O_5 and the flow rate and pump amperage tracked over time. The trial was designed to last the equivalent of a normal control cycle that was run immediately prior to the testing of the antiscalant. Listed below are the salient results from the trial:

- No additional load (measured by pump amps) was exerted on the pump indicating an absence of scale.
- The flow of acid did not deteriorate during the 72 hour trial also indicating an absence of scale.
- Two spool pieces were attached at the end of the pipeline for visual observation and gravimetric measurement of the scale. The control cycle had a significant layer of scale weighing 5.86 kilograms. The trial where PHOSFLOW™ was utilized showed no observable scale and the weight recorded was 0.25 kilograms, a greater than 95% reduction in accumulated scale mass.
- Clarifier and granulation data and observations showed no fouling, foaming, adverse settling or other negative effects and product quality acid was produced.

The trial met all of the objectives and was deemed successful by Cytec Industries and the customer. Subsequently, the customer indicated that the true bottleneck within their plant was in the heat exchanger and feed acid line to the heat exchanger where significant scale buildup occurs and creates a greater loss in production. Further testing of the antiscalant was therefore planned at this point in the process.

3. Trial of PHOSFLOW™ technology in phosphoric acid plant heat exchanger and feed acid line

As stated previously, the customer identified the feed acid line to the heat exchanger and the heat exchanger as areas that suffer from scale buildup and requires periodic cleaning to maintain acid flow. The typical cycle length of the heat exchanger was 3 weeks and a clean out of the feed acid line was necessary approximately 10 days into the cycle. The cleanout time for the feed acid line was 4 hours and 3 days for the heat exchanger. Cleanout of the heat exchanger entails mechanical cleaning with a high pressure water lance that takes approximately 15 hours with an average of 150 tubes visually plugged out of a bundle of 868 tubes. During a cycle, the flow rate of acid to the evaporator decays from an initial rate of approximately 50 m^3/hr to less than 39 m^3/hr. A two-trial evaluation was proposed where the first trial of the antiscalant would replicate their normal operating cycle time of 3 weeks. The data generated from the trial would be compared with historical data as well as data from a control cycle run immediately after to ensure similar environmental conditions and ore chemistry were encountered. If the results looked promising, a second trial would be conducted looking to extend the cycle beyond the typical 3 weeks. The process parameters chosen as indicators of performance for the feed line and heat exchanger are listed below:

- Heat transfer coefficient – Gives an indication as to the efficiency of heat transfer. Values greater than 450 W/m^2 K are considered sufficient.
- Percent valve open reading – the valve opening is modulated to attain a set point flow rate. When the line is scaled or a blockage develops, the valve will need to be fully open (100%) to achieve the set point flow.
- Current load on recirculation pump in the heat exchanger. If the tubes in the heat exchanger become plugged, the current load on the recirculation pump will increase.
- The number of tubes plugged in the heat exchanger and the time required for cleaning the heat exchanger.
- The flow rate of acid through the system.

3.1. Historical Cycle Data

In preparation for the trial, the customer provided 5 cycles worth of historical data. The process parameters of interest described above were plotted versus production hours for the historical cycles. One cycle of data is shown in figure for each process parameter of interest. Appendix A contains the remaining 4 cycles of historical data for each process parameter.

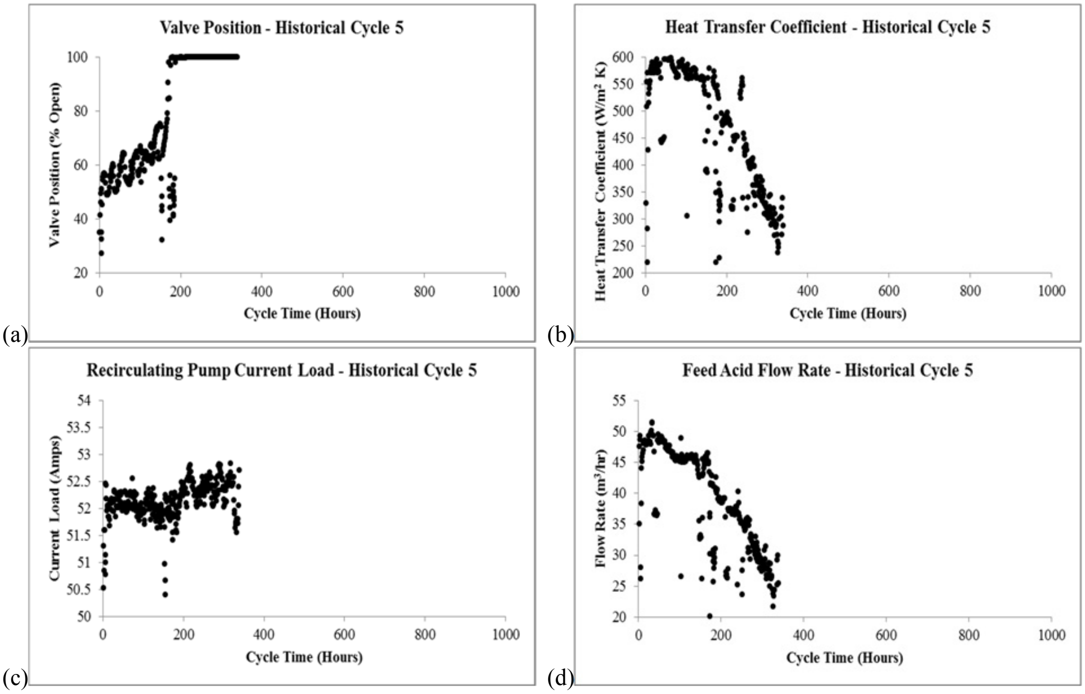


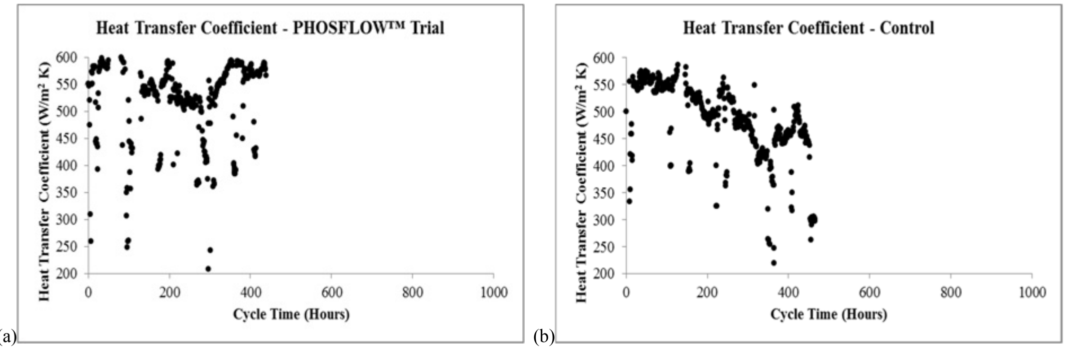
Figure 2. Historical data for a select cycle including (a) valve position; (b) heat transfer coefficient; (c) current load on recirculating pump; (d) feed acid flow rate

The historical data illustrates the degree of variability that occurs in plant processes. Nevertheless, some general observations can be drawn from the data and are summarized in the points below:

- The valve position during each cycle typically starts around 50% open and gradually rises as scale builds up in the pipeline and begins to restrict flow. A washout of the feed acid line typically occurs around mid-cycle when the acid flow rate slips below 39 m^3/hr.
- The heat transfer coefficient typically decays throughout most cycles. This parameter is confounded with acid feed rate so it must be taken in context with that. The customer process engineers indicated a value above 450 W/m^2 K with flow rate equal or above 45 m^3/hr indicates the heat exchanger and feed line are running well.
- Current load on the recirculating pump can be an indicator of tubes being plugged restricting flow. In general, a gradual increase in current load is observed in all cycles with several cycles having severe upward trend (see appendix A).
- The feed acid flow rate shows a general trend of decreasing flow rate as the cycle time increases.

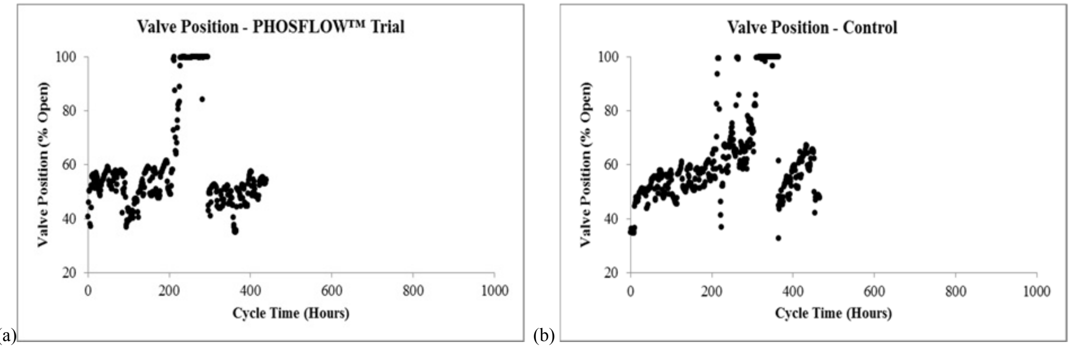
3.2. Results from three week trial of PHOSFLOW™ antiscalant

The antiscalant was dosed into the outlet side of the feed line pump carrying 28% P_2O_5 acid from a storage tank to a heat exchanger designed to increase the acid concentration to 54% P_2O_5. The dose was set at 50 ppm (vol/vol) for the duration of the trial and monitored regularly. Figures 3-6 below show a comparison of the process parameters for the antiscalant treated cycle as well as the cycle immediately after designated as a control cycle.



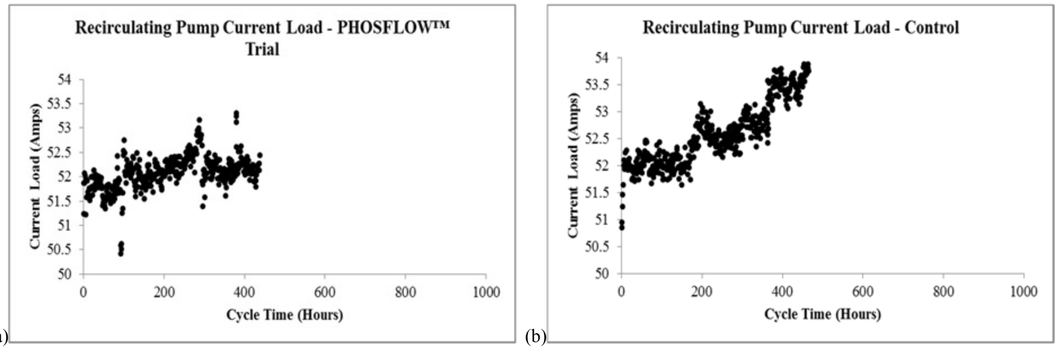
(a) (b)

Figure 3. Data for heat transfer coefficient for (a) PHOSFLOW™ treated cycle and (b) control cycle



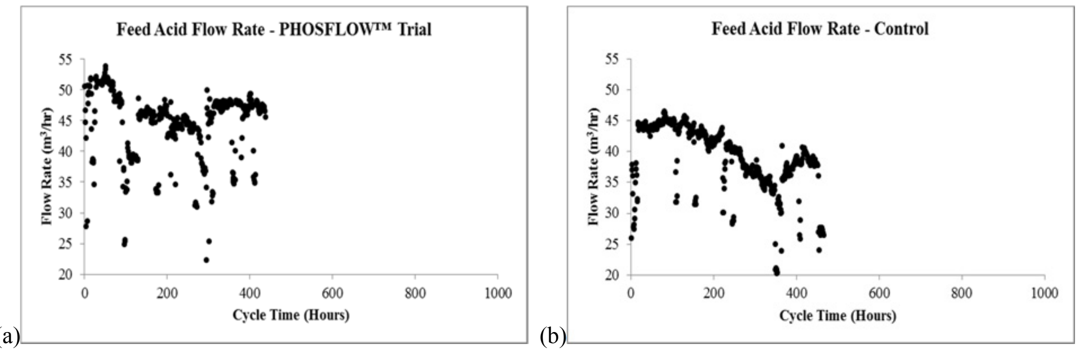
(a) (b)

Figure 4. Data for valve position for (a) PHOSFLOW™ treated cycle and (b) control cycle



(a) (b)

Figure 5. Data for current load on recirculating pump for (a) PHOSFLOW™ treated cycle and (b) control cycle



(a) (b)

Figure 6. Data for feed acid flow rate for (a) PHOSFLOW™ treated cycle and (b) control cycle

With the exception of the valve position parameter, all other data points indicated that the antiscalant effectively controlled the scale buildup in the feed acid line and heat exchanger, especially compared to the control cycle. It can be observed that the flow rate, heat transfer coefficient and current load were all maintained to a greater degree than in the control cycle. With respect to the feed acid line, it did require a washout as the data indicated a blockage occurred however it should be noted that the slope of the curve before jumping to 100% open and after the washout (where it returned to baseline) was very low in contrast to the control cycle. Additionally, the increase in valve position was not accompanied by a large drop off in flow rate as in the control cycle indicating a reduced scaling rate. Thus a higher rate of production was realized in the antiscalant treated cycle.

When the heat exchanger was opened and inspected, it was observed that only 18 tubes were plugged compared to a historical average of 150. Additionally, the cleanout using a high pressure water lance took approximately one hour compared with a historical average of 15 hours.

The data and visual inspection results showed great promise for extending the cycle length of the heat exchanger, thus it was decided to continue the evaluation with a trial aimed at doubling the cycle time.

3.3. Results from extended 6 week trial of PHOSFLOW™ antiscalant

As with the 3 week trial, the antiscalant was dosed into the outlet side of the feed line pump carrying 28% P_2O_5 acid from a storage tank to a heat exchanger designed to increase the acid concentration to 54% P_2O_5. The dose was set at 50 ppm (vol/vol) for the duration of the trial and monitored regularly. Figures 7 and 8 show the data from the process parameters of interest for the antiscalant treated cycle.

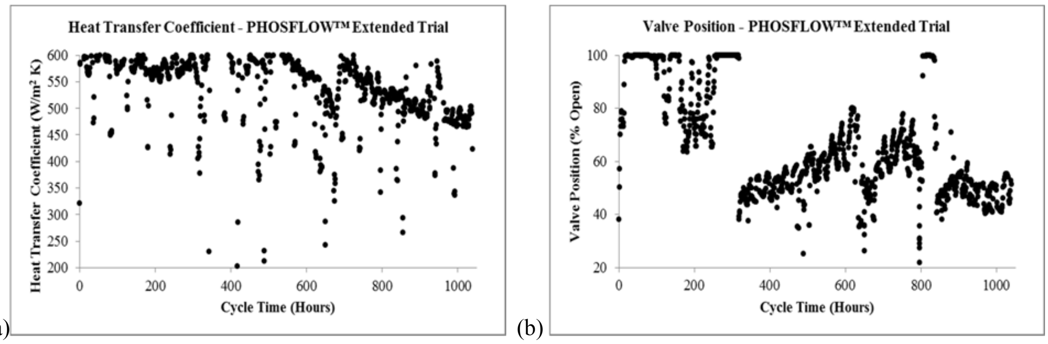


Figure 7. Data for heat transfer coefficient and valve position for extended evaluation of PHOSFLOW™

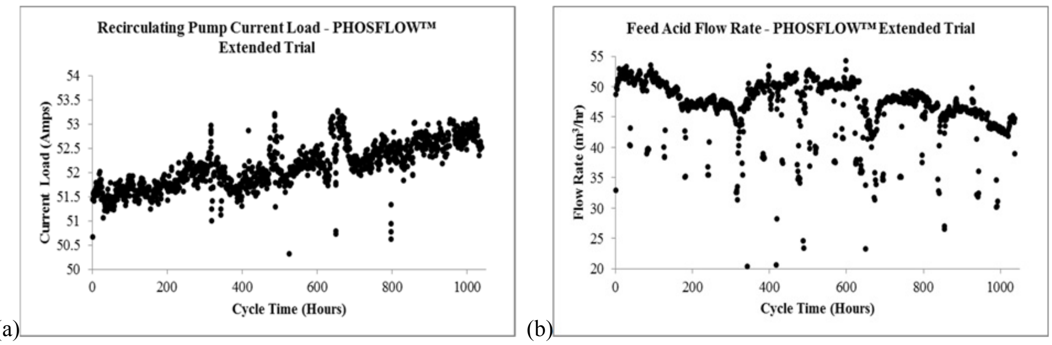


Figure 8. Data for current load on recirculating pump and feed acid flow rate for extended evaluation of PHOSFLOW™

The data for the process parameters show a successful extension of the cycle time without as significant degradation in heat transfer coefficient, feed acid flow rate, or increase in pump current load. In the case of valve position, it can be observed that the line was not cleaned out sufficiently from the start and that it had already developed a blockage. Nevertheless, the antiscalant allowed for production level flow rates for a significant period of time before the line was washed. No additional line cleanouts were necessary during the remainder of the trial which lasted an additional 700 hours past the first cleanout. This is significantly more than their average cycle time from historical data of 486 hours so a mid-cycle wash was effectively eliminated.

When the heat exchanger was opened and inspected, it was observed that only 66 tubes were plugged compared to a historical average of 150 tubes for a 3 week cycle. Additionally, the cleanout time using a high pressure water lance took approximately 2.5

hours compared with a historical average of 15. The operators observed that the scale was very soft and easy to remove from the heat exchanger tube walls.

4. Conclusion

The plant trial results demonstrate that Cytec Industries PHOSFLOW™ antiscalant technology provided a significant benefit in terms of controlling scale buildup within process pipelines and heat exchangers of a phosphoric acid plant. Figures 9 and 10 summarize the results of the three trials and new process option available by applying the antiscalant. The trials were considered a success and are leading to further evaluations of the technology at this customer's plant and others to help establish the robustness of the technology.

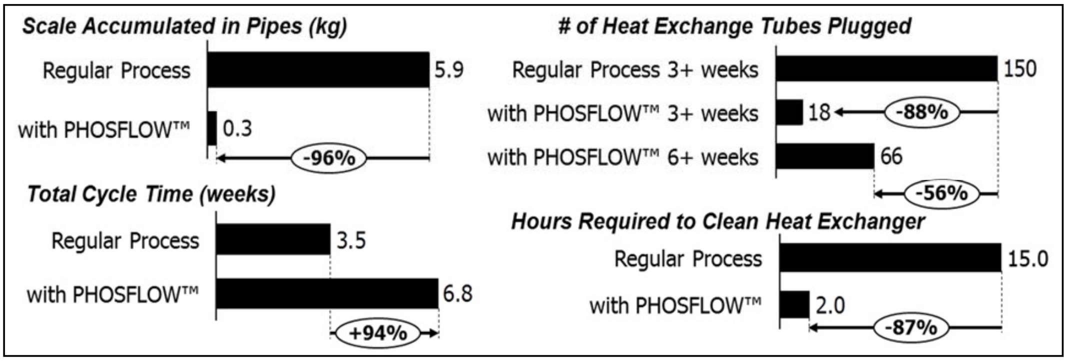


Figure 9. Compilation of plant trial results for application of PHOSFLOW™ antiscalant technology

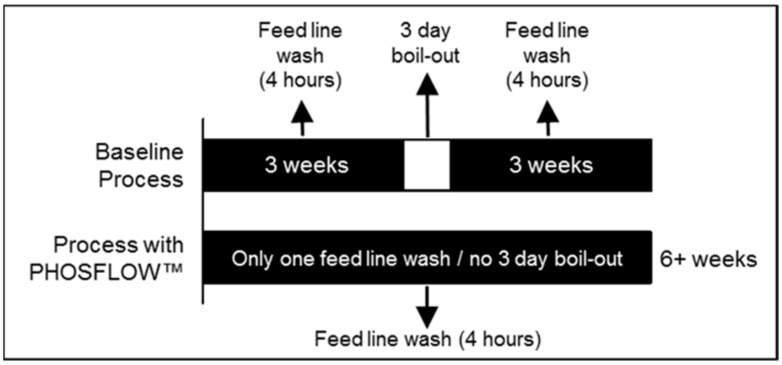


Figure 10. Comparison of customer's historical process with one using PHOSFLOW™ antiscalant

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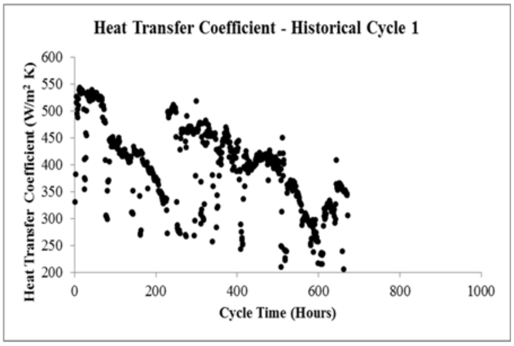
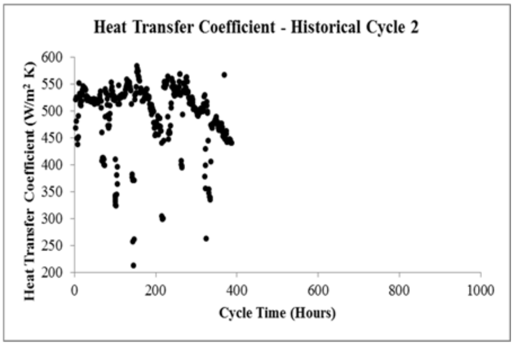
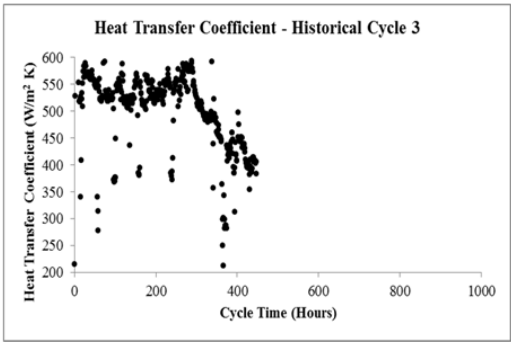
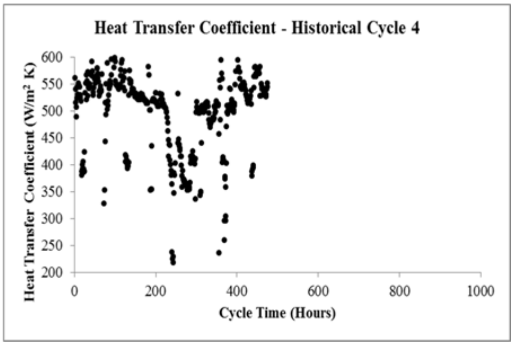
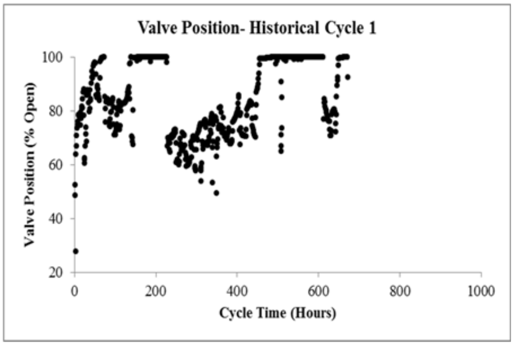
Appendix A. Historical cycle data graphs; heat transfer coefficient, valve position, recirculating pump current load, and acid feed flow rate.

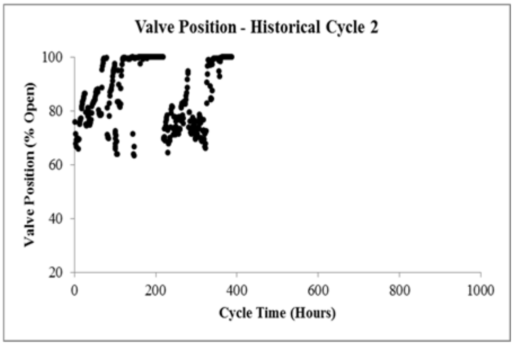


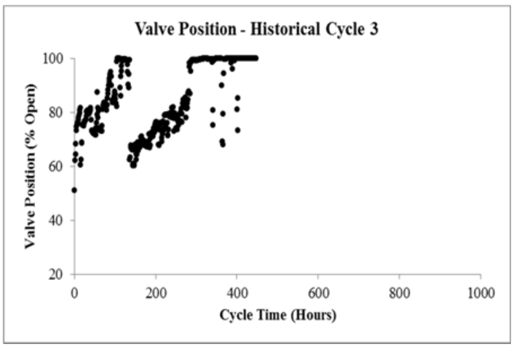


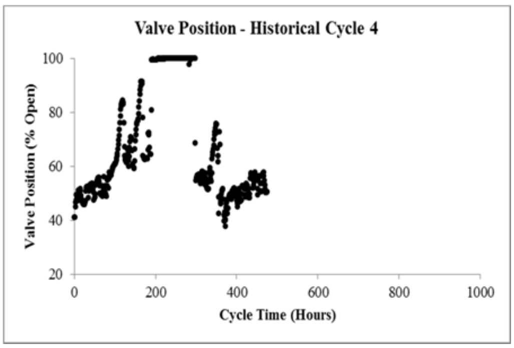


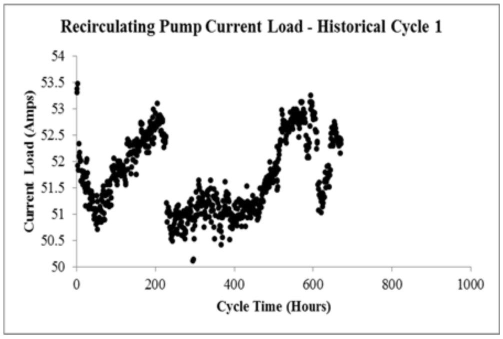


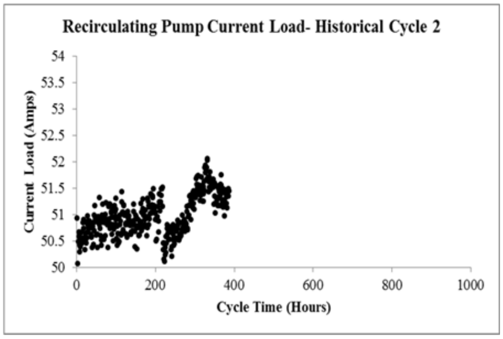


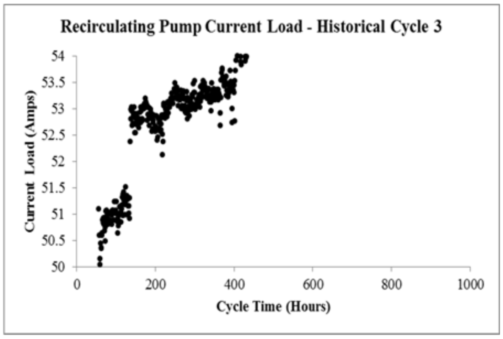


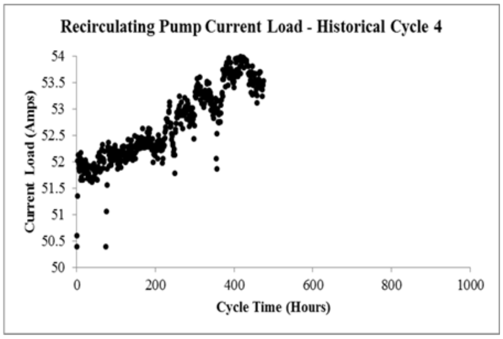


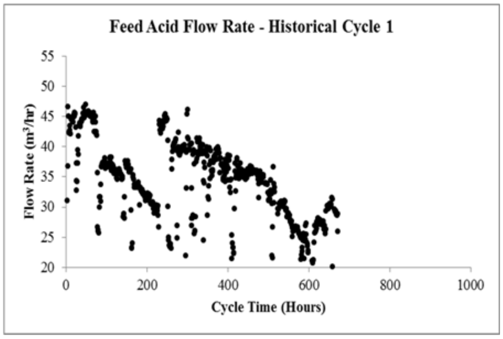


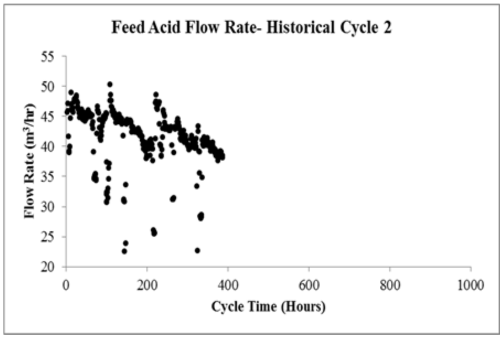


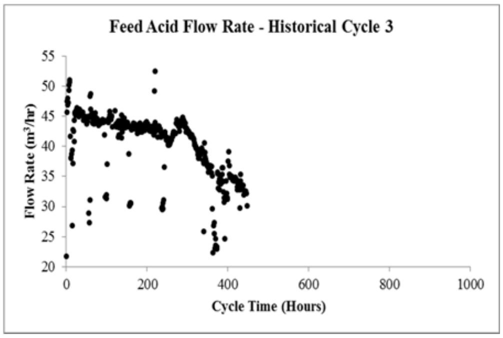


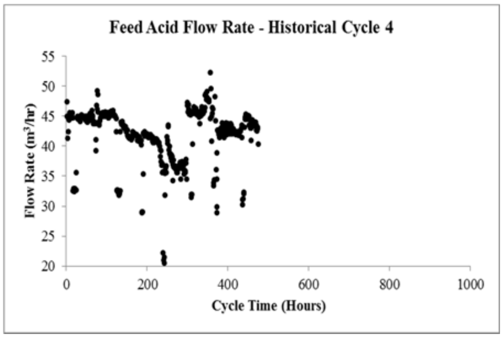












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