Six Sigma Evaluation of the High Level Waste Tank Farm Corrosion Control Program at the Savannah River Site

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ABSTRACT

Six Sigma is a disciplined approach to process improvement based on customer requirements and data. The goal is to develop or improve processes with defects that are measured at only a few parts per million. The process includes five phases: Identify, Measure, Analyze, Improve, and Control. This report describes the application of the Six Sigma process to improving the High Level Waste (HLW) Tank Farm Corrosion Control Program. The report documents the work performed and the tools utilized while applying the Six Sigma process from September 28, 2001 to April 1, 2002.

During Fiscal Year 2001, the High Level Waste Division spent $5.9 million to analyze samples from the F and H Tank Farms. The largest portion of these analytical costs was $2.45 million that was spent to analyze samples taken to support the Corrosion Control Program. The objective of the Process Improvement Project (PIP) team was to reduce the number of analytical tasks required to support the Corrosion Control Program by 50 percent.

Based on the data collected, the corrosion control decision process flowchart, and the use of the X-Y Matrix tool, the team determined that analyses in excess of the requirements of the corrosion control program were being performed. Only two of the seven analytical tasks currently performed are required for the 40 waste tanks governed by the Corrosion Control Program. Two additional analytical tasks are required for a small subset of the waste tanks resulting in an average of 2.7 tasks per sample compared to the current 7 tasks per sample.

Forty HLW tanks are sampled periodically as part of the Corrosion Control Program. For each of these tanks, an analysis was performed to evaluate the stability of the chemistry in the tank and then to determine the statistical capability of the tank to meet minimum corrosion inhibitor limits. The analyses proved that most of the tanks were being sampled too frequently. Based on the results of these analyses and the use of additional Six Sigma tools, the team identified improvements that allow sampling frequencies to be extended without increasing the overall risk associated with the Corrosion Control Program. Overall, the team identified improvements to the process that would reduce the number of analytical tasks required to support the corrosion control program by approximately 77 percent reducing analytical costs by $1.2 million per year.

INTRODUCTION

The High Level Waste Division at the Savannah River Site is responsible for safely storing and processing approximately 38 million gallons of radioactive waste. This waste is stored in 49 tanks each having a capacity of one million gallons. One of the aspects of safely storing this material is ensuring that a non-corrosive environment exists inside the storage tanks at all times. Studies have shown that, for the carbon steel storage tanks, nitrates, chlorides, and sulfates are corrosion aggressors and that nitrites and free hydroxides are corrosion inhibitors. The basis of the Corrosion Control Program at the Savannah River Site is to ensure that the proper ratio of corrosion inhibitors to corrosion aggressors is maintained. This ratio is monitored in the 40 waste tanks that contain liquid waste by periodically sampling the waste tanks and analyzing the waste for inhibitor and aggressor concentrations. These samples are analyzed by an on-site laboratory.

In fiscal year 2001 the cost for the analytical services by the onsite lab was $2.45 million. The charges for these laboratory services are based on the number of analytical tasks that the laboratory performs to obtain the results for the requested analytes; therefore, to reduce the cost of analytical services, the number of analytical tasks had to be reduced. This reduction could be obtained by two methods: 1) Reduce the number of analytical tasks per sample, and 2) reduce the number of samples analyzed. A Six Sigma PIP team was established to achieve these reductions. The team members included representatives from High Level Waste Process Engineering, High Level Waste Operations, the Analytical Laboratory Department, a Savannah River Technology Center (SRTC) analytical scientist, and the SRTC corrosion scientist who authored the Corrosion Control Plan. A Six Sigma Black Belt facilitated the team's activities.

TASK REDUCTION

When a corrosion sample was pulled in support of the Corrosion Control Program the analytical laboratory was asked to analyze the sample for pH, density, potassium, total gamma, free hydroxide, nitrate, nitrite, sulfate, chloride, carbonate, aluminate, oxylate, fluoride, and sulfate. To obtain the results for these 14 analytes, the laboratory performed seven analytical tasks. (See Table I which shows the seven analytical tasks and the corresponding analytes obtained from performing the task.)

Table I. Analytical Tasks and Corresponding Analytes for Corrosion Control Samples at the Savannah River Site Before Six Sigma Process Improvement

Analytical Task	Analytes	Number of Tanks (of 40)
Anion (IC)	Fluoride, Chloride, Phosphate, Sulfate, Oxylate	40
Anion (NO2/NO3)	Nitrate, Nitrite	40
Density	Density	40
Gamma PHA	Total Gamma	40
Hydoxide	Aluminate, Carbonate, Free Hydroxide	40
pH	pH	40
Potassium	Potassium	40

The first tool used to reduce the number of tasks per sample was to map the decision process that was used to evaluate each set of corrosion control sample results (Figure 1). This decision tree is used to determine if additional corrosion inhibitors are needed in the tank and to establish temperature limits for the tank wall (T_w), the tank supernate (T_{sup}), and the salt/sludge in the tank (T_{ss}). In the decision tree, S is the total inhibitor concentration (Nitrite + Free Hydroxide) and R is total inhibitor concentration divided by the nitrate concentration.

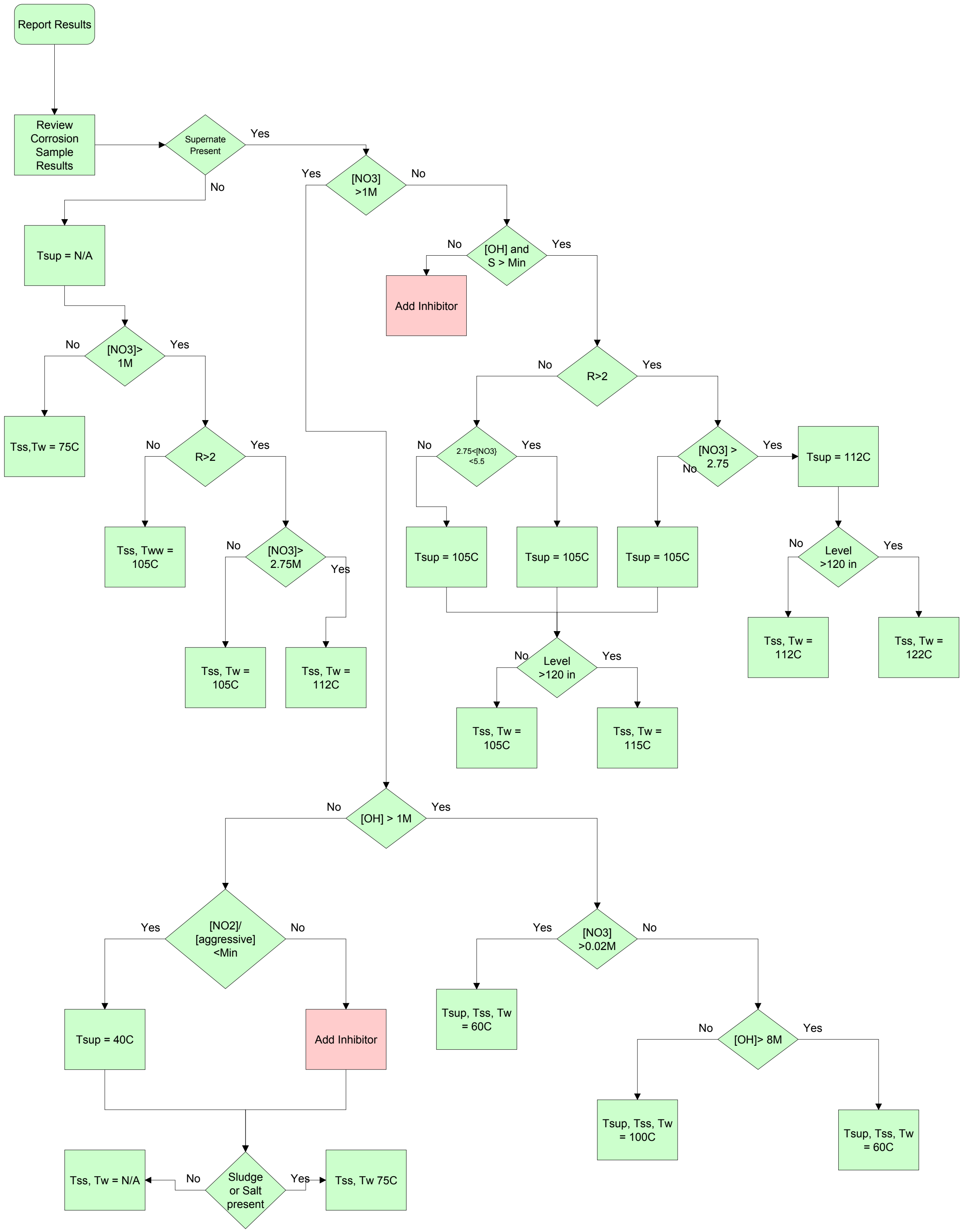

Fig. 1. Savannah River Site Corrosion Control Program Decision Tree

The corrosion control decision process was used as input to two additional Six Sigma tools, the X-Y Matrix and the Failure Mode and Effect Analysis (FMEA). The X-Y Matrix measured the impact of the individual analytes to the output of the decision process. Through the use of this tool, six of the requested analytes (density, total gamma, potassium, aluminate, phosphate, and oxylate) were identified as having no impact on the corrosion control decision process. The FMEA evaluated the effect that not obtaining the results for an individual analyte would have on the decision making process. This tool demonstrated that in addition to the six analytes identified from the X-Y Matrix, the results for pH, fluoride, and carbonate were never required to support the decision making process. The FMEA also identified that the chloride and sulfate concentrations were only required when the nitrate concentration in the waste tank was less than 0.07 Molar. Although it was not required to support the corrosion control decision, the FMEA also revealed that the total gamma number was required for about half of the tanks to support other Authorization Basis commitments.

The result of the task reduction phase was to reduce the number of analytical tasks per sample was from 7 to an average of 2.7. Table II shows the analytical tasks and corresponding analytes that were not eliminated.

Table II. Analytical Tasks and Corresponding Analytes for Corrosion Control Samples at the Savannah River Site After Six Sigma Process Improvement

Analytical Task	Analytes	Number of Tanks (of 40)
Anion (NO2/NO3)	Nitrate, Nitrite	40
Hydroxide	Free Hydroxide	40
Anion (IC)	Chloride, Sulfate	5
Gamma PHA	Total Gamma	22

SAMPLE REDUCTION

The focus of the sample reduction phase of the process improvement was to reduce the number of samples that were sent to the lab for analysis. The strategy for reducing samples was to determine the likelihood of having insufficient corrosion inhibitor in a tank and then determine the new sampling frequencies. When the Corrosion Control Plan was developed in 1991, the waste tank sampling frequencies were established based on bounding assumptions about the how rapidly the corrosion chemistry in a waste tank could change based on the type of service the tank was in and on the nitrate concentration in the tank. See Table III for the original sampling frequencies that were prescribed by the Corrosion Control Program.

Table III. High Level Waste Tank Sampling Frequencies from the Corrosion Control Program at the Savannah River Site Before the Six Sigma Process Improvement

Tank Status	Tank Category	Sampling Frequency
Active Waste Tanks	Evaporator System Tanks	3 Months
	Nitrate Concentration Less Than 1 Molar	3 Months
	Nitrate Concentration Greater Than or Equal to 1 Molar	6 Months
Static Waste Tanks	Nitrate Concentration Less Than 1 Molar	3 Months
	Nitrate Concentration Greater Than 1 Molar and Hydroxide Concentration Less Than 3 Molar	1 Year
	Nitrate Concentration Greater Than 1 Molar and Hydroxide Concentration Greater Than 3 Molar	4 Years

The probability of having out-of-spec chemistry (insufficient corrosion inhibitor) in a tank was determined by calculating the statistical capability for each of the tanks. The statistical capability was determined by first compiling into a data set the tank’s sample results from samples that were pulled since the last bulk material transfer into the tank. A normality test was then performed on the data set and in the few instances when the distribution was not normal, a transformation was applied to obtain a normal distribution. The mean of this distribution was then compared to the Lower Specification Limit (LSL). The LSL is the minimum corrosion inhibitor concentration that is required to maintain a non-corrosive environment inside of the waste tank. The capability was then calculated by dividing the difference between the mean of the distribution by the standard deviation of the distribution. See Figure 2 for example of this calculation.

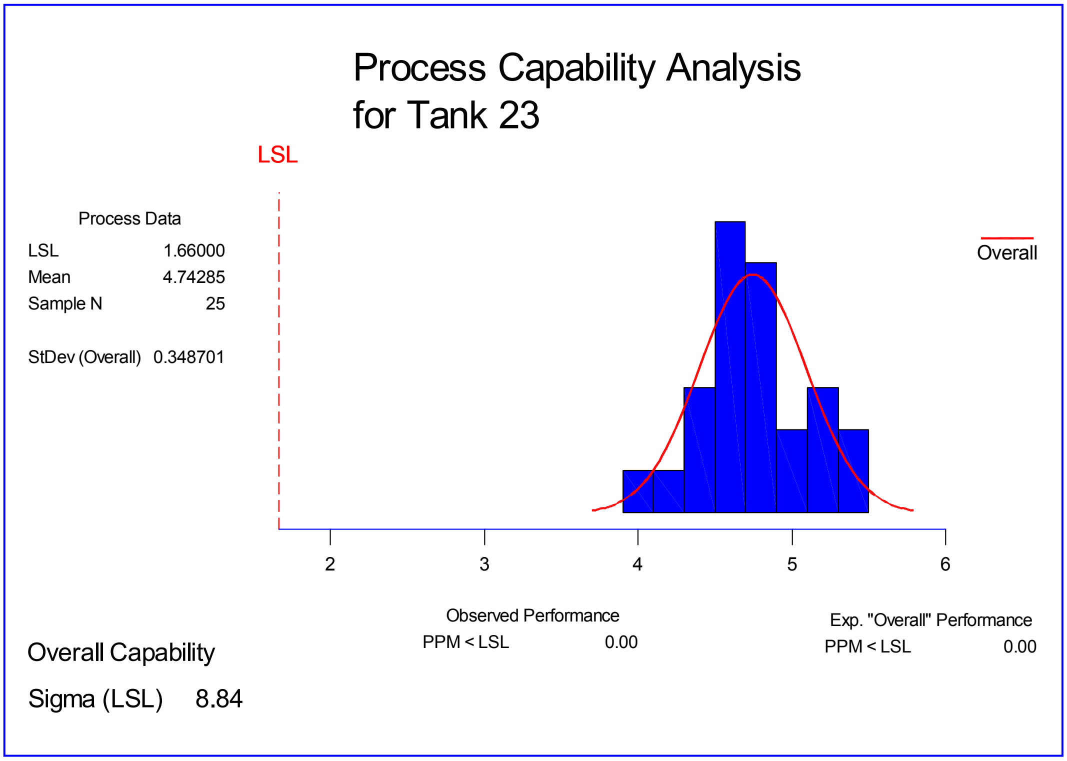

Fig.2. Corrosion Capability Analysis for High Level Waste Tank 23 at the Savannah River Site

Once the capability for a tank was known, the probability of having out-of-spec chemistry was calculated using the properties of the Laplace-Gaussian normal probability distribution. The capability and associated probability of out-of-spec chemistry for the SRS HLW tanks are listed in Table IV. In a few instances there was insufficient data available to calculate a tank's capability, therefore an estimated capability was developed for informational purposes only.

Table IV. Corrosion Capability and Probability of Out of Specification Chemistry for High Level Waste Tanks at the Savannah River Site

Tank #	Sigma Level	Probability of Out-of-Spec Chemistry (ppm)	Tank #	Sigma Level	Probability of Out-of-Spec Chemistry (ppm)
4	4.5	3	32	3.5	233
5	? (est 3.5)	233	33	4	32
6	4.4	5	34	5.7	0.06
7	4.5	3	35	4.8	1
8	? (est 9)	<0.0001	36	7	<0.0001
11	4.2	13	37	? (est 2.3)	10724
13	8.2	<0.0001	38	1.4	80757
18	Closing	N/A	39	4.8	1
19	Closing	N/A	40	? (est 4.5)	3
21	8	<0.0001	41	14	<0.0001
22	4.6	2	42	9	<0.0001
23	6	0.001	43	9	<0.0001
24	15	<0.0001	44	6.5	<0.0001
25	5.4	0.03	45	5	0.28
26	4.2	13	46	2.5	6210
27	5.6	0.01	47	5	0.28
28	9.8	<0.0001	48	4.5	3
29	1	158655	49	? (est 4)	32
30	4.3	9	50	6.8	<0.0001
31	4.4	5	51	4.5	3

Once the capabilities were determined for each tank, the team developed a methodology for establishing a tank’s sampling frequency based on the tank’s capability. A process simulation model was developed to perform a Monte Carlo type analysis that would correlate sigma level to expected minimum time between out-of-spec samples. The model was used to simulate approximately 250,000 consecutive samples at each sigma level from 2.5 to 4 (in 0.1 sigma increments). For sigma levels less than 3, there were instances in which two consecutive samples were out of spec. For sigma levels between 3 and 3.5 the shortest time between out-of-spec results was 9 months. Between 3.5 and 4 sigma the shortest time between out-of-spec results was 15 months and at 4 sigma or greater the shortest time between out-of-spec results was 4.75 years. Based on these results, Table V was developed to equate capability to sampling frequencies.

Table V. Corrosion Control Sampling Frequencies for Active High Level Waste Tanks at the Savannah River Site

Capability	Sampling Frequency
0 - 2.99	3 Months
3.00 - 3.49	6 Months
3.50 - 3.99	12 Months
4.00 or greater	24 Months

The frequencies established in Table V are for Active tanks only. The frequencies for static tanks (tanks that are not receiving new waste) are double the frequencies established in Table V. As part of the development of Table V, the team desired to determine the level of risk associated with the new sampling frequencies and compare these risks to risks that were already being accepted within the Corrosion Control Program. The risk was calculated by multiplying the probability of out-of-spec chemistry (in ppm) by the consequence expressed in Corrosion Units (CU). A Corrosion Unit was defined as three months of a corrosive environment inside of a waste tank. The calculated risks are listed in Table VI. The risk associated with Tanks 37 and 46 under the old Corrosion Control Program are included as a reference.

Table VI. Calculated Risks Associated with New Corrosion Control Sampling Frequencies for High Level Waste Tanks at the Savannah River Site

Sigma Level	Frequency	Probability of Out-of-Spec Chemistry	Risk (in ppmCU)
3	6 Months	1350 ppm	4053
3.5	12 Months	233 ppm	2320
4	24 Months	32 ppm	1152
Reference tanks (capability)			
Tank 37 (2.3 sigma)	3 Months	10724 ppm	10724
Tank 46 (2.4 sigma)	3 Months	8198 ppm	8198

As seen in Table VI, the risks associated with the new sampling frequencies are less than the risks that were already considered to be acceptable in the Corrosion Control Program.

While the frequencies established in Table V reduced the frequencies for tanks that have calculated capabilities, the team also developed an alternate methodology that would take credit for excess inhibitor in tanks that have not been stable for a long enough period to determine the capability. Corrosion chemistry for the waste tanks was examined during periods when the waste tanks were stable. An unstable period was defined as any time that the bulk waste was being stirred in the tank or when a waste tank to waste tank transfer was occurring. The standard deviation for each of these "strings" of data was calculated and plotted in a histogram. Using the properties of the Laplace-Gaussian normal probability distribution, it was determined that there was less than 0.17% probability that any future tank chemistry parameter would have a standard deviation greater than 0.5 Molar (Fig. 3).

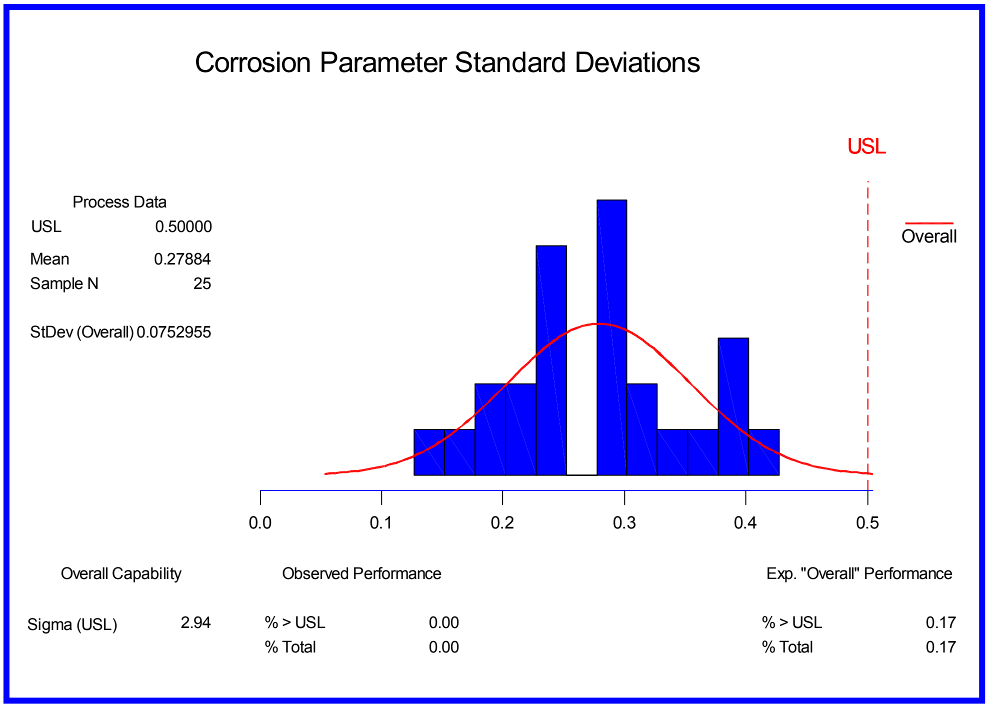

Fig. 3. Standard Deviations for Corrosion Control Parameters in Stable Waste Tanks at the Savannah River Site

This value (0.5 Molar) was then defined as the Historical Worst Case Standard Deviation (HWCSD). This information was then combined with the minimum corrosion inhibitor concentrations defined by the Corrosion Control Plan (See Table VII). If the minimum inhibitor concentration was exceeded by 3 HWCSD, then the sampling frequency could be doubled; and, if the minimum inhibitor concentration was exceeded by 5 HWSCD, then the sampling frequency could be quadrupled. Table VIII was developed to implement this methodology.

Table VII. Minimum Corrosion Inhibitor Concentrations for High Level Waste Tanks at the Savannah River Site

Applicability	Parameter	Minimum Needed	Units
Case 1. $5.5 < [NO_3^-] \leq 8.5$ Molar	$[OH^-]$	0.6	Molar
	$[OH^-] + [NO_2^-]$	1.1	Molar
Case 2. $2.75 < [NO_3^-] \leq 5.5$ Molar	$[OH^-]$	0.3	Molar
	$[OH^-] + [NO_2^-]$	1.1	Molar
Case 3. $1.0 \leq [NO_3^-] \leq 2.75$ Molar	$[OH^-]$	$0.1[NO_3^-]$	Molar
	$[OH^-] + [NO_2^-]$	$0.4[NO_3^-]$	Molar
Case 4a. $0.02 < [NO_3^-] < 1.0$ Molar Either Inhibit with $[OH^-]$	$[OH^-]$	1.0	Molar
Case 4b. $0.02 < [NO_3^-] < 1.0$ Molar OR Inhibit with $[NO_2^-]$	$[NO_2^-]$	$1.66 \times [NO_3^-]$	Molar

Table VIII. Extended Corrosion Control Sampling Frequencies based on Excess Corrosion Inhibitor Concentrations for High Level Waste Tanks at the Savannah River Site

Status	Category	Inhibitor Levels**	Frequency
ACTIVE WASTE TANKS	Evaporator Feed and Drop	If $[NO_3^-] < 1M$ or $[OH^-] < 2.35$ M or $[S] < 3$ M	3 months
		If $[NO_3^-] \geq 1M$ and $[OH^-] \geq 2.35$ M and $[S] \geq 3$ M	6 months
	Fresh Canyon Waste Receiver with Nitrate Concentration greater than or equal to 1 molar	$[OH^-] < 3$ M or $[S] < 4$ M	6 months
		$[OH^-] \geq 3$ M or $[S] \geq 4$ M	12 months
	Receiver with Nitrate Concentration less than 1 molar	$[NO_2^-]/[NO_3^-] < 3.4$ or $[OH^-] < 0.02$ M	3 months
		$3.4 \leq [NO_2^-]/[NO_3^-] < 4.8$ and $0.02 M \leq [OH^-] < 2.35$ M	6 months
		$[NO_2^-]/[NO_3^-] \geq 4.8$ or $[OH^-] \geq 2.35$ M	12 months
	Receiver with Nitrate Concentration greater than or equal to 1 molar	$[OH^-] < 2.35$ M or $[S] < 3$ M	6 months
		$2.35 M \leq [OH^-] < 3$ M and $3 M \leq [S] < 4$ M	12 months
		$[OH^-] \geq 3$ M or $[S] \geq 4$ M	24 months
STATIC WASTE TANKS	Nitrate Concentration less than 1 molar	$[NO_2^-]/[NO_3^-] < 3.4$ or $[OH^-] < 0.02$ M	6 months
		$3.4 \leq [NO_2^-]/[NO_3^-] < 4.8$ and $0.02 M \leq [OH^-] < 2.35$ M	12 months
		$[NO_2^-]/[NO_3^-] \geq 4.8$ or $[OH^-] \geq 2.35$ M	24 months
	Nitrate Concentration greater than or equal to 1 molar	$[OH^-] < 2.35$ M or $[S] < 3$ M	12 months
		$2.35 M \leq [OH^-] < 3$ M and $3 M \leq [S] < 4$ M	24 months
		$[OH^-] \geq 3$ M or $[S] \geq 4$ M	48 months

** [S] is the total inhibitor concentration (nitrite and hydroxide).

CONCLUSIONS

The Six Sigma process improvement methodology was used to identify ways to reduce the cost resulting from analyzing samples that were pulled to support the Corrosion Control Program for the High Level Waste storage tanks located at the Savannah River Site. To reduce the analytical costs, improvements were identified in two areas. First, the analytical effort associated with each sample analysis was reduced by over 50 percent and second, the number of samples the program required to be pulled was reduced by 50 percent. The net reduction in analytical effort was 77 percent. The Total cost reduction for the High Level Waste Division is $5.82 million and for the Savannah River Site, $3.22 million. The reduction in the number of samples pulled will also make operators available to perform an additional 7,084 hours of work ($304,612). Cost savings for these improvements are for fiscal years 2002 through 2007.