Use of Reclamation for Amine Hygiene Management

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ABSTRACT

The build-up of heat stable salts and amine degradation products (residue) has long been a concern for refinery and gas plant amine treating systems. Historically, when disposal and amine prices were low, a bleed and feed approach was often an economical solution. As amine and disposal prices have risen along with more stringent environmental concerns, refineries and gas plants have focused on amine management. While this has resulted in system optimization and amine make-up minimization, it has also resulted in faster residue build-up and thus more frequent action to maintain or improve amine hygiene. Several reclamation technologies including both on-site and off-site options exist to assist in amine hygiene management. Choosing the right technology for each operating unit is a critical step with regards to proper amine hygiene management. System size, amine type, contaminant level, contaminant type, utilities, waste disposal, permitting and of course cost all influence the reclamation decision. This paper provides an overview of three refineries and their respective amine hygiene management techniques.

COST CONSTRAINED REFINERY GAS TREATING

Over the past twenty years refinery margins have fluctuated widely, often causing operating companies to enforce severe cost constraints. When evaluating opportunities for cost savings and world class performance, amine consumption in refinery gas/liquid treating service was an early target. The cost of consumable products is easy to track, so early efforts focused on minimizing amine consumption. The studies revealed that treating systems that ran well and were initially in the top quartile for reliability began to falter over time.

Fifteen to twenty years ago Shell spent considerable effort in defining the parameters that needed to be maintained in order to achieve top quartile cost and reliability for refinery gas/liquid treating systems. Instead of examining only amine consumption cost, Shell decided to focus on total cost of operations. This effort was inspired by the Amine Best Practices Group and their survey publication results, and buoyed by a focused directive from central or corporate technical groups.

Operating parameters were studied and refined. As the data were evaluated, world class reliability and performance could be tied to proper operating windows as well as proper amine hygiene control. Over the course of time, Shell developed key parameters for each refinery treating system. Specific clear guidelines were also developed so that each refinery could be "graded" at the end of the year. Key areas could then be addressed the following year. These parameters eventually evolved into the Shell Amine Recovery Unit (ARU) Annual Score Card.

ARU SCORE CARD

Senior Shell senior management and key personnel use the ARU Score Card to compare performance among operating units. (See Table 1) This concise piece of information focuses future efforts and is also one part of The Amine Solvent Management Program utilized by Shell and administered by Shell Global Solutions (US) Inc.

The ARU Score Card was developed in response to the realization that the amine inventory in refineries represents a serious investment of millions of dollars, and there is a desire to protect this asset as well as the associated process equipment. The global initiative is to continue to minimize amine purchases without compromising solvent hygiene and unit reliability. The Score Card is a way to ensure that all Shell manufacturing locations are utilizing Best In Class practices, and provides direction for detailed investigation into any deficiencies that may exist.

The key aspects covered in the ARU Score Card are as follows;

1. <u>Amine Inventory Replacement</u>
   Tracks amine purchases and compares them to the total amine inventory of each individual unit. Tracking is for primary treating systems only. The goal is for a world class performance compared to the rest of the industry.

2. Reclaim Cost Per Pound Of Amine Inventory
   Track reclaiming or solvent hygiene quality cost compared to the amine inventory of each individual unit. Some reclaiming technologies are more robust than others so cost adjustment factors are taken into account (plus or minus). Logistics can make this value site specific and while cost adjustment factors may be necessary, areas for improvement are easily identified.

3. Amine Quality (Solvent Hygiene)
   Six specific measured guidelines are monitored and ranked versus Best In Class targets. Some of these targets are global, but many are specific for individual systems.

4. Scheduled Sample Analysis
   Track the sample frequency to ensure that all values are properly monitored. This also maintains historical data for each individual system. Sample frequency global guidelines are firmly established and adjusted for specific individual systems.

5. Shell Global Solutions Technical Services
   Scheduled visits by Shell technical experts promote knowledge management to refinery and central engineering staff. These visits are also part of a young professional's development program.

TOTAL COST OF OWNERSHIP

The unit operator and support staff track the total cost of ownership for refinery gas/liquid treating systems. Capacity utilization and energy index are all tracked from a corporate staffing level and reported accordingly. Other than plant reliability, the items most closely tracked by the plant and support personnel are amine purchases and cost of maintaining solvent hygiene. The costs of these two items are closely related to each other. Shell has studied these costs in detail to find the most effective means of maintaining solvent hygiene while maintaining optimum cost of ownership.

AMINE QUALITY (SOLVENT HYGIENE)

Shell gas/liquid treating systems monitor the amine solution on a frequent basis. Detailed analysis of the solution provides a historical perspective on the various contaminants present in the circulating amine solution. Each component that is measured and tracked is important to ensure reliable unit operations. The treating effectiveness and corrosion potential of the solution is a function of the concentrations of all components. Specific guidelines for essentially all of the contaminants measured have been established based on careful study and years of experience.

Accurate monitoring of data are required to adequately project a reclaiming frequency (onsite/batch), to adequately budget and plan logistics for offsite reclaiming, and in some jobs to determine the cost of each option. Monitoring data involves not only obtaining accurate analytical data, but also a complete knowledge of solvent inventory (which includes amine losses and makeup). Site management should be able to correctly assess and manage the overall hygiene control to avoid *surprise* reclaiming jobs that are not part of the annual budget.

For the ARU Score Card and for a quick overview of each solvent analysis, Shell has established six key items to be tracked as indicators warranting action or further investigation. As previously mentioned, these six items (Big Six) provide a quick overview of the solvent quality and may be used as a basis for developing targets for solvent hygiene guidelines. Solvent hygiene guidelines for each gas/liquid treating system will have specific targets for these six items, as well as individual contaminant guidelines unique to each operating unit.

PROPER RECLAIMING TECHNOLOGY SELECTION

A "bleed and feed" type of approach has generally been found to be the least desirable method to maintain solvent hygiene due to environmental cost considerations. Conventional thermal reclaiming has been successfully used for MEA and DGA® systems, but an alternative technology must be selected for the other types of amines typically used in refinery gas/liquid treating systems due to higher boiling points. The options for third party or "merchant" reclaiming technologies currently offered to the industry are:

1. <u>Vacuum Distillation</u>
   Off-Site/On-Site/Permanent Options Available
2. <u>Ion Exchange</u>
   On-Site/Permanent Options Available
3. <u>Electrodialysis</u>
   On-Site/Permanent Options Available

The first step in the selection process for the various reclaiming technologies is to select the option that will remove all of the contaminants that are required to properly improve the solvent hygiene to the desired levels. Diethanolamine (DEA) is widely used in the Shell system, so global and DEA specific contaminant removal must be considered for reclaiming technology selection. Based on technical investigation and years of experience Shell has selected vacuum distillation for their refinery gas/liquid treating systems. See Table 2.
It is important to stress that the technology selection must be based on the ability to remove the desired contaminants and remove them to the level that is required.

The second step in the selection process for the various reclaiming technologies is to select the off-site or on-site option based on site-specific requirements, areas of concern, or potential limitations. Other than the cost of the services from the reclaiming supplier, there are many items to consider when evaluating any potential reclaiming project cost and logistics. Some of the items for consideration would include;

1. Duration of contractor onsite
2. Contactor safety performance
3. Supervision requirements for on-site contractor
4. Permitting requirements from state agencies
5. MOC and site permitting requirements

6. Utilities availability and cost
7. Piping and containment cost
8. Chemical requirements and cost
9. Waste/process stream storage requirements and cost
10. Waste classification, disposal options and cost
11. Available footprint and foundation
12. Transportation cost
13. System volume
14. Schedule criticality and risk

PERMANENT RECLAIMING FACILITIES

As mentioned earlier, MEA and DGA® systems do employ a slip-stream thermal reclaimer due to their respective low boiling points. Shell has reasonably good experience operating these types of reclaimers as well as similar slip-stream thermal reclaimers for Flexsorb® and Sulfinol-D™. Over the past few years improvements in design and operating guidelines have made these reclaimers an efficient part of Shell's overall solvent hygiene philosophy.

Currently all three reclaiming technologies are offered on a permanent basis in the form of a skid mounted unit available for purchase or lease. Shell has evaluated these permanent solutions for the majority of its manufacturing locations*)*. The annualized cost for the skid unit does not compare favorably when costs for merchant reclaiming in the form of on-site and off-site were annualized. Also additional required technical, operational or maintenance attention is very unattractive to manufacturing locations.

VACUUM DISTILLATION RECLAIMING

Shell has evaluated each of the reclaiming technologies from an investigative standpoint and has tested each technology at manufacturing locations supplied by current vendors. Based on that experience and the requirements for proper solvent hygiene management, Shell chose vacuum distillation for improving solvent hygiene quality in most applications. Historically, solvent hygiene has been improved by using on-site vacuum distillation technology services, and Shell will continue to be evaluate this service ; however, during the past few years it has been found that off-site vacuum distillation technology services has been cost effective. Detailed economic evaluations have been completed with regards to the total cost of the project. Following are three case studies where off-site vacuum distillation met Shell requirements in a cost effective manner.

CASE STUDY ONE – WEST COAST REFINERY

A manufacturing location on the West Coast of the United States has very stringent solvent hygiene parameters. These parameters have been refined over time based on study and actual experience so as to maintain optimal system performance. This location has specific issues that must be included when evaluating reclaiming options.

The system has a moderately high system volume and the containments that must be removed include HSS, DEAF, THEED and oxidative degradation products. This location has stringent state permitting requirements for merchant reclaimers that include environmental emissions/liabilities that must be included in the manufacturing site state reporting. Waste produced from any type of reclaiming also has a high costs associated with its generation and subsequent disposal. Manpower for supervising operation and set up of merchant reclaiming efforts must also be considered.

This location has used merchant vacuum distillation previously with a high degree of success and satisfaction. However, due to the total costs of the on-site option, a detailed evaluation was made in consideration of off-site vacuum distillation, and off-site vacuum distillation was the option selected. Parameters were set for post evaluation and included: contaminant removal, amine recovery, and total cost. For system decline curve, please see Figure 1.

Off-Site Job Summary

	Project Basis	Actual
Contaminant Removal	1	4
Amine Recovery	1	1.17
Total Cost	1	0.84

Contaminant removal was four times better than the target level, and amine recovery was about 17% better than the target level. Both of these targets were based on expectations of the technology selected as well as previous experience. The total cost of the job was approximately 84% of the cost associated with the on-site vacuum distillation option based on actual numbers. Based on the data, the project exceeded all expectations for the manufacturing location and this option is a cost effective, low manpower requirement option for the Shell Amine Solvent Management Program.

Case 1: Project Highlights

- 80% of the system volume sent off-site for reclaiming (batch = best efficiency)
- Low manpower requirements, loading and off-loading by outside operator
- Contractor liability limited/minimized
- Environmental permitting/liability eliminated
- Significant project savings from set-up costs (manpower, etc)
- Significant project savings from utility and waste disposal costs
- Project costs and duration met +/- 5%

CASE STUDY TWO – LARGE REFINERY MAIN SYSTEM

A manufacturing location in the United States has very stringent solvent hygiene parameters for corrosion "avoidance". These parameters have been refined over time based on study and actual experience so as to maintain optimal system performance. This location has specific issues that must be included when evaluating reclaiming options.

The system has a large system volume and the containments to be removed include HSS, DEAF, and THEED. This location has less stringent state permitting requirements for merchant reclaimers, but it does still include environmental emissions and liabilities that must be included in the manufacturing site state reporting. Waste produced from any type of reclaiming has moderate costs associated with its generation and subsequent disposal. This Manpower for supervising operation and set-up of merchant reclaiming efforts must also be considered for this location.

This location has used various merchant reclaiming technologies on-site without a high degree of success and satisfaction. Due to the liabilities and issues of the on-site options, a detailed evaluation was made in consideration of off-site vacuum distillation. This option was selected for technical merits and convenience. During the evaluation process this manufacturing location was willing to pay more for the simplicity of an off-site option based on their previous on-site experience. Parameters were set for post evaluation and these included: contaminant removal, amine recovery, and total cost. For system decline curve, please see Figure 2.

Off-Site Job Summary

	Project Basis	Actual
Contaminant Removal	1	2
Amine Recovery	1	1
Total Cost	1	0.99

Contaminant removal was two times better than the target level, and amine recovery was at the target level. Both targets were based on expectations of the technology selected as well as previous experience. The total cost of the job was approximately 99% of the cost associated with the on-site vacuum distillation option based on actual numbers. Based on the data, the project exceeded all expectations for the manufacturing location and this option is a cost effective, low liability, and low manpower requirement option for the Shell Amine Solvent Management Program.

Case 2: Project Highlights

- 100% of the system volume sent off-site for reclaiming (batch = best efficiency)
- Low manpower requirements, loading and off-loading by outside operator
- Project met the goal of no on-site contractor
- Environmental permitting/liability eliminated
- Significant project savings from set-up costs (manpower, etc)
- Significant project savings from utility and waste disposal costs
- Project costs 10% under budget

CASE STUDY THREE – MID-SIZE REFINERY MAIN SYSTEM

A manufacturing location on in the United States has very stringent solvent hygiene parameters due to the fact that chemical feed stocks are treated with the main system. Any treating issues with the main treating system will greatly affect downstream polishing processes as well as catalyst performance in the chemical plant. These parameters have been refined over time based on study and actual experience so as to maintain optimal system performance. This location has specific issues that must be included when evaluating reclaiming options.

The system has a mid-size system volume and the containments that must be removed include HSS, DEAF, and THEED. This location has less stringent state permitting requirements for merchant reclaimers, but it does still include environmental emissions/liabilities that must be included in the manufacturing site state reporting. Waste produced from any type of reclaiming has moderate costs associated with its generation and subsequent disposal. Manpower for supervising operation and set-up of merchant reclaiming efforts must also be considered for this location.

Due to the liabilities and issues of the on-site options, a detailed evaluation was made in consideration of off-site vacuum distillation. This option was chosen for technical merits and also for the ability of the location to maintain a fairly consistent solvent hygiene. For the past four years, this location has chosen to reclaim on a frequent basis in the form of a Chem Group Services Maintenance Program. For system hygiene curve, please see Figure 3.

As seen from Figure 3, the manufacturing location is able to maintain good solvent hygiene by using the robust vacuum distillation technology for contaminant removal. Parameters are controlled within guidelines and the flexibility is there to adjust reclaiming schedule as required. The system is optimized from an absorption and stripping efficiency standpoint while also minimizing amine losses with a well maintained system. This location was in the top rankings for reclaiming cost and solvent hygiene in the annual Shell ARU Score Card.

SUMMARY

As seen in the above discussion and case studies, vacuum distillation has been shown to fit well within the Shell Amine Solvent Management Program.

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ADDITIONAL SOURCES

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TABLE 1

ARU Score Card

	A	B	C	D	E	F	US Refining
Amine Inventory Replacement	%	%	%	%	%	%	%
Reclaim Cost Per Pound Of Amine Inventory	$	$	$	$	$	$	$
Amine Quality Score	#	#	#	#	#	#	#
Scheduled Sample Analysis Score	#	#	#	#	#	#	#
SGS Technical Services Score	#	#	#	#	#	#	#
Combined Score	#	#	#	#	#	#	#

Key

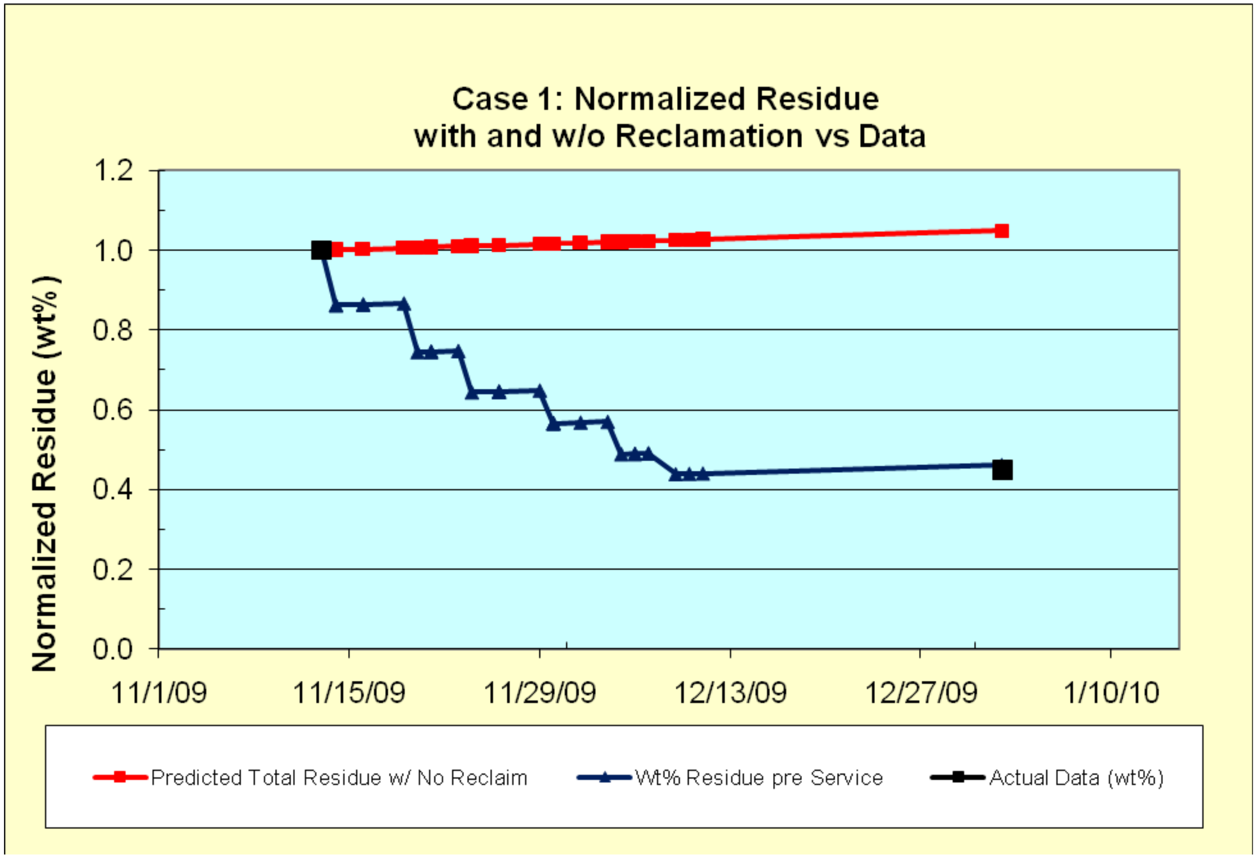
Amine Inventory Replacement	<X%	X-Y%	>Y%	Control Costs and Track Performance
Reclaim Cost Per Pound Of Amine Inventory	<$0.X	$0.X-$0.Y	>$0.Y	Balance Amine Replacement and Solvent Quality
Amine Quality (Perfect Score = AA)	>X	X-Y	<Y	Unit Performance and Reliability
Scheduled Sample Analysis Score	>X	X-Y	<Y	Track Amine Quality
SGS Technical Services Score	>X	X	<X	Knowledge Management
Combined Score	A-B	B-C	<C	

Table 2: DEA Quality (Solvent Hygiene) Management with Merchant Reclaiming Options: Vacuum Distillation, Ion Exchange, Electrodialysis

Control of HSS	All
Control of DEAF (Slip-Stream Processing)	All
Control of DEAF (*Batch Processing)	Vacuum Distillation Only
Control of Bicine	All
Control of THEED	Vacuum Distillation Only
Control of Polymeric Material	Vacuum Distillation Only
Control of Oxidative Degradation Products	Vacuum Distillation Only

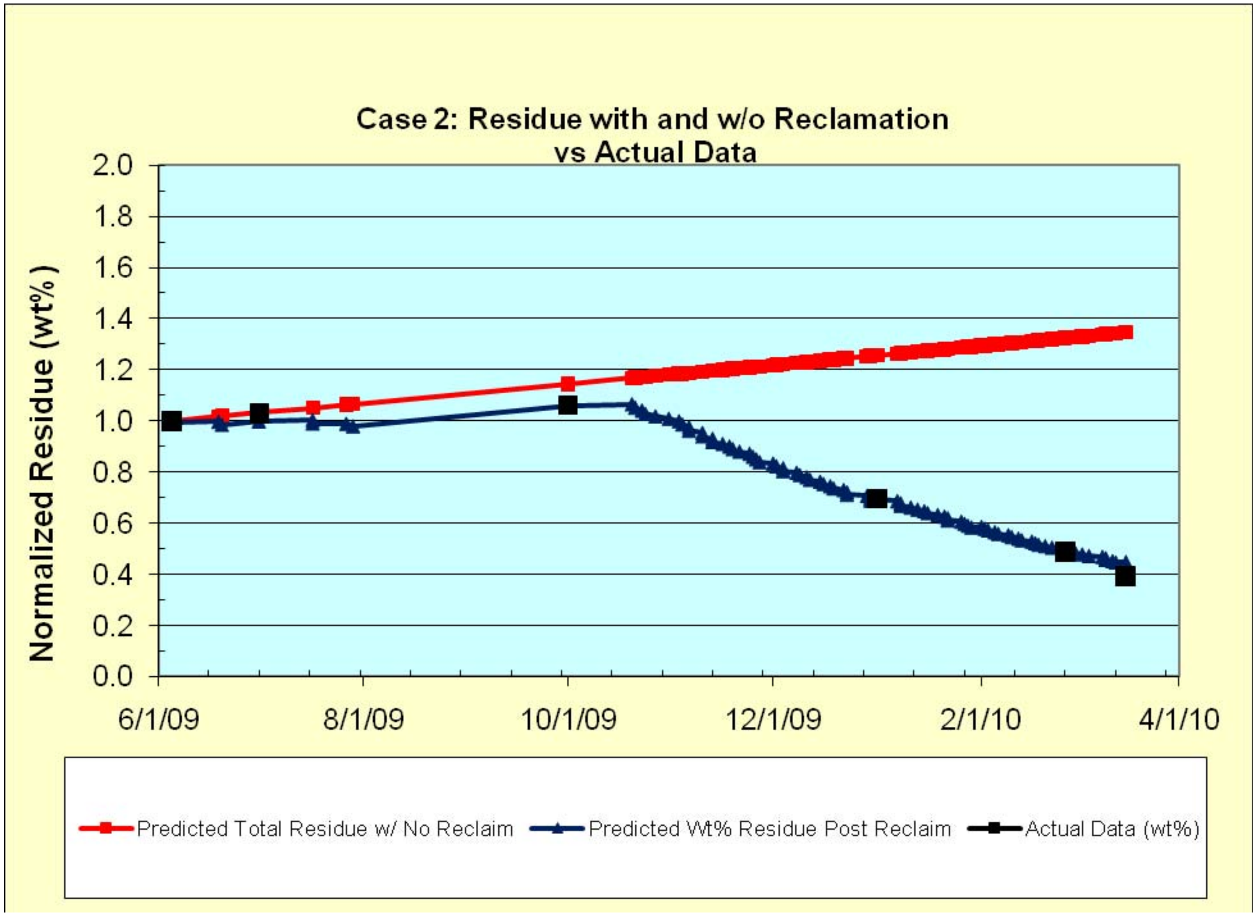
**Best Efficiency = Batch Processing*

FIGURE 1



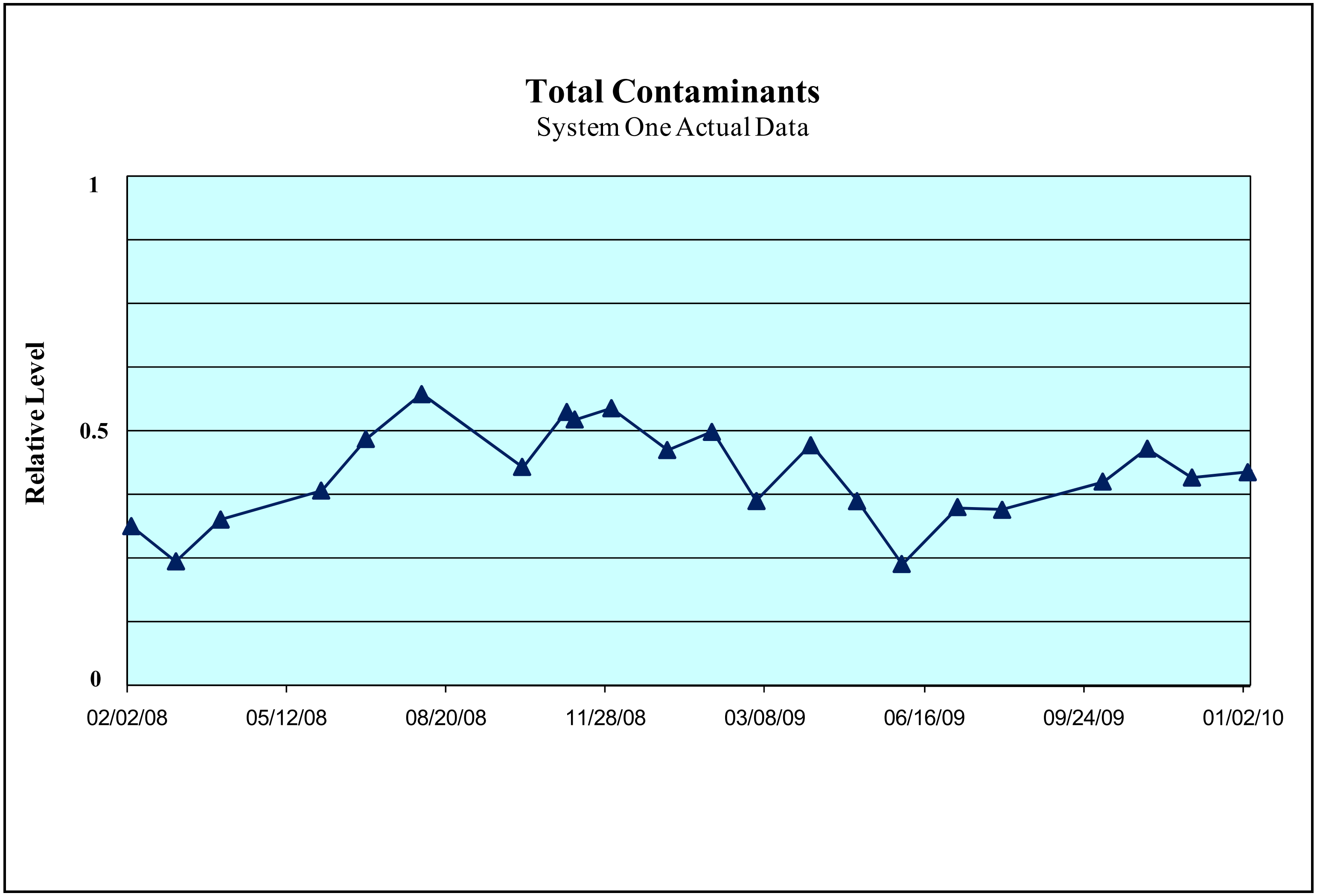
Case 1: Normalized Residue
with and w/o Reclamation vs Data
Normalized Residue (wt%)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
11/1/09
11/15/09
11/29/09
12/13/09
12/27/09
1/10/10
Predicted Total Residue w/ No Reclaim
Wt% Residue pre Service
Actual Data (wt%)

FIGURE 2



Case 2: Residue with and w/o Reclamation
vs Actual Data
Normalized Residue (wt%)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
6/1/09
8/1/09
10/1/09
12/1/09
2/1/10
4/1/10
Predicted Total Residue w/ No Reclaim
Predicted Wt% Residue Post Reclaim
Actual Data (wt%)

FIGURE 3


Total Contaminants
System One Actual Data
Relative Level
1
0.5
0
02/02/08
05/12/08
08/20/08
11/28/08
03/08/09
06/16/09
09/24/09
01/02/10