3D TRASAR and the MOC Approach – Treating the Whole Cooling Water System with an Example from ExxonMobil (Esso), Campana, Argentina

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Refining and petrochemical cooling water systems often provide the most difficult challenges in the water treatment industry. High skin temperatures and low water velocities, degrading quality of incoming make up water streams, tightening environmental restrictions combined with shrinking capital and variable budgets continue to increase the difficulty in treating these systems. The combination of stresses can adversely impact reliable operation of the asset. Poor performance of a cooling water system will increase the unit's total costs and reduce the assets reliability and throughput.

Corrosion and scale will adversely impact the site's ability to operate reliably. Corrosion can lead to unplanned outages due to exchanger leaks. These can result in lost production/profit opportunities, increased maintenance costs and possible environmental issues. Scale deposition inside exchangers will reduce heat transfer, increasing energy consumption and possibly requiring unscheduled outages to clean exchangers.

In this paper we will review Nalco Company's approach to addressing the whole system. This approach has been utilized with great success within Nalco during the past 5 years. It can be summarized into two broad application points: **3D TRASAR** technology and the **"MOC Approach."** This total system approach was utilized at ExxonMobil (Esso) Refinery in Campana, Argentina and the results are shared in this report.

3D TRASAR

The term "3D TRASAR" is Nalco's platform technology in treating all cooling water. It is a combination of chemistries, hardware and integrated data management designed to reliably deliver the targeted results. 3D TRASAR is successfully treating over 1,000 petrochemical and refining cooling towers globally. Since Nalco's initial deployment of 3D TRASAR in 2004, Nalco has installed over 9,000 operating 3D TRASAR units across all cooling water systems globally.

3D TRASAR - Chemistries

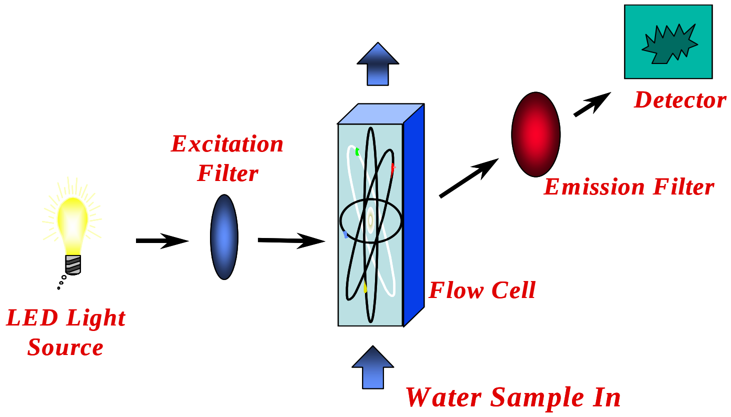
3D TRASAR for open recirculating cooling systems is designed to provide superior corrosion and scale protection, even during upset conditions. The 3D TRASAR program was developed from the need to create one simplified program that could cost effectively operate across a wide range of our customers operating conditions. The backbone of the new program is a combination of Nalco's proprietary PSO (Phosphinosuccinic Oligomer), THSP (Tagged High Stress Polymer) and "Traced" orthophosphate molecules. PSO overcomes the shortcomings of traditional cathodic corrosion inhibitors like pyrophosphate and zinc. The THSP polymer allows the program to perform in today's variable and high stress operating conditions with automated response to upsets. The result is one basic program that can be optimized to deliver superior performance across most of our customers operating conditions.

A typical 3D TRASAR based program includes the following chemistries:

1. **PSO (Phosphinosuccinic Oligimer)** - A non-reverting, dual function phosphinate that provides cathodic (pitting) corrosion inhibition (replacing pyrophosphate and/or zinc) it also replaces HEDP/MoO_4 based programs. It provides moderate calcium carbonate inhibition (replacing HEDP, PBTC). The PSO overcomes the reversion/degradation issues of pyrophosphate and is many times more soluble than zinc at high pH's and does not require polymer to maintain its solubility.

2. **Traced Ortho-phosphate** - Provides anodic (general) corrosion protection with the advantage of on-line dosage automation to ensure correct dosage application. Too much ortho-phosphate can lead to scale deposition in low flow or high heat flux exchangers. Too little ortho-phosphate will allow increased corrosion. The fluorescent tracer greatly improves PO_4 control.

Figure 1 - Basics of fluorescence measurement.



3. **THSP (High Stress Polymer)** - A stress resistant polymer for CaPO4, FePO4 and general silt dispersion that allows for on-line, real-time automation of active polymer control. The on-line automation allows the system to respond to system demand or upsets by immediately feeding the amount of product required to always maintain the targeted dosage of active polymer. The active polymer dosage is analyzed every 6 seconds via fluorescent and does not require the use of chemical reagents to complete the analysis. A schematic showing the functionality of traditional polymer control is shown in Figure 2 below. The use of fluorescence tagged polymer control is in Figure 3.

Figure 2 – Traced Polymer Control

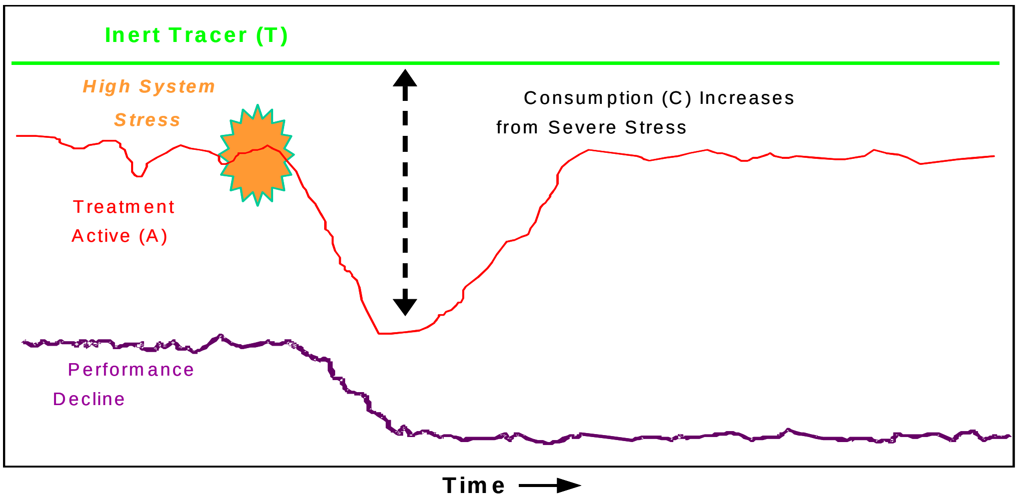
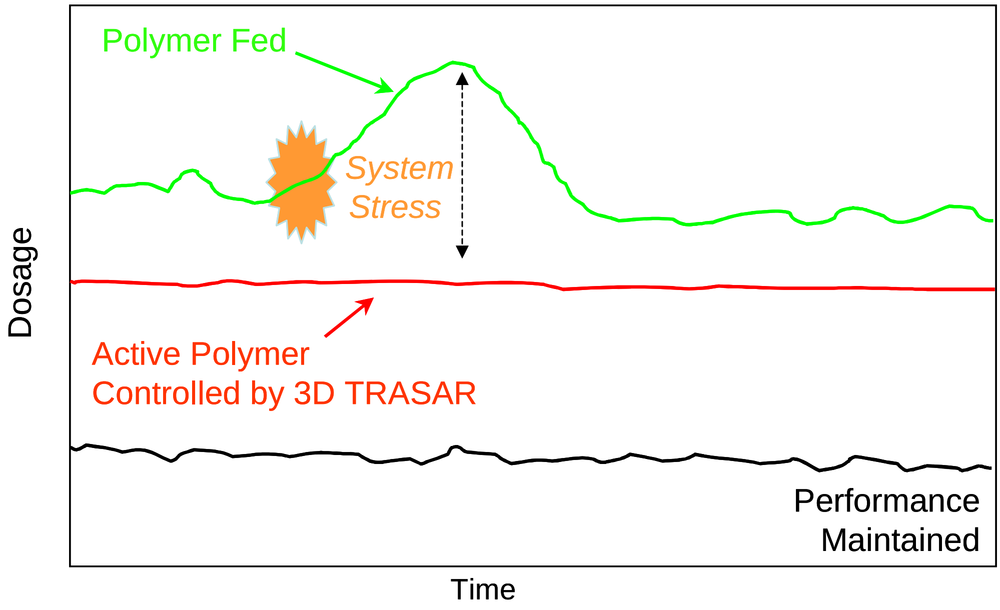


Figure 3 – Active Polymer Control using 3D TRASAR



The 3D TRASAR program is a very robust chemistry, applicable over a wide pH range similar to heavy metal programs of the 70's. The program application can be simple, PSO and Traced ortho PO4 is all that is needed for corrosion control and polymer for deposit control. If yellow metal is present in the system, an azole product is also included. Highly stressed systems with unusual levels of sulfate, chlorides or other aggressive ions might include the addition of zinc.

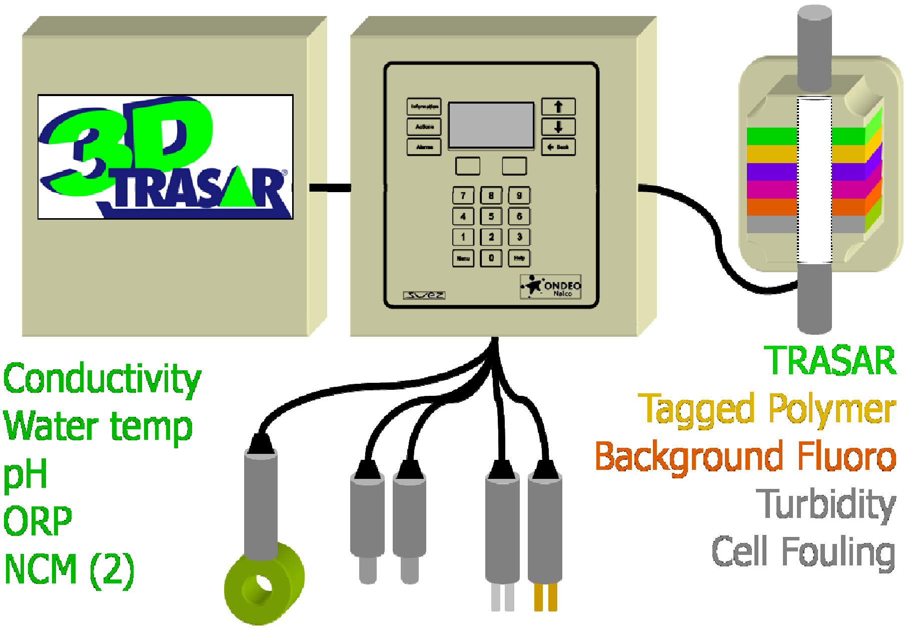
PSO is a halogen and calcium stable cathodic inhibitor that does not revert or require polymer and pH to maintain solubility. It has been proven to be as effective as pyrophosphate and zinc as a cathodic inhibitor. Since it is stable, feed and control problems are eliminated making the program more robust. Overfeed of the inhibitor will not cause any precipitation problems. It is effective from neutral pH all the way through high pH applications. It will not revert in the drum upon storage and is completely stable in cooling systems to the presence of oxidizing biocides.

Ortho PO_4 is the anodic inhibitor. This can be obtained from make up water sources or from the addition of phosphate. The effectiveness of the 3D TRASAR hardware to continuously monitor the ppm dosage level of the Traced ortho-phosphate product feed is key to ensuring the tower's ortho-phosphate remains inside its targeted control range. Also the THSP polymer is very effective calcium phosphate dispersant, maintaining the phosphate's solubility to prevent scale and improve corrosion inhibition.

3D TRASAR programs use THSP (Tagged High Stress Polymer). THSP solves the problem of polymer consumption caused by varying system stresses and upset conditions. A fluorescent tag is incorporated onto the THSP molecule, allowing the 3D TRASAR controller to maintain a specified active polymer level in the system at all times, even under varying stresses and upset conditions when polymer consumption increases. The 3D TRASAR controller constantly monitors the active polymer level in the system, when system stresses increase polymer consumption; the controller automatically reacts by feeding more polymer to compensate for increased consumption. Likewise, when system stress decreases, the feed rate of THSP polymer is reduced automatically.

3D TRASAR – Hardware

A key component of the 3D TRASAR offering is the equipment. This hardware is capable of monitoring all measured parameters every 6 seconds, recording the data at any desired rate and can send the data and alarms over the internet for rapid response to upset conditions. The hardware includes pH, conductivity, ORP and product dosage control as well as containing 2 NCM (on-line corrosion monitoring probes) and turbidity monitoring. This is shown below (Figure 4).



A variety of automatic control conditions can be set up in the controller to respond to upset conditions. This smart-response logic allows the user to set up various types of responses to multiple alarm settings. This can respond by either with the pump on, with the pump off, or at a constantly learned feed rate setting that is an "average" feed rate. This is based on a running average of the past seven days of % of the pump operating. Then if the system goes into this specified alarm mode, the pump will operate at this average feeding every 15 minutes. A photograph of a typical 3D TRASAR industrial installation is shown in Figure 5 below.

Figure 5 – Industrial 3D TRASAR Installation

3D TRASAR – Integrated Data Management

The 3D Trasar controller holds a variety of data – it collects and stores the on-line data, it records a variety of calculated data and an event log to record alarm conditions. This data can be stored and retrieved locally or sent over a land or wireless device to a central server for display and archiving. Any automatically generated alarms are sent immediately via the local communication method to up to 25 recipients. This data is available to view and analyzed with software that can provide multiple statistical analysis methods, allowing you to view multiple parameters in relationship to one and other for diagnostic analysis. Below in Figure 6, is an example of the "Data Dashboard" for the control parameters of a cooling tower. Any of these parameters can be individually or grouped together for statistical analysis comparison.

Figure 6 – "Data Dashboard" Monitoring

Intervalo estadístico:
7 días

Haga clic en un parámetro para abrir los informes.

CLAVE: ADVERTENCIA - PELIGRO -

Nombre del parámetro	Fecha y hora	Último valor	PROM.	Mín.	Máx.	Desv. est.	Límite crítico bajo	Límite bajo	Límite alto	Límite crítico alto	Último valor
Yokogawa pH (pH)	20/07/2009 12:00:00	7,61	7,56	7,24	7,73	0,08	6,75	7	8	8,25	
Hach CL-17 (ppm)	20/07/2009 12:00:00	0,29	0,29	0,1	0,83	0,11	0,1	0,15	1	1,25	
Steel Corr. Rate (mpy)	20/07/2009 12:00:00	1,15	1,28	0,9	1,96	0,27	---	---	2	2,5	
Brass Corr. Rate (mpy)	20/07/2009 12:00:00	0,12	0,14	0	0,23	0,03	---	---	0,75	1	
Conductividad (µS/cm)	20/07/2009 12:00:00	2313,3	2507,26	2213,35	3152,53	259,7	2500	3000	4000	4500	
Potencial redox (mV)	20/07/2009 12:00:00	349	312,98	218	478	49,97	50	100	500	600	
pH	20/07/2009 12:00:00	7,8	7,44	6,33	8,01	0,32	6,75	7	8	8,25	
Dosis de polímero marcado (ppm)	20/07/2009 12:00:00	74,57	76,81	72,97	89,46	2,42	40	50	100	110	
Temperatura (°C)	20/07/2009 12:00:00	28,76	31,05	23,38	40,11	-12,48	0	4,44	48,89	60	
Dosis de TRASAR (ppm)	20/07/2009 12:00:00	15,43	16,44	14,7	20,02	0,87	5	10	25	30	
Turbidez (NTU)	20/07/2009 12:00:00	10,91	9,77	7,25	13,89	1,74	---	---	30	50	

"MOC" Approach

Mechanical Survey

Yet prior to any implementation of the various components of the 3D TRASAR technologies, the first step in successfully treating the cooling water system is understanding the unique characteristics of that specific system. The initial step is a system audit. This audit process is used to identify ways to maximize the performance in each area to improve system reliability and throughput while lowering the total system costs. A Mechanical analysis helps develop a cooling water system profile of all exchangers. On-line measurements of water flow rates and temperatures are compared to exchanger design to identify any gaps. These gaps are assets where the increased stresses at the exchanger could lead to increased potential for corrosion and/or scale. Detailed line diagrams are completed as well and compared to existing P&ID drawings to ensure a full understanding of where problem exchangers are located across the cooling water circuit. This can also provide insight into the stresses that are impacting that exchanger's performance.

Operational Survey

Another area of importance is an assessment of the system's capability to control the various operational components needed for achieving targeted performance. This is frequently a main contributor to a program's inability to succeed. Inability to adequately control pH, active polymer, ortho phosphate, conductivity and halogen levels are common issues. Historical performance data versus targeted control ranges is statistically assessed to determine if the system is capable of the desired control. This exercise will identify gaps in control capability and lead to recommendations necessary to improve the system's capability.

Chemical Survey

Mineral Solubility Sensitivity Analysis is used to determine potential scaling or corrosion conditions using the physical data from the mechanical survey, with control window determined by the operation survey and combining it with any make up water variations. This provides a highly detailed analysis of water chemistry scenarios that can initiate corrosion of scale at a given exchanger location.

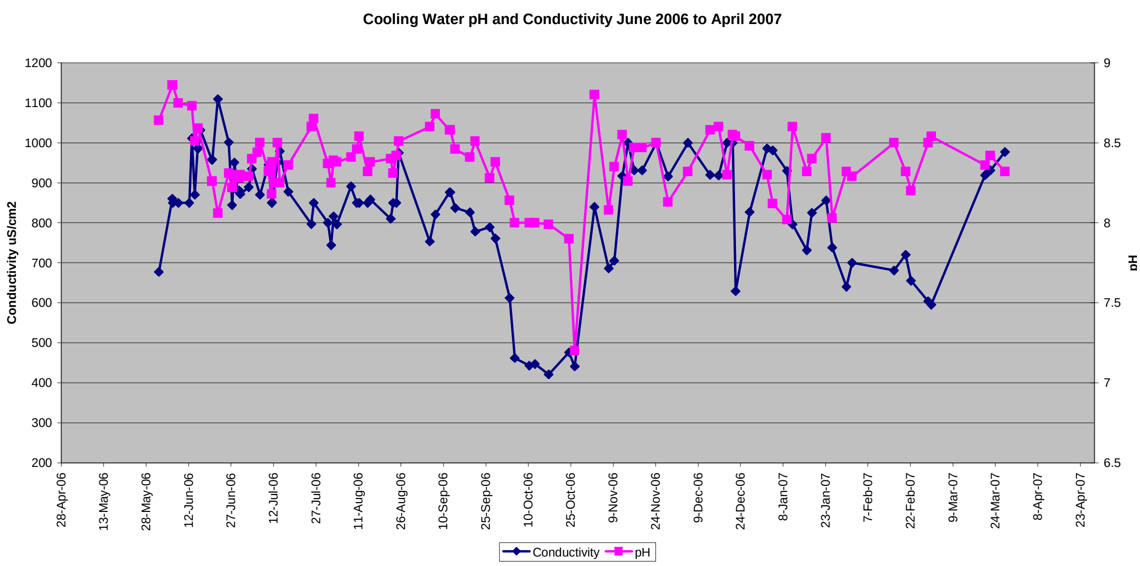
Implementation

The rest of this paper is designed to show how these principles were applied to the ExxonMobil (Esso) refinery in Campana, Argentina. The initial MOC survey noted a variety of issues within the cooling water system that reduced the reliability of the cooling water utility in the refinery operation. These included items such as: highly stressed exchangers, manual feed and control of corrosion inhibitor and dispersants with a highly variable Make Up River water source, the desire to not feed acid for pH control, single cooling tower serving a variety of operating units, and debris and chip scale fouling issues due to a lack of routine exchanger back-flushing.

The initial Mechanical review showed that the plant was monitoring ~25 exchangers on a monthly basis or ~20% of the plants total. During the summer months, several exchangers experienced outlet water temperatures of ~50 °C with one (designated E-006) that would range from 70-80 °C. This one hot exchanger was critical to the plants operation and could not be taken off line to clean without shutting down entire sections of the plant. Additionally, 5 of the exchangers operated below minimum flow rate needed to maintain 1 m/s cooling water flow velocity necessary to minimize fouling and maintain corrosion protection. While 4 exchangers appeared to see very high flow rates that could promote erosion corrosion as these were copper alloyed exchangers.

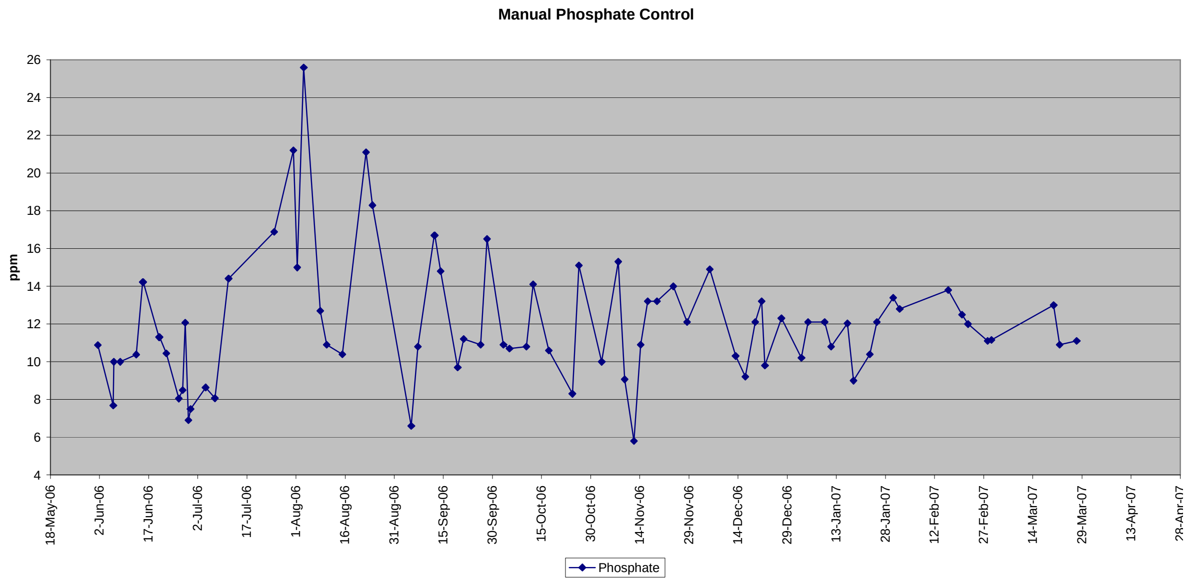
The operation survey showed the challenges of trying to maintain cycles of concentration and a stable pH when using variable river water as a MU source to the cooling tower. This is shown in Figure 7 with the conductivity and pH both seeing wide variations.

Figure 7 – Cooling Water pH and Conductivity Control



This is also reflected on the affect of manual control on the orthophosphate corrosion inhibitor portion of the treatment program prior to Nalco servicing the system.

Figure 8 – Manual Control, Cooling Water PO4 Treatment Levels



The Chemical analysis of the MU water shows typical seasonal variations on water composition. The MU water in the chart below is an analysis period of over 16 months.

Figure 9 – Historical Variation of Make up water

Parameter	Average	3 σ Standard Deviation
pH	7.23	0.87
Conductivity (uS/cm)	126	92
M Alkalinity (as $CaCO_3$) ppm	29	44
Calcium (as $CaCO_3$) ppm	19	23
Total Hardness (as $CaCO_3$) ppm	33	45
Silica (as SiO_2) ppm	15	5

The largest issue with this make up water variability is the resulting impact it has on the cooling water:

- pH is highly dependent on the control of cycles of concentration (concentration of alkalinity)
- Calcium to conductivity ratio is not constant

This is important because acid is not used for pH control. The fluctuating pH and calcium levels will impact scale potential in the cooling water if only controlled to a set conductivity level. Computer modeling of the water chemistry variability, control limits (no acid feed) and exchanger conditions shows that even a 0.2 pH unit difference can greatly increase the scale potential of the recirculating cooling water in exchangers operating with high outlet water temperatures.

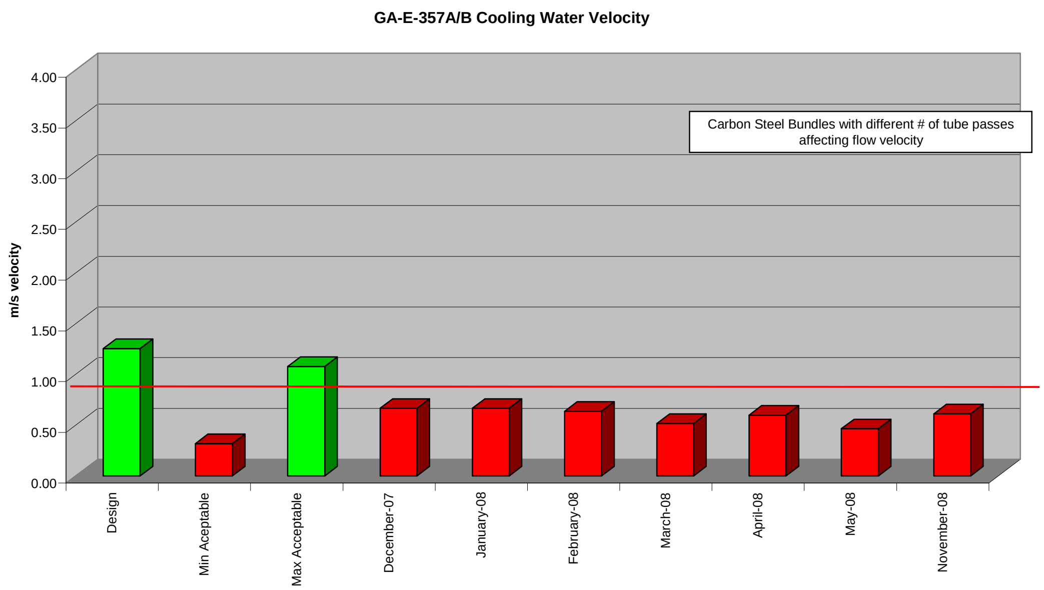
With these known conditions, it was determined that the 3D Trasar based program would be an appropriate fit for the refinery. This program would provide more automation and monitoring as well as automated response to upset conditions and fluctuating water chemistry.

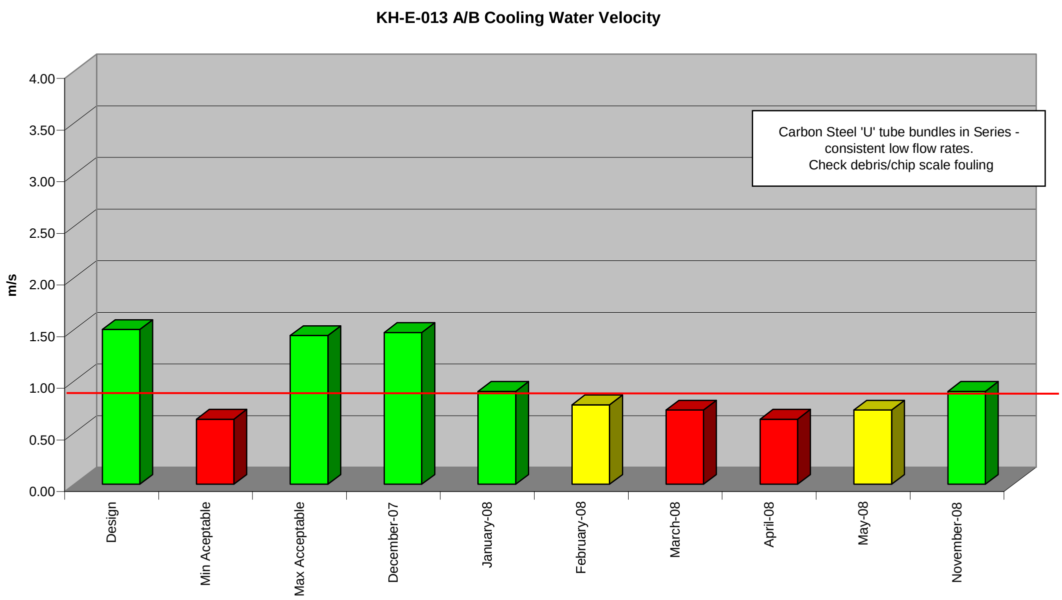
Application

The 3D Trasar program was implemented at the end of August, 2007. Almost immediately the system experienced a series of exchanger leaks, with 11 occurring in the first 8 months after the switch to the new program. The result of an investigation into the causes concluded much of the damage that initiated the leaks was due to a 1 week emergency shut down in May of 2007 when the plant lost electricity and the plant sat idle.

Mechanically the new approach increased the level of monitoring that took place. A baseline study was implemented on every cooling water exchanger, with data comparing baseline and current operation provided on all exchangers. Two examples are shown in Figure 10. In addition, a series of recommendations Nalco made to help improve system performance. One was the restarting of regular back-flushing of exchangers. Also the plant has the ability to flush sludge accumulation from the cooling water basin. This sludge can be a source of bacteria that could continue to inoculate the system with microbiological growth, decreasing microbio control. Other recommendations centered on minimizing debris in the cooling water and minimizing the build up of chip scale in exchangers after unit outages (Turnarounds), etc.

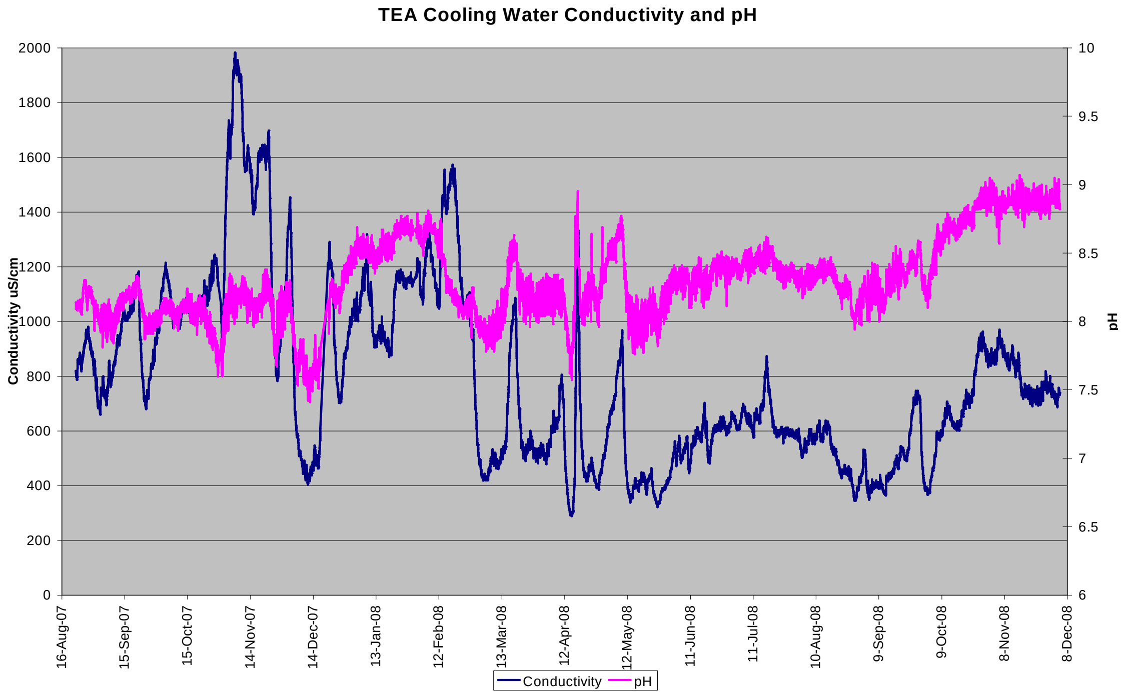
Figure 10 – Exchanger Survey Results versus Design, Water Velocity





Operationally, the overall control of the cooling water system has improved. The tower's conductivity and pH were still variable due to the makeup water fluctuations and the lack of installed automation for the pH or cycles control. Also the initial process leaks that occurred in the system also caused an increase in conductivity variation. This data is shown below in Figure 11.

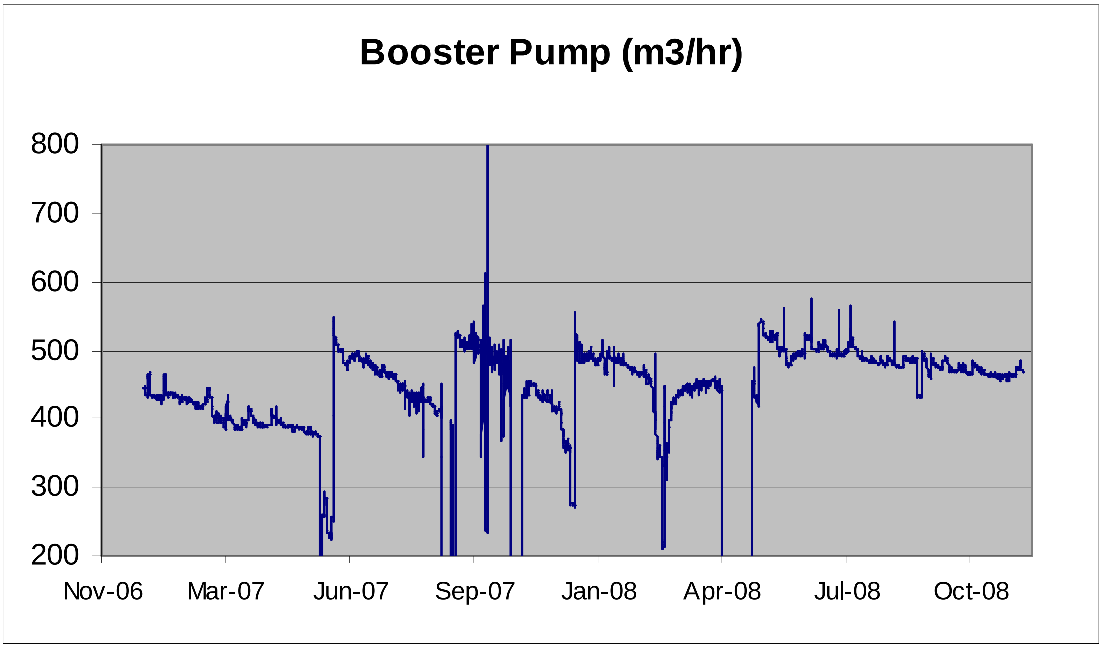
Figure 11 – Cooling Water Conductivity and pH



Control of product actives such as ortho phosphate used for corrosion protection improved from an average of 12.1 $\pm$ 3.3 ppm PO_4 using manual control to 9.8 $\pm$ 1.3 ppm with automated Trasar control. Active polymer control also increased from manual control of 13.7 $\pm$ 2.8 ppm to 9.8 $\pm$ 1.4 ppm with improved fouling and scale inhibition control.

The improved fouling control is shown as by the output of a booster pump used to improve flow at the back end of the plant. This is shown in Figure 12 where the old program would typically see a 100 m^3/hr loss of flow over a 4 month period to the Nalco controlled program where to booster pump loss of flow was only 40 m^3/hr over a 7 month time frame.

Figure 12 - Booster pump output loss due to fouling



A series of chemical treatment improvements were also implemented. The basic program was converted to one utilizing Trasar technology for the basic control algorithm. The anodic corrosion inhibitor used is ortho-phosphate. The total level of ortho-phosphate was reduced due to computer modeling. This showed that high levels of PO_4 with the high operating temperature of E-006 and uncontrolled pH could easily cause fouling. Using a combination of PSO and zinc provided cathodic corrosion control. The zinc provides a fast acting inhibitor while PSO provides a more stable film that takes slightly longer to form. In this way pH fluctuations or sour leaks would have minimal impact on overall corrosion protection. Dispersancy was provided by THSP (tagged high stress polymer) that would respond to MU water and operational changes automatically via the 3D TRASAR controller to minimize or eliminate scale formation in the exchangers.

Computer modeling shown in Figure 13 shows the impact of pH, temperature and cycles of concentration with 10 ppm of phosphate on the scale potential of the water. An increase of the phosphate levels would increase the fouling potential. Figure 14 shows the same conditions only with an increase of total phosphate to 14 ppm.

Figure 13 – Cooling Water Chemistry Modeling

Esso Campana - Cooling Water Calcium Phosphate French Creek Analysis (Scale Reliability)

		Cycles of Concentration				
50 C	Calcium	69	78	87	95	104
10 PO4	8.0	80	98	117	137	157
	8.1	117	144	171	199	228
	8.2	167	204	243	283	324
	8.3	230	282	336	391	448
	8.4	309	378	450	525	601
	8.5	400	490	584	681	781

		Cycles of Concentration				
60 C	Calcium	69	78	87	95	104
10 PO4	8.0	151	184	219	254	290
	8.1	216	263	312	363	414
	8.2	300	366	434	504	576
	8.3	405	494	586	680	777
	8.4	528	644	765	888	1014
	8.5	665	811	964	1120	1279

		Cycles of Concentration				
70 C	Calcium	69	78	87	95	104
10 PO4	8.0	283	343	406	470	535
	8.1	395	479	567	656	747
	8.2	536	650	769	890	1013
	8.3	703	853	1009	1169	1330
	8.4	891	1082	1279	1482	1688
	8.5	1086	1321	1564	1813	2067

		Cycles of Concentration				
80 C	Calcium	69	78	87	95	104
10 PO4	8.0	496	600	708	818	930
	8.1	678	820	967	1116	1269
	8.2	897	1086	1280	1478	1680
	8.3	1148	1389	1638	1893	2152
	8.4	1415	1715	2024	2341	2662
	8.5	1681	2040	2411	2790	3176

Figure 14 - Water Chemistry at 14 ppm PO4

Esso Campana - Cooling Water Calcium Phosphate French Creek Analysis (Scale Reliability)

		Cycles of Concentration				
50 C	Calcium	69	78	87	95	104
14 PO4	8.0	165	218	275	335	397
	8.1	241	318	401	488	578
	8.2	342	452	570	694	822
	8.3	474	626	789	960	1137
	8.4	634	839	1058	1288	1527
	8.5	822	1089	1374	1674	1984

		Cycles of Concentration				
60 C	Calcium	69	78	87	95	104
14 PO4	8.0	259	340	426	515	608
	8.1	370	485	607	735	866
	8.2	513	673	843	1019	1202
	8.3	690	906	1134	1372	1617
	8.4	898	1179	1477	1787	2107
	8.5	1126	1480	1855	2245	2648

		Cycles of Concentration				
70 C	Calcium	69	78	87	95	104
14 PO4	8.0	487	635	792	954	1121
	8.1	679	886	1104	1330	1562
	8.2	918	1198	1493	1799	2111
	8.3	1202	1569	1956	2355	2766
	8.4	1517	1982	2471	2980	3501
	8.5	1844	2411	3011	3635	4275

		Cycles of Concentration				
80 C	Calcium	69	78	87	95	104
14 PO4	8.0	626	818	1021	1232	1449
	8.1	873	1140	1423	1717	2018
	8.2	1180	1543	1925	2322	2728
	8.3	1544	2019	2521	3039	3573
	8.4	1949	2549	3185	3845	4523
	8.5	2367	3102	3881	4690	5522

Summary

The total system approach to addressing the problems at this refinery's cooling water system have eliminated the process leaks and sharply improved the scale, fouling and corrosion inhibition. On-going performance monitoring is accomplished in a number of ways. Exchanger performance will be monitored be the comparison of the exchangers' design data versus their operating data with respect to heat flux, skin temperature and water velocity. On-going wet chemistry testing will also supplement the on-line analyzer of the 3D TRASAR system. This will include pH, conductivity, ORP, carbon steel and admiralty corrosion rates and turbidity. Variations in targeted control parameters are quickly detected statistically analyzed and corrective measures applied. Implementation of new, all-soluble chemistries such as PSO will help minimize the scaling potential in highly stressed exchangers. The total system approach has successfully improved the performance of this cooling water system, increasing reliability and improved the total profitability for the site.