STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

# Analysis of Tank Chemistry Compliance with Chemistry Specification in Double-Shell Tanks

## DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

**Date submitted:**

October 17, 2014

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**Submitted to:**

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0000598

FIU | Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

## DISCLAIMER

# ABSTRACT

During the summer of 2014, Carmela Vallalta participated in an internship at the Hanford Site located in Richland, WA. Throughout the summer, Carmela worked with Mr. Dennis Washenfelder as part of the Tank and Pipeline Integrity Group of Washington River Protection Solutions LLC (WRPS). Her primary task during the internship was to investigate the waste chemistry history of double-shell tank AY-102 which was determined to be leaking in August of 2012, find instances when the tank was out of specification, and devise a way to present this information in a clear and concise manner. Lastly she investigated the history of other similar double-shell tanks to compare the data to AY-102.

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# INTRODUCTION

In August 2012, radioactive waste was discovered in the annulus space separating the primary and secondary tank of double-shell tank AY-102. A formal leak investigation documented in RPP-ASMT-53793 determined that the primary tank was leaking.

During the investigation, historical sample analyses were reviewed to determine the susceptibility of the metal primary tank to waste corrosion. The investigation did not consider the efforts that had been made to mitigate waste that was outside of the chemistry specification. In some cases, there were significant lapses of time between the discovery of the out-of-specification condition and the response of adding chemicals needed to return the waste to specification. These lapses may have contributed to the eventual tank failure. Current corrosion control specifications are published in OSD_T_151_00007.

Discovery of out-of-specification waste was a frequent occurrence between startup of the first double-shell tank (AY-102) in 1971 and the mid 2000's. Out-of-specification waste could result in a reduction of the tank service life if left unmitigated. For example, in 1994, ten double-shell tanks were known or suspected to be out-of-specification as described in Occurrence Report RL--WHC-TANKFARM-1994-0046. Summaries of the sampling and waste mitigation histories for the 28 double-shell tanks do not exist.

The corrosion testing programs that have been underway for many years under the general sponsorship of the Department of Energy (DOE) and other agencies provide a technical basis for the assessment of the propensity for general, pitting, and cracking corrosion. The original specifications for liquid in the AY Farm required the pH to be between 8 and 10 (ARH-205, Design Criteria PUREX AY Tank Farm). The first major change in chemistry specifications occurred in 1983.The current specifications improved the 1983 specifications over time as more testing was completed and are contained in OSD-T-151-00007. Table 1 shows the specifications currently used for all DSTs.

**Table 1. Waste Chemistry Limits**

| $NO_3$ | CONDITION | | |
|---|---|---|---|
| | T < 167 °F | 167 °F ≤ T ≤ 212 °F | T > 212 °F |
| $0 \le NO_3 \le 1$ | $0.01 \le OH \le 8$ | $0.01 \le OH \le 5$ | $0.01 \le OH \le 4$ |
| | $0.011 \le NO_2 \le 5.5$ | $0.011 \le NO_2 \le 5.5$ | $0.011 \le NO_2 \le 5.5$ |
| | $NO_3/(OH + NO_2) < 2.5$ | $NO_3/(OH + NO_2) < 2.5$ | $NO_3/(OH + NO_2) < 2.5$ |
| $1 < NO_3 < 3$ | $0.1\ NO_3 \le OH < 10$ | $.1\ NO_3 \le OH < 10$ | $0.1\ NO_3 \le OH < 4$ |
| | $NO_3/(OH + NO_2) \le 2.5$ | $OH + NO_2 \ge 0.4\ NO_3$ | $OH + NO_2 \ge 0.4\ NO_3$ |
| $3 < NO_3 \le 5.5$ | $0.3 \le OH < 10$ | $.3 \le OH < 10$ | $0.3 \le OH < 4$ |
| | $OH + NO_2 \ge 1.2$ | $OH + NO_2 \ge 1.2$ | $OH + NO_2 \ge 1.2$ |

In addition to out-of-specification chemistry inside the tank, a radiation mechanism capable of creating acidic conditions on the outside of the tank during humid conditions has been identified. The mechanism would be present whenever that tank's annulus ventilation system is off-line, allowing stagnant air to accumulate.

Tank AY-102 is one of two 1-million gallon (Mgal) tanks in the 241-AY Tank Farm (AY Farm) located in the southeast portion of the Hanford 200 East Area. Tank AY-102 is a double-shell tank (DST) system that consists of a primary tank and secondary liner structure; concrete shell, insulating pad (refractory), and foundation; central pump pit; sluice pits; annulus pump pit; leak detection pit (and well); air lift circulators; and monitoring and alarm systems; and the capability for a mixer pump. Figure 1 shows an illustration of a DST.

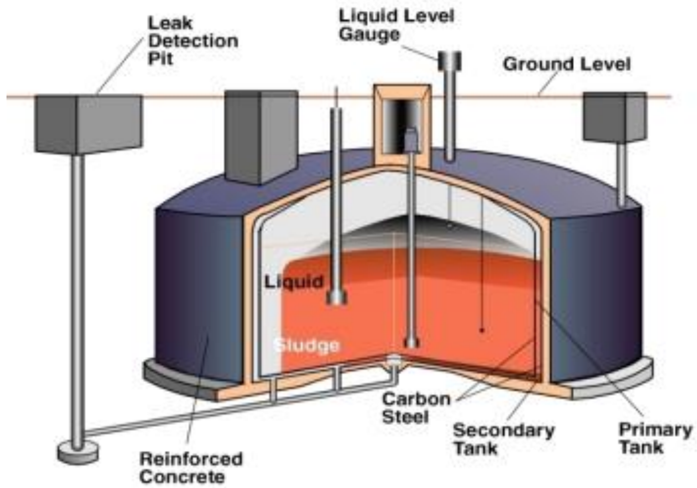



**Figure 1. Double-shell tank.**

The primary steel tank rests inside the secondary steel liner and is supported by the refractory on the floor of the secondary liner. An annular space of 2.5 ft. is formed between the primary tank and secondary liner. The primary tank and annulus have separate ventilation systems, both of which are kept at negative pressures to the environment with the use of exhaust fans. The primary tank is a fully enclosed structure with the only penetrations being side fill lines and dome risers. The secondary steel tank provides containment up to a height of 39 ft. 8 in. from the bottom to where the secondary liner meets the dome of the primary tank.

The annulus has 22 risers that allow for the insertion of inspection equipment and placement of instruments in the annulus. Six additional risers act as annulus ventilation outlets. The liquid level in the tank is limited to 362 in. because of the side fill lines, which are positioned at about 372 in. The height difference between the waste level and height of the containment allows for more than 8 ft. of freeboard above the maximum liquid level in the primary tank, if the annulus ever fills and equalizes with the level in the primary tank.

The secondary liner meets at a working point where both radii of the curvatures of the haunches are coincident. This joint is not welded or fastened, but is offset ½ in. by the use of backup copper bars and covered by an 18-gauge, 14-in. wide metal flashing that is tack-welded to the primary tank. This allows for movement from expansion or contraction between the two tanks after the concrete shell has been cast over the tanks.

Tank AY-102 was the first double-shell radioactive waste storage tank constructed at Hanford. The tank was completed in 1970 and entered service in 1971. It currently stores the Waste Treatment and Immobilization Plant hot commissioning feed.

In August of 2012, an accumulation of material was discovered at two locations on the floor of the annulus that separates the primary tank from the secondary liner, and at a third location on the primary tank dome above the waterline. None of the material was present during inspections completed in December 2006 and January 2007. A formal leak assessment team was established August 10, 2012, to review Tank AY-102 construction and operating histories, and determine whether the material found on the annulus floor resulted from a primary tank leak.

The panel consisted of engineering, base operations, and environmental protection individuals representing a broad cross-section of the company. The team met between August 28, 2012 and October 10, 2012, to gather and analyze information, formulate tank leak and non-leak hypotheses, and reach a consensus on the source of the floor material. Tank AY-102 construction records detail a tank plagued by first-of-a-kind construction difficulties and trial-and-error repairs. The result was a tank whose as-constructed robustness was much lower than intended by the double-shell tank designers. For example:

- Bulges created in the secondary liner from welding the thin floor plates, and from reworking rejected welds, were eventually accepted so construction could proceed. The rigid insulating refractory cast on top of the secondary liner cracked as the bulges moved, leaving the pad bridged in places.
- The primary tank floor plate weld rejection rate was 36 percent. Weld maps show welds being reworked as many as four times before passing radiography examination.
- Rainwater saturated the insulating refractory pad in the weeks before the primary tank was scheduled for post-weld stress-relief. During stress relief, the tank bottom temperature could not be raised above 210°F for two days, while steam escaped from the water-soaked refractory. The tank temperature eventually reached the required annealing temperature and was held at temperature for the required time.
- After stress relief and the hydrostatic leak check, part of the insulating refractory pad was found to be too damaged to be used. The outside 21 in. of the refractory were excavated from beneath the primary tank and replaced with structural concrete. Pieces of Styrofoam were used to fill gaps between the primary tank bottom and the refractory surface further

under the tank when they were found. The initial pours of the structural concrete filled the area under the primary tank knuckle, but did not flow to the back of the excavation. The slump was increased on later pours to ensure that the primary tank bottom was supported.

# EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2014, a DOE Fellow intern (Carmela Vallalta) spent 10 weeks doing a summer internship at the Hanford Site in Richland, WA, under the supervision and guidance of Dennis Washenfelder, manager of the Tank and Pipeline Integrity Group at Washington River Protection Solutions- LLC. The intern's project was initiated on June 23, 2014, and continued through August 29, 2014, with the objective of assisting in the analysis of the chemistry history in numerous double-shell tanks and preparing waste mitigation and annulus ventilation operating chronologies for the double-shell tanks, beginning with the earliest tanks, AY-102 and AY-101, and finishing with AN-102 and AN-107.

# RESEARCH DESCRIPTION

The work scope designated for the duration of the internship consisted of the following tasks:

1. Investigate the waste mitigation and annulus ventilation operating chronologies for the double-shell tanks, beginning with the earliest tanks, AY-102 (the leaking tank) and AY-101.
2. Create visual representation to present the waste chemistry in the double-shell tanks in ways that allow useful conclusions to be made.
3. Develop a template in Microsoft Excel to summarize the sampling history for the 28 double-shell tanks, showing when the tanks were found to be not compliant with the waste chemistry specifications described in the report OSD-T-151-00007 and in Table 1 in the introduction. Note that the current waste chemistry specifications have only been active since the year 1983; before then, they were less strict. The analysis took that into consideration when looking at sample data from that period.
4. Develop an Excel "calculator" to quickly determine if a sample from a specific sampling event meets the chemistry specifications for hydroxide (OH), nitrite ($NO_2$), and nitrate ($NO_3$) concentrations as well as temperature.

Within the duration of the internship, a complete analysis of the earliest double-shell tanks in the AY-farm (AY-101 and AY-102) and two of the seven tanks in the AN-farm (AN-102 and AN-107) was completed.

Resources that were available to the intern and useful for providing the chronologies of the waste in the tanks included:

- Tank Waste Information Network System (TWINS) - very useful for finding information on sampling events after 1994, does not include anything before that date.
- Integrated Data Management System (IDMS) - online database compilation of numerous reports that may contain information on waste chemistry and samples.
- Document Management & Control System (DMCS) - online database compilation of numerous reports that may contain information on waste chemistry and samples.
- Technical Safety Requirements Recovery Plans - when tank chemistry was found to be out of specification, one of these reports was issued. These reports are useful to determine when the chemistry in the tank was returned to chemistry limits.
- Occurrence Reports and Event Fact Sheets - issued for many reasons including when tank chemistry was found to be out of specification.

- Caustic Limits Reports
- Any other references mentioned in this report

The main deliverable for this scope of work was a complex Excel worksheet describing the waste corrosion chemistry mitigation chronology and annulus ventilation chronology for each tank, including a time line showing sampling, sample results, and mitigation activities, waste levels and waste temperatures.

# RESULTS AND ANALYSIS

As a way to better understand the waste chemistry specifications in Table 1, a graph was created to compare the hydroxide levels and the nitrate levels (Figure 2). After analyses of many samples across different tanks, it was concluded that this relationship of hydroxide to nitrate was the most predictive when determining if a sample was in specification or not.

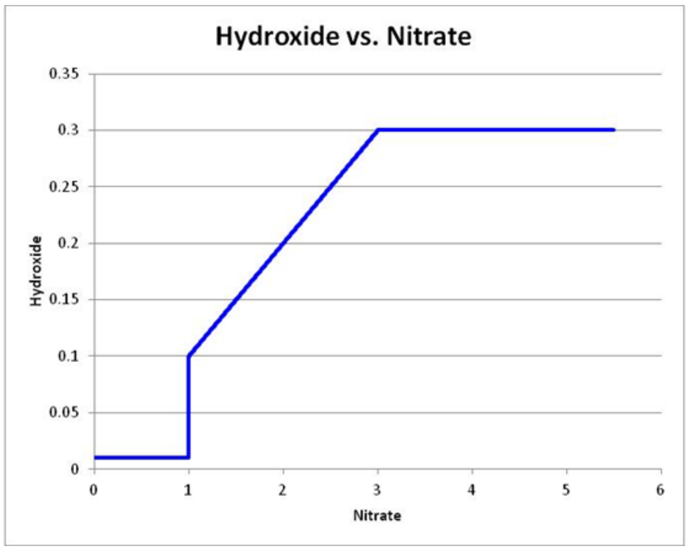



**Figure 2. Min. hydroxide vs nitrate graph.**

Figure 2 provides a very simple way to look at the chemistry specifications. The line represents the minimum hydroxide concentration levels (in M) needed at a specific nitrate concentration. As long as the hydroxide concentration is above the blue line, the waste chemistry is in specification and the tank integrity is at a low risk of corroding.

In order to quickly and efficiently analyze waste samples and determine whether or not they met chemistry specifications, a calculator (Figure 3) was created in Excel.

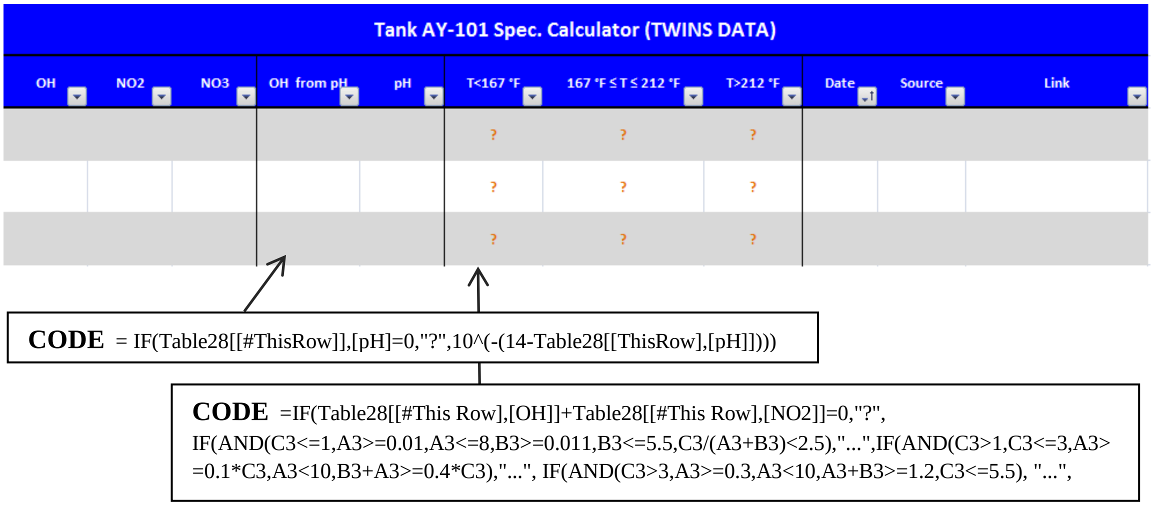



**Figure 3. Specification calculator.**

The calculator was programmed so that the user plugs in the values for nitrate, nitrite and hydroxide concentrations. The calculator then determines whether or not, and at which temperatures, those values are in specification. The calculator displays an "F" if the values are not in specification and "..." if they are. Figure 3 shows a "?" instead because the data is incomplete as there are no values plugged in. The value of pH can be entered in the calculator where the hydroxide values are not known. The following formulas allow for the conversion of pH into OH.

1. $pH + pOH = 14$

2. $pOH = -log\,[OH^-]$

3. $1 * 10^{-14} = [H^+] * [OH^-]$

The calculator includes columns to keep track of the sample identification and sampling event dates. A table for each tank is located in Appendix A. The information for these tables was organized and analyzed in Excel. For convenience, the results and analysis section is divided into subsections that contain information for each tank individually, starting with AY-102.

## AY-102

The TWINS data on the double-shell tanks is updated regularly and includes a Data Loading Summary of all the tanks with information on the last supernatant and core samples taken.

A supernatant sample is taken from the liquid layer of the tank; a core sample is a sample taken from the solid layer that forms at the bottom of a tank. It is more difficult and much more expensive to collect core samples. However, the leak in AY-102 was caused at the bottom of the tank and, therefore, the chemistry of this layer is much more likely to be responsible.

**Table 2. Data Loading Summary AY-102 (TWINS)**

| Tank Name | Core/Segment Date | Surface Date | Supernate Date | Historical Data Exists | Best Basis Date | TCR Date | HTCE Date | Report As Of Date |
|---|---|---|---|---|---|---|---|---|
| AY-102 | 8/10/2005 | | 11/5/2002 | YES | 2/12/2014 | | 1/31/1997 | 7/20/2014 |

According to Table 2, taken from the TWINS data, the last core sample was taken about ten years ago in 8/10/2005 and the last supernatant sample was taken in 2002. This means that there is a lack of data from the last decade for AY-102 samples.

In investigating the history of AY-102, several interesting points where discovered:

- The first steps to intervene with out-of-specification waste appear to have been taken ~ 1994 (per the occurrence reports).
- The first core sample was taken in 1988, ten years after the solid layer was first reported.
- There are little sample data on which to base the extent of compliance with the corrosion specification.
- Corrosion chemistry looked to be out-of-specification for about 1/3 of tank’s life. This could have contributed to the tank leak.

Figure 4 is a representation of the data that is available for AY-102. The TWINS data provided information from 1997 to 2005. Before that, the data taken from numerous reports found in the IDMS and DMCS databases.

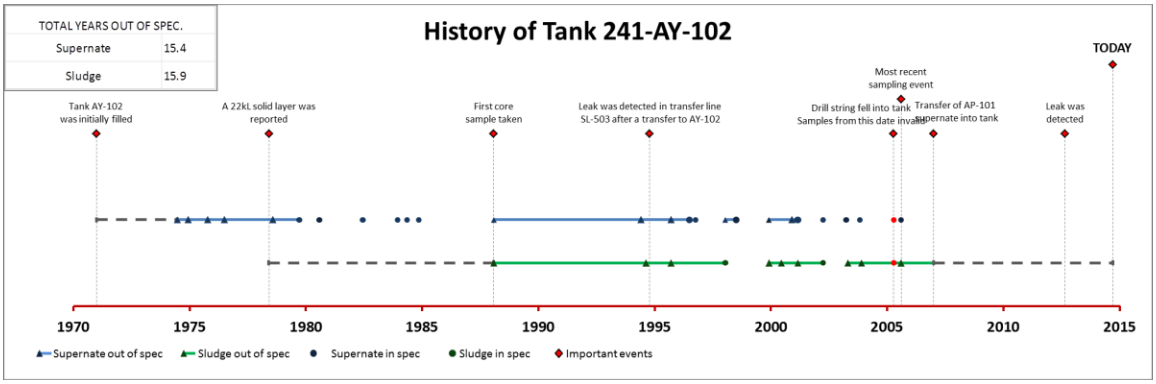



**Figure 4. History of Tank AY-102.**

The blue line in this graph represents periods of time when the supernatant was found to be out of compliance with the current waste chemistry specifications; the green line represents when the sludge/solid layer did not meet the specifications. The top row has some important events that may have either affected the results of the samples or are significant events in the tank's lifetime.

This graph as well as all the other graphs in this section will be included in Appendix A.

The following graph is a different representation of the same data. In many sampling events, there turned out to be many different results. This might have been due to varying samples from different sections in the tank or just as a result of different analysis and measurement methods.

Figure 5 plots hydroxide levels at different sampling event dates.

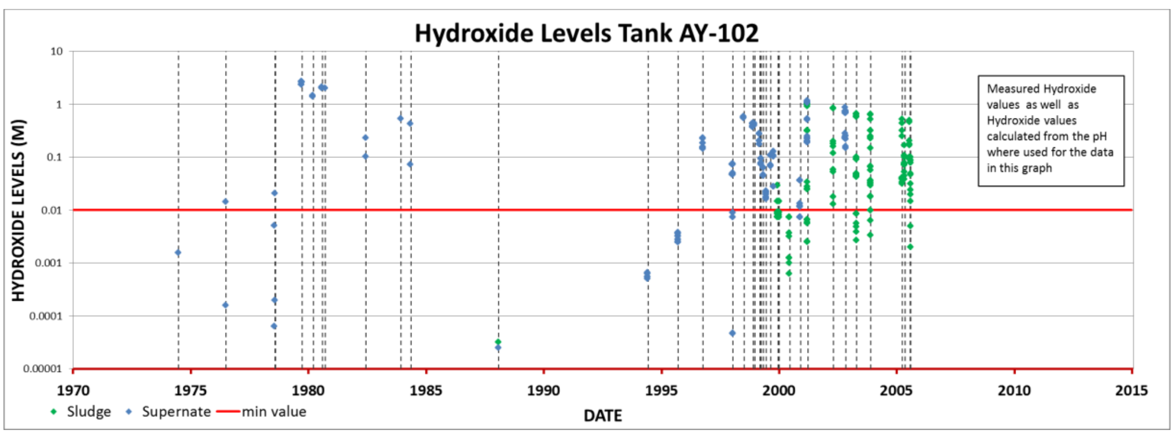



**Figure 5. Hydroxide levels in Tank AY-102.**

Tank AY-102 historically has always had low concentrations of nitrate, constantly below 1M, keeping the minimum hydroxide also pretty low at 0.01M. Note that the majority of samples at many of the sampling event dates are above the minimum and therefore in specification; however, the samples that turned out to be out of specification should not be ignored as they may have contributed to the tank leak.

## AY-101

The Data Loading Summary for AY-101 shows that there are more recent samples for this particular tank.

The most recent core sample was taken in April of 2008 and the most recent supernatant sample was taken in February of 2014. Table 3 shows the hydroxide levels for Tank AY-101.

**Table 3. Hydroxide Levels in Tank AY-101**

| Tank Name | Core/Segment Date | Surface Date | Supernate Date | Historical Data Exists | Best Basis Date | TCR Date | HTCE Date | Report As Of Date |
|---|---|---|---|---|---|---|---|---|
| AY-101 | 4/8/2008 | | 6/13/2013 | YES | 2/12/2014 | | 1/31/1997 | 7/20/2014 |

The same graphs were completed for AY-101 to compare the results with AY-102. There is a lot less data of the sludge layer in this tank because the layer took longer to form.

This tank started operating just a few years after AY-102

Looking at the graph in Figure 6, the supernatant layer was out of specification longer than the supernatant layer in AY-102: 19 yrs. (AY-101) vs. 15 yrs. (AY-102). However, the solid layer appears to have been out of compliance less than half as long as the solid layer in AY-102: 6 yrs. (AY-101) vs. 16 yrs. (AY-102). This is a good sign because, as mentioned before, the solid layer was likely to have been the cause of the leak in the first place.

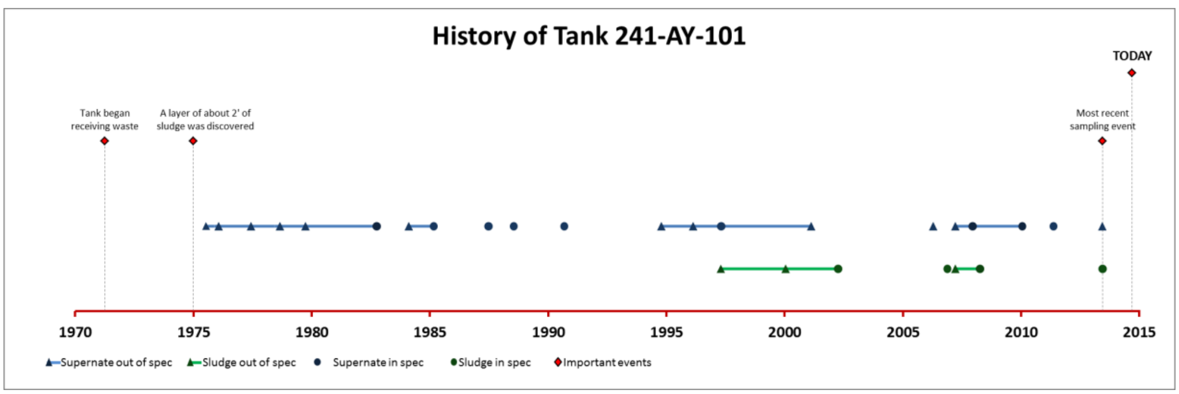



**Figure 6. History of Tank AY-101.**

The waste in tanks AY-101 and AY-102 is very similar. They are both low nitrate so, like in AY-102, the minimum hydroxide level for AY-101 stayed constant at 0.01M (Figure 7).

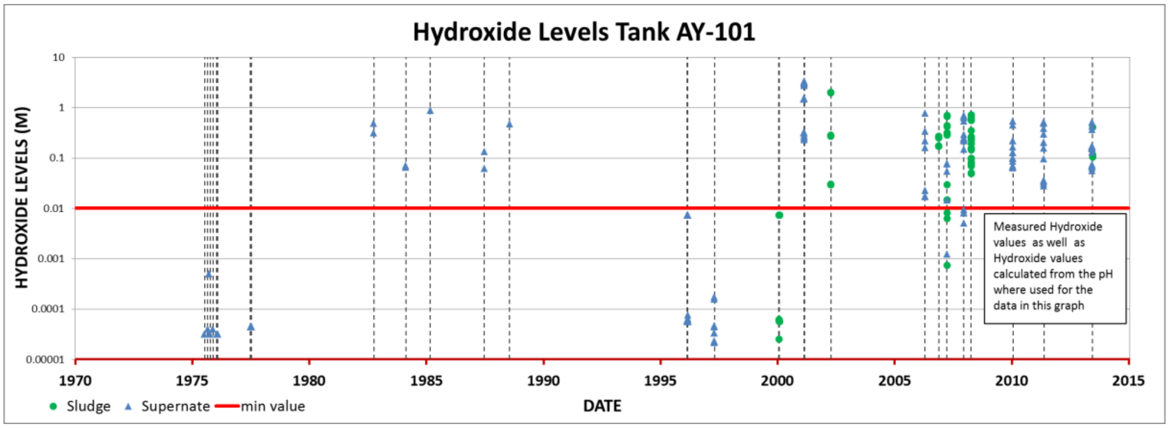



**Figure 7. Hydroxide levels in Tank AY-101.**

## AN-102

Due to the limited time of the internship, less data was found for the tanks AN-102 and AN-107. These tanks are different from the tanks in the AY farm in these following key characteristics:

- They started service in the early 1980's, about 6 years after the tanks in the AY farm.
- They are "hotter," which means the waste they contain is much more radioactive and have higher concentrations of nitrate. These tanks should be monitored more closely and have frequent caustic addition events to keep the chemistry within limits.

The Data Loading Summary shows that there is a fairly recent supernatant grab sample. However, the last core sample was taken over a decade ago and, in the TWINS data, there is only a record of one core sampling event. This leaves an incomplete picture of the history of the waste chemistry in this tank (Table 4).

**Table4. Data Loading Summary AN-102 (TWINS)**

| Tank Name | Core/Segment Date | Surface Date | Supernate Date | Historical Data Exists | Best Basis Date | TCR Date | HTCE Date | Report As Of Date |
|---|---|---|---|---|---|---|---|---|
| AN-102 | 3/19/2003 | | 7/11/2013 | YES | 1/6/2014 | | 1/31/1997 | 8/11/2014 |

A timeline was also produced for this data. Even though very little actual data was found for AN-102, it still shows about 16 years of out of specification chemistry in the supernatant layer (Figure 8). The estimate on the time that the sludge of this tank was out of spec. was determined by the single core sample on the overlying supernatant chemistry and on the record of caustic additions.

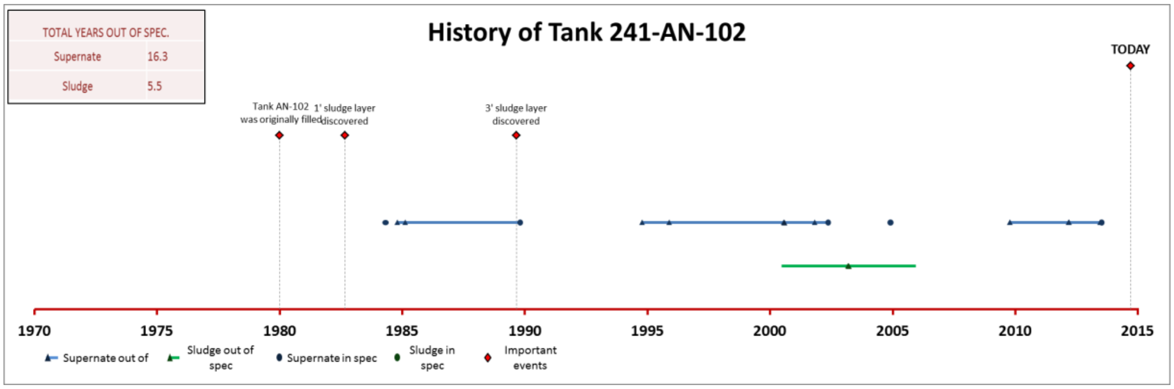



**Figure 8. History of Tank AN-102.**

Since the waste in this tank has higher nitrate concentrations, it falls at a place on the graph with a variable minimum hydroxide level, as shown in Figure 9.

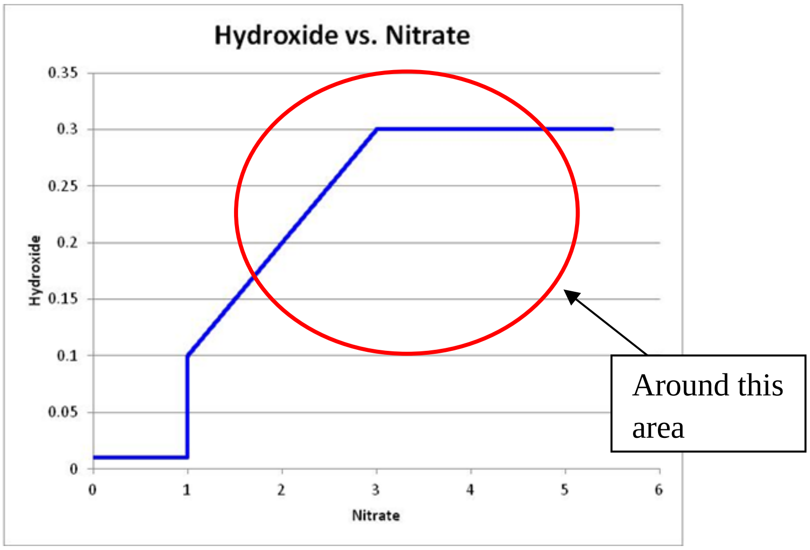



**Figure 9. Hydroxide vs nitrate levels for tank AN-102.**

Therefore, the graphs plotting the hydroxide levels over time do not look the same as they did for the tanks on the AY-farm. In order to make the graphs as easy to read and as accurate as possible, the y-axis was changed to read the deviation from the minimum hydroxide which was calculated in an extra row in the specification calculator (Figure 10).

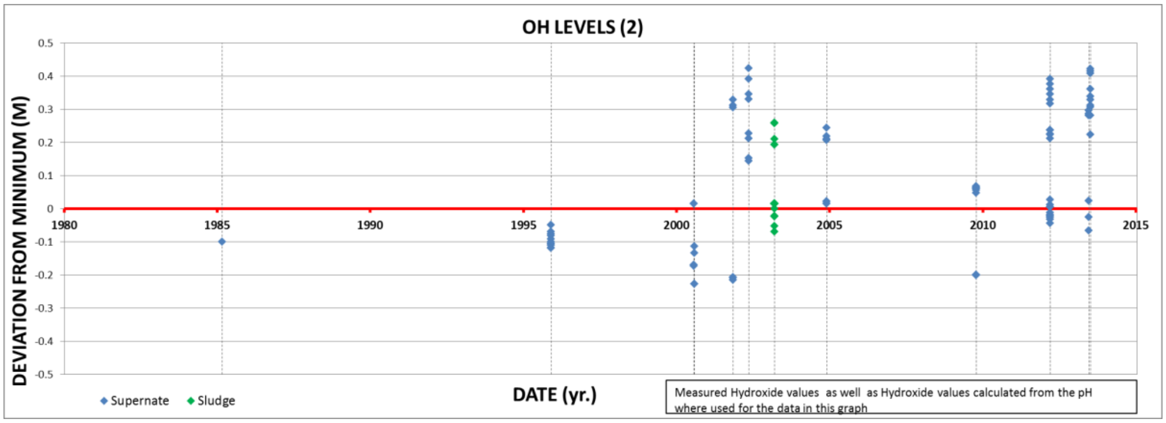



**Figure 10. Hydroxide levels in Tank AN-102.**

## AN-107

Table 5 shows the data loading summary for Tank AN-107.

**Table 5. Data Loading Summary AN-107 (TWINS)**

| Tank Name | Core/Segment Date | Surface Date | Supernate Date | Historical Data Exists | Best Basis Date | TCR Date | HTCE Date | Report As Of Date |
|---|---|---|---|---|---|---|---|---|
| AN-107 | 6/19/2003 | | 6/16/2010 | YES | 12/20/2010 | | 1/31/1997 | 8/11/2014 |

Tank AN-107 is the tank that looks the best so far. It has spent less time out of specification than any other tank (Figure 11). However, very little data was found for this tank so that result could be misleading.

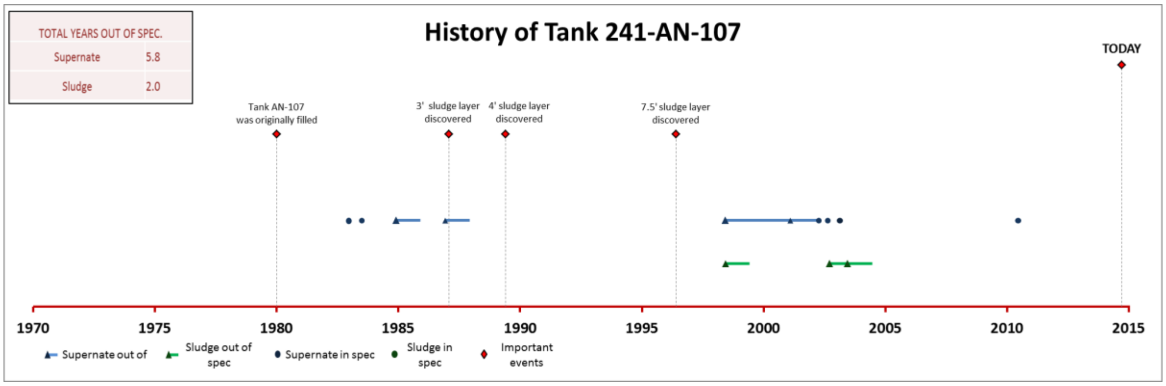



**Figure 11. History of Tank AN-107.**

Like tank AN-102, AN-107 has waste with higher nitrate concentrations, requiring the same type of graph (Figure 12).

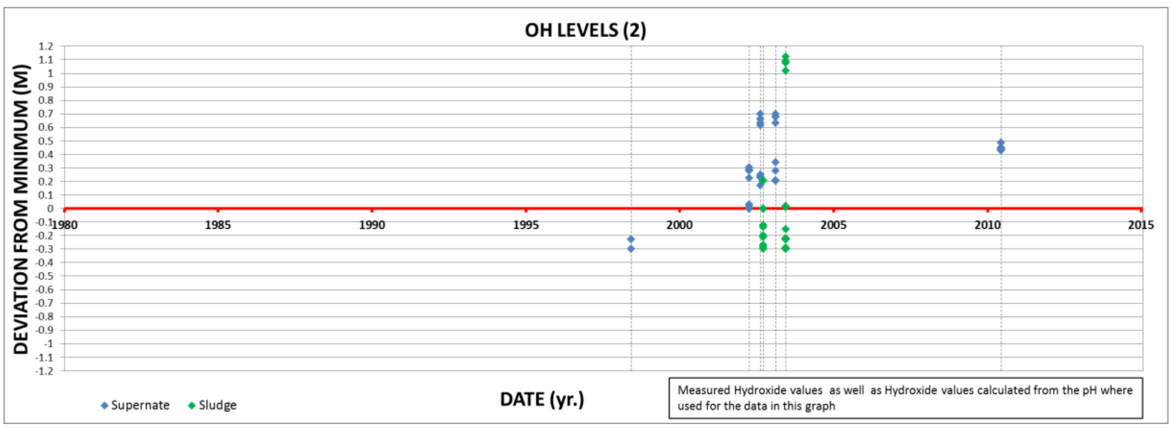



**Figure 12. Hydroxide levels in Tank AN-107.**

# CONCLUSIONS

The waste chemistry in Tank AY-102 could have been a factor contributing to the tank leak. The tank sludge was recorded to have out of spec. chemistry for almost a third of its lifetime, roughly 16 years, far greater than any of the other double-shell tanks that were investigated. This is partly because the state of the chemistry within the tanks was often uncertain. For example, there was only one core sample taken from AY-102 in its entire lifetime. Periodic samples should be collected for a more accurate history and better monitoring of the tank's chemistry.

Other factors could also have caused the premature corrosion of Tank AY-102, such as inconsistencies and error in construction (since it was the first double-shell tank to be built). A possible measure of external corrosion to the bottom of the tank could also have been due to multiply ventilation outage events that occurred to the tank. However, due to time restraints of the internship, this could not be further investigated.

# REFERENCES

Tank Waste Information Network System (TWINS), Hanford Site

Integrated Data Management System (IDMS), Hanford Site

Document Management & Control System (DMCS), Hanford Site

RPP-ASMT-53793, Tank 241-AY-102 Leak Assessment Report

OSD-T-151-00007, Operating Specifications for Double-Shell Storage Tanks

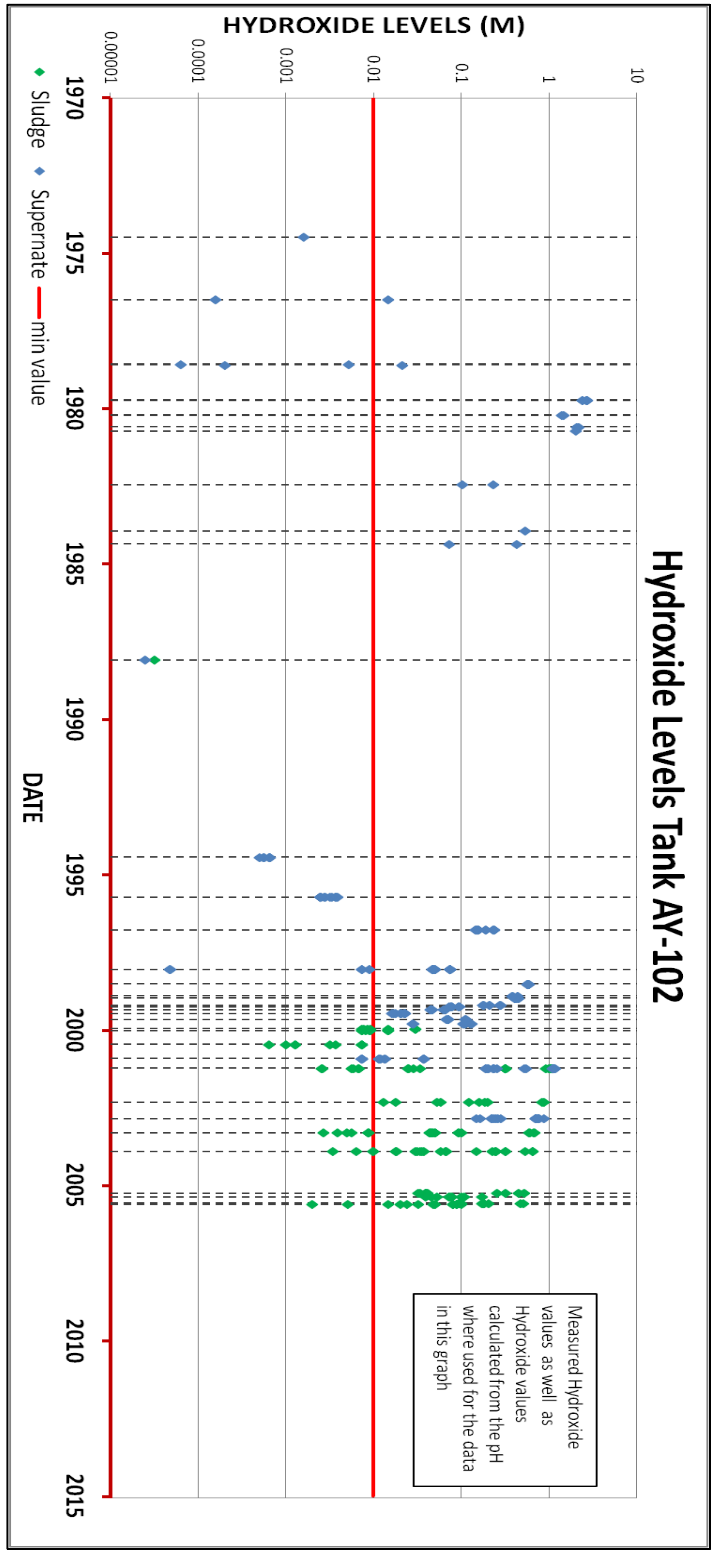
Occurrence Report RL--WHC-TANKFARM-1994-0046, Analysis of Waste Sample Results in Discovery of Out-of Specification Levels of Dioxide in 200 East Area Waste Tanks

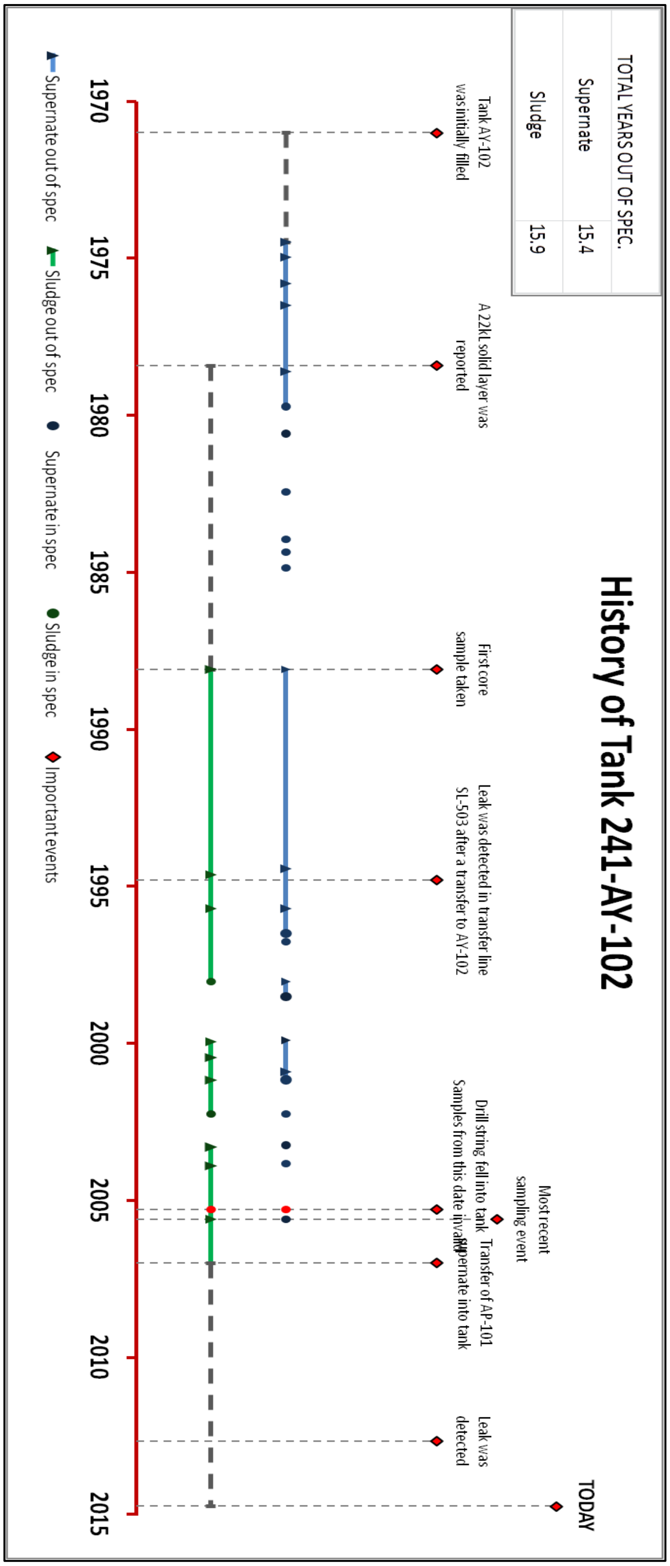
ARH-205, Design Criteria PUREX AY Tank Farm

OSD-T-151-00017, Operating Specifications for Aging Waste Operations in 241-AY and 241-AZ

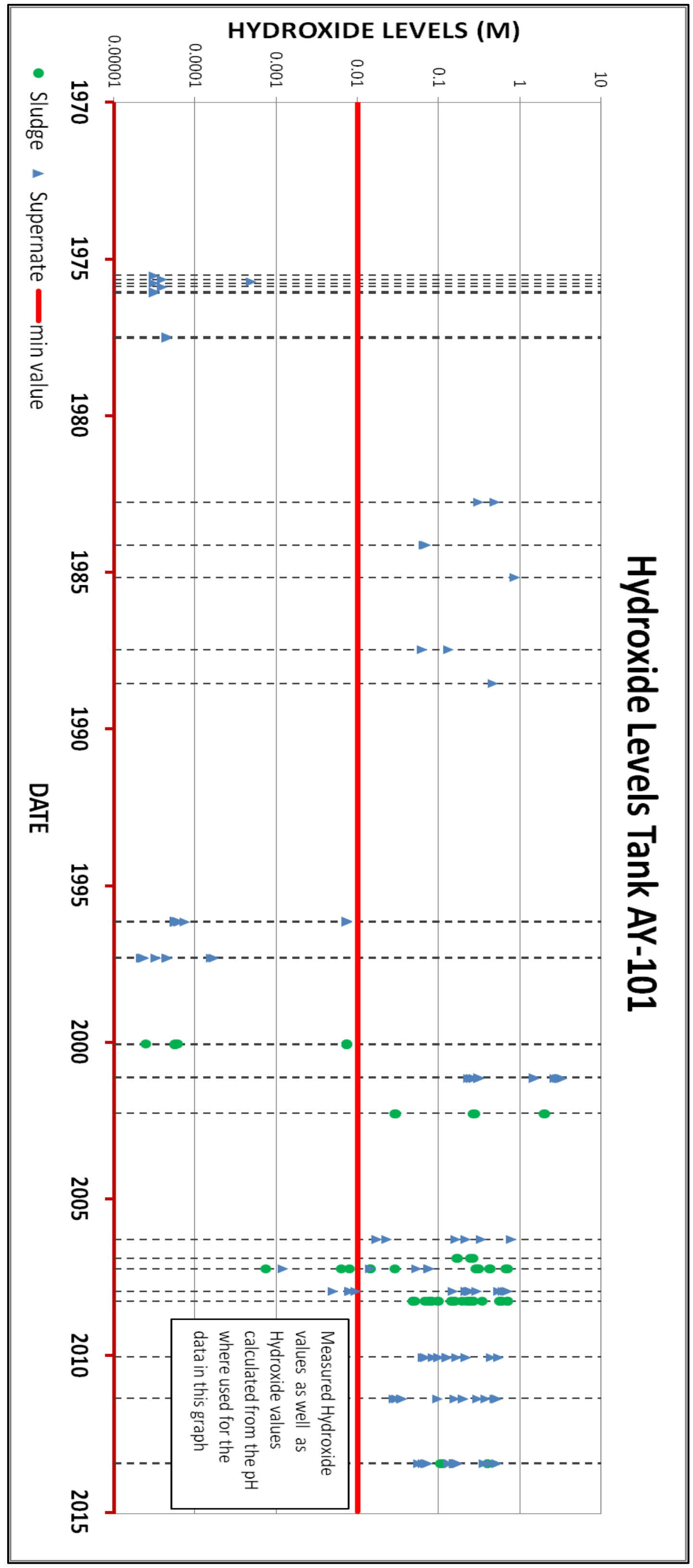
# APPENDIX A: GRAPHS

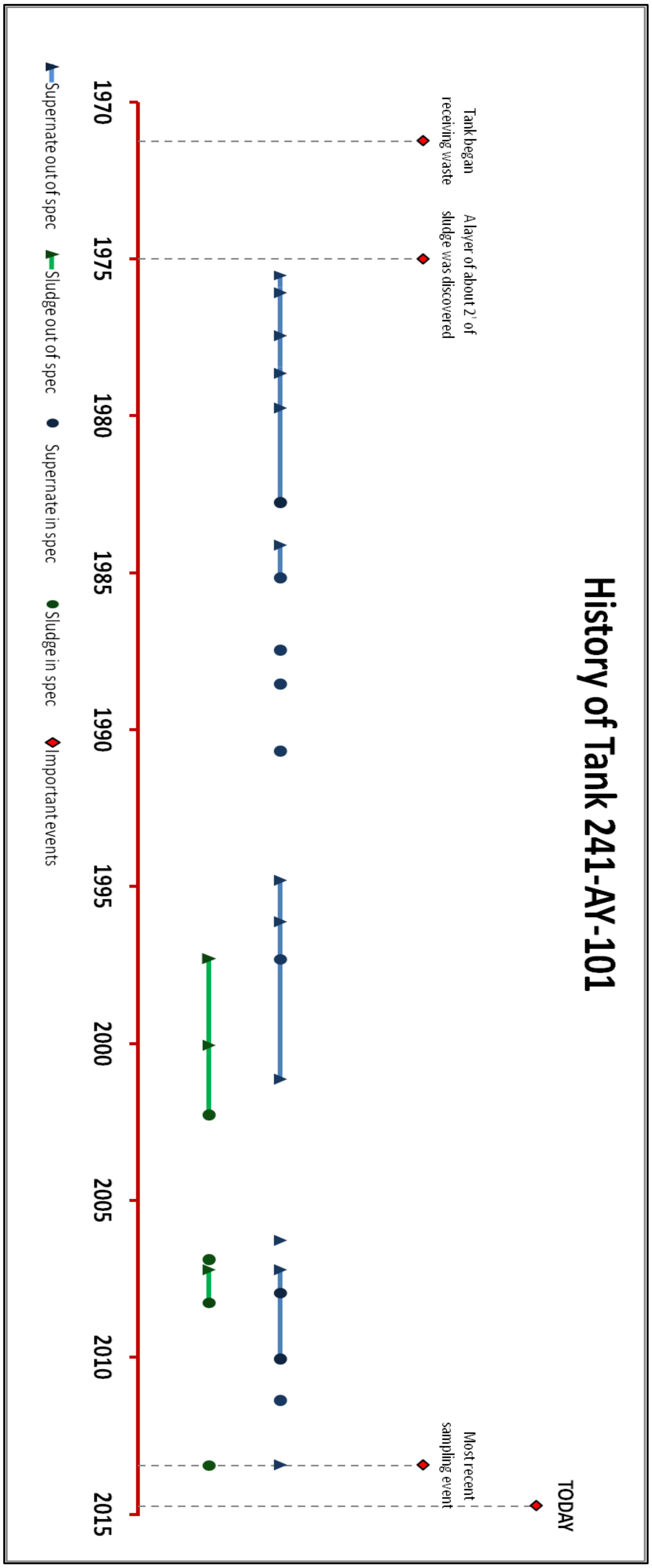
## AY-102



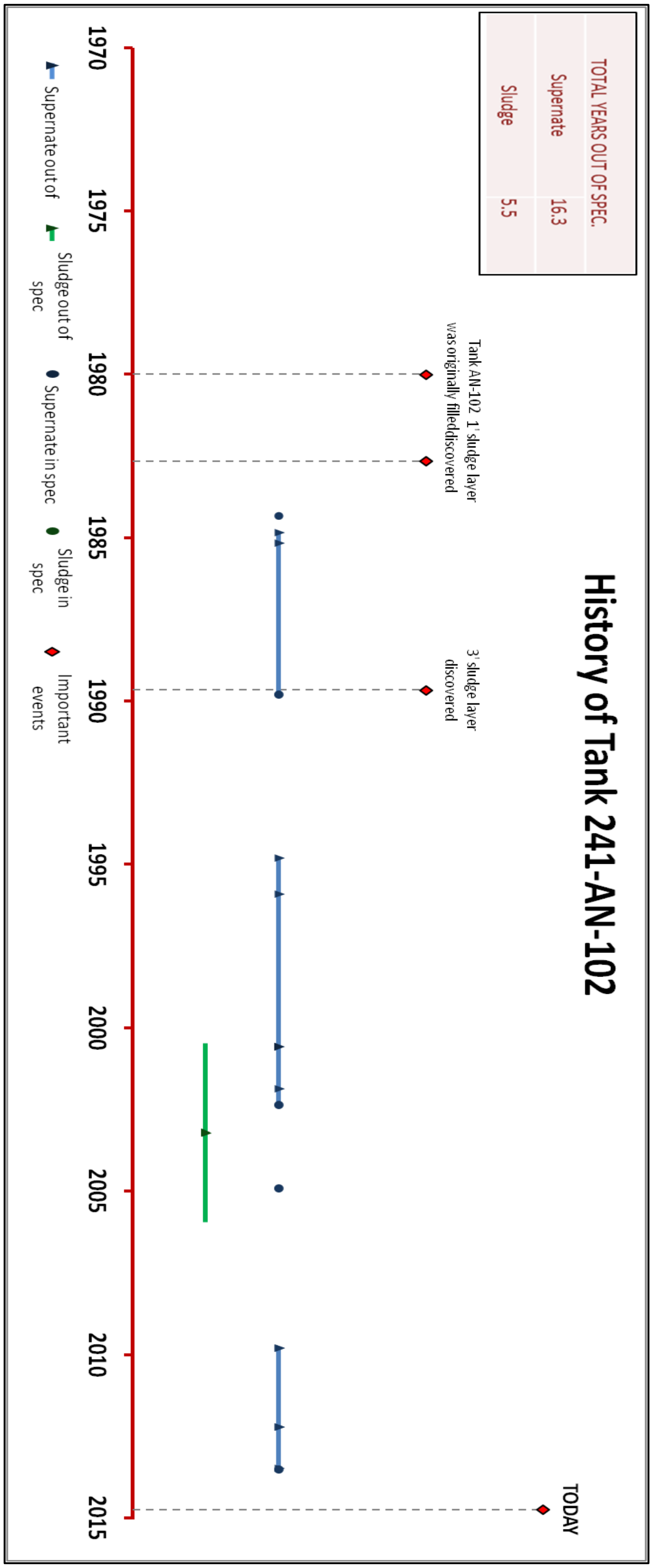



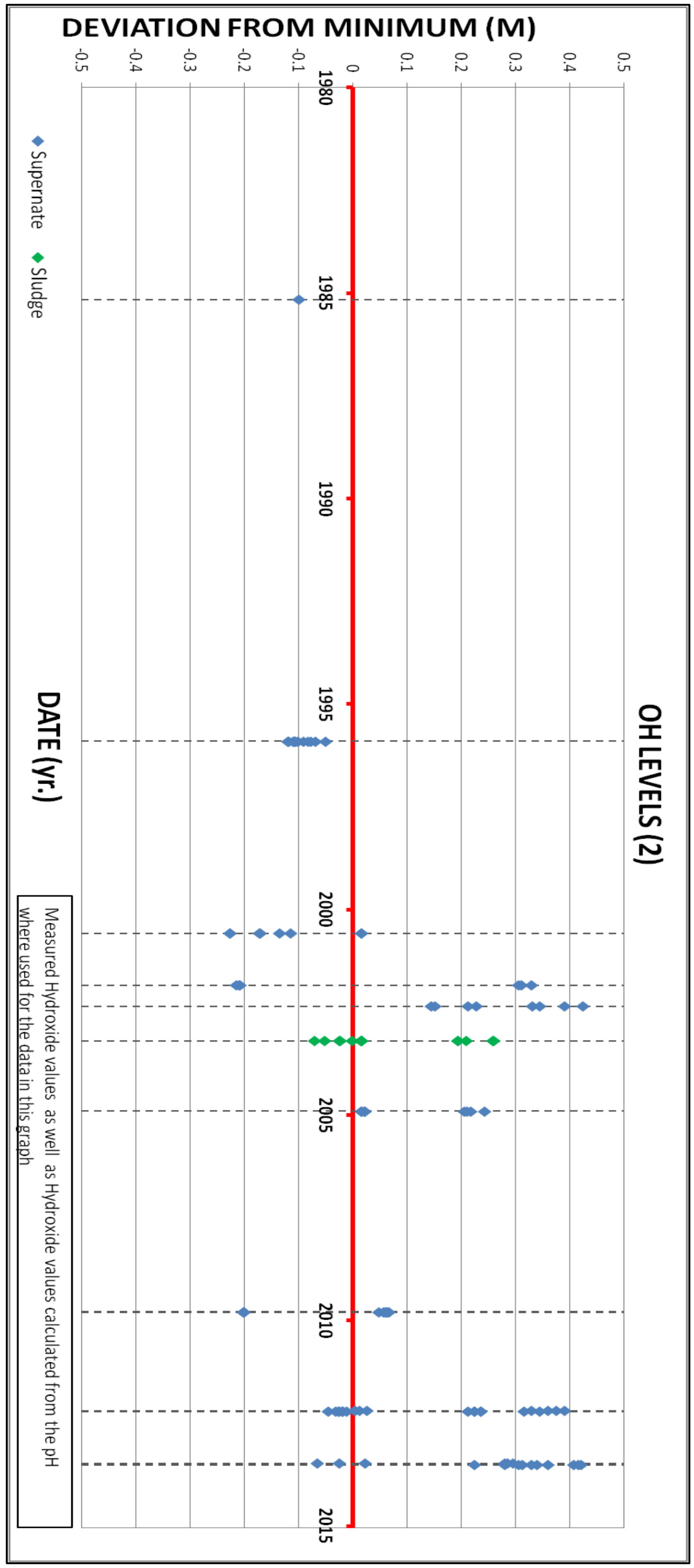
## AY-101


Hydroxide Levels Tank AY-101
HYDROXIDE LEVELS (M)
10
1
0.1
0.01
0.001
0.0001
0.00001
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
DATE
Measured Hydroxide values as well as Hydroxide values calculated from the pH where used for the data in this graph
Sludge
Supernate
min value

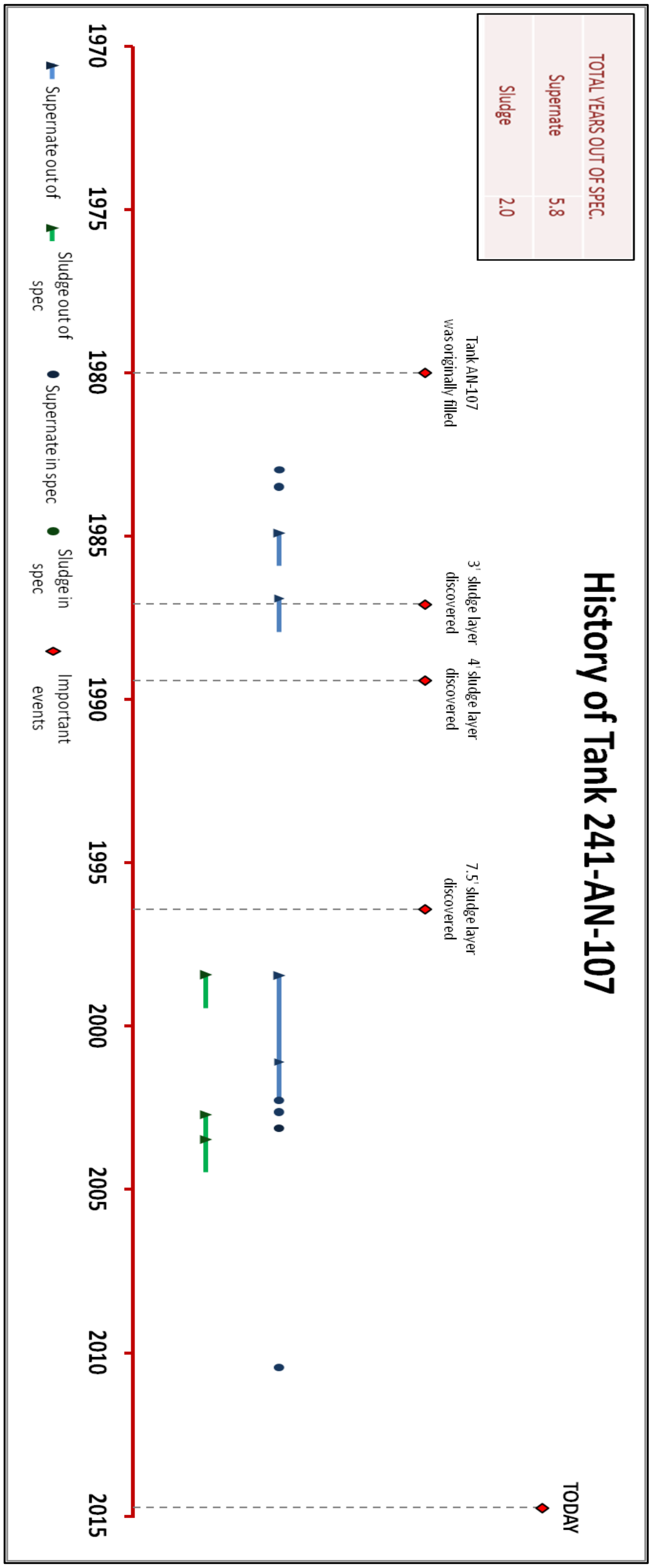

History of Tank 241-AY-101
Tank began receiving waste
A layer of about 2' of sludge was discovered
Most recent sampling event
TODAY
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Supernate out of spec
Sludge out of spec
Supernate in spec
Sludge in spec
Important events

## AN-102

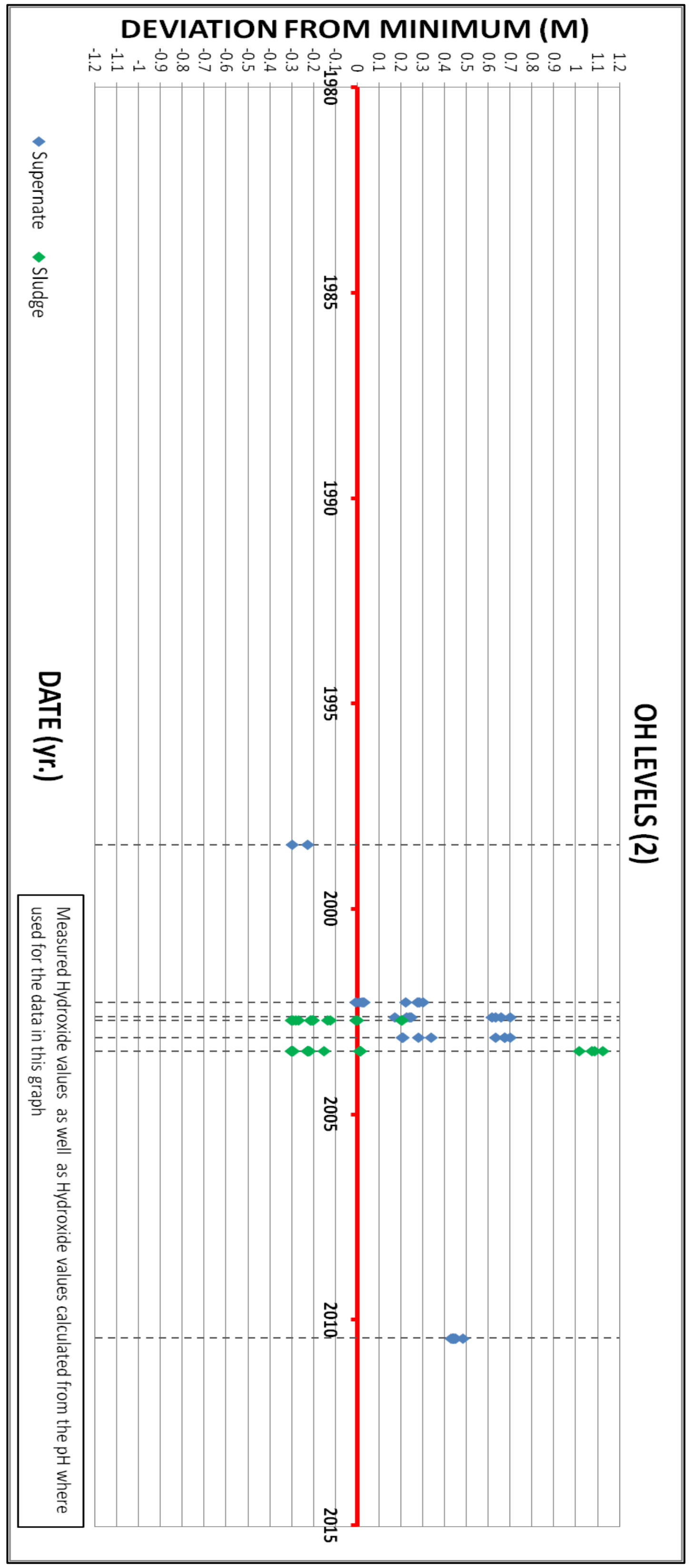

History of Tank 241-AN-102
TOTAL YEARS OUT OF SPEC.
Supernate 16.3
Sludge 5.5
Tank AN-102 was originally filled
1' sludge layer discovered
3' sludge layer discovered
TODAY
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Supernate out of spec
Sludge out of spec
Supernate in spec
Sludge in spec
Important events


OH LEVELS (2)
DEVIATION FROM MINIMUM (M)
DATE (yr.)
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
1980
1985
1990
1995
2000
2005
2010
2015
Supernate
Sludge
Measured Hydroxide values as well as Hydroxide values calculated from the pH where used for the data in this graph

**AN-107**



History of Tank 241-AN-107
TOTAL YEARS OUT OF SPEC.
Supernate 5.8
Sludge 2.0
Tank AN-107 was originally filled
3' sludge layer discovered
4' sludge layer discovered
7.5' sludge layer discovered
TODAY
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Supernate out of spec
Sludge out of spec
Supernate in spec
Sludge in spec
Important events

OH LEVELS (2)
DEVIATION FROM MINIMUM (M)
DATE (yr.)
Measured Hydroxide values as well as Hydroxide values calculated from the pH where used for the data in this graph
Supernate
Sludge

# APPENDIX B: TEMPERATURE MEASUREMENTS