Accession #: D196034232

Document #: SD-WM-ER-538

Title/Desc:

EVALUATION OF ALTERNATIVES FOR UPGRADING DST CORROSION MONITORING AT HANFORD

Pages: 43

Sta.4 (E)

FEB 23 1996

ENGINEERING DATA TRANSMITTAL

1. EDT № 614264

2. To: (Receiving Organization) TWRS Transition Projects	3. From: (Originating Organization) TWRS Materials & Corrosion Engineering	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: 1N1F82	6. Cog. Engr.: J. L. Nelson	7. Purchase Order No.: N/A
8. Originator Remarks: Approval/Release		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: N/A
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date:

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-WM-ER-538		0	Evaluation of Alternatives for Upgrading Double Shell Tank Corrosion Monitoring at Hanford	N/A 2/22/96	1	1	1

16. KEY

Approval Designator (F)	Reason for Transmittal (G)		Disposition (H) & (I)	
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 2. Release 3. Information	4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment	4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.
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18.	19.	20.	21. DOE APPROVAL (if required)
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BD-7400-172-2 (04/94) GEF097

Evaluation of Alternatives for Upgrading Double Shell Tank Corrosion Monitoring at Hanford

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U.S. Department of Energy Contract DE-AC06-87RL10930

EDT/ECN: 614264 UC: 2030
Org Code: 74A40 Charge Code: N1750
B&R Code: EW3130010 Total Pages: 39

Key Words: Double Shell Tank, Corrosion, Trade Study, Corrosion Probe, Uniform Corrosion, Pitting Corrosion, Stress Corrosion Cracking

Abstract: Recent discovery of low hydroxide conditions in Double Shell Tanks have demonstrated that the current corrosion control system of waste sampling and analysis is inadequate to monitor and maintain specified chemistries for dilute and low volume waste tanks. Moreover, waste sampling alone cannot provide adequate information to resolve the questions raised regarding tank corrosion. This report evaluates available technologies which could be used to improve on the existing corrosion control system. The evaluation concludes that a multi-technique corrosion monitoring system is necessary, utilizing ultrasonic and visual examinations for direct evaluation of tank liner condition, probes for rapid detection (alarm) of corrosive conditions, and waste sampling and analysis for determination of corrective action. The probes would incorporate electrochemical noise and linear polarization resistance techniques. When removed from the waste tank, the probe electrodes would be physically examined as corrosion coupons. The probes would be used in addition to a modified regimen of waste sampling and the existing schedule for ultrasonic examination of the tank liners. Supporting information would be obtained by examination of in-tank equipment as it is removed.

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DATE: STA: 4 HANFORD RELEASE ID:
FEB 23 1996

Release Approval Date 2/23/96 Release Stamp

Approved for Public Release

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Executive Summary

Recent discovery of low hydroxide conditions in Double Shell Tanks have demonstrated that the current corrosion control system of waste sampling and analysis is inadequate to monitor and maintain specified chemistries for dilute and low volume waste tanks. Moreover, waste sampling alone cannot provide adequate information to resolve the questions raised regarding tank corrosion. This report evaluates available technologies which could be used to improve on the existing corrosion control system. The evaluation concludes that a multi-technique corrosion monitoring system is necessary, utilizing ultrasonic and visual examinations for direct evaluation of tank liner condition, probes for rapid detection (alarm) of corrosive conditions, and waste sampling and analysis for determination of corrective action. The probes would incorporate electrochemical noise and linear polarization resistance techniques. When removed from the waste tank, the probe electrodes would be physically examined as corrosion coupons. The probes would be used in addition to a modified regimen of waste sampling and the existing schedule for ultrasonic examination of the tank liners. Supporting information would be obtained by examination of in-tank equipment as it is removed.

1.0 Introduction

Assessment of corrosion mechanisms for Double Shell Tanks (DSTs) containing high-level waste at Hanford indicates that recent waste composition excursions outside of established Operating Safety Document (OSD) limits have the potential to shorten DST service lives to less than their design service lives [1]. The current implementation of corrosion control for DSTs is that of waste sampling and analysis to infer corrosive characteristics of the waste and control waste composition. Six occurrences of DST operation outside of established corrosion limits in the past two years indicate that this implementation is inadequate to maintain compliance with applicable regulations (Section 2.2.1). The trade evaluation in this report defines an upgrade to the DST corrosion control system. The format of the trade study is based on System Engineering Procedure 6.0 "Trade Studies and Alternatives Evaluation" of WHC-IP-1117 "WHC Hanford Site Systems Engineering Manual" [2].

1.1 Purpose

The purpose of this study is to identify a combination of corrosion monitoring techniques that will improve the ability to evaluate DST liner condition and improve the ability to detect and evaluate waste corrosivity. The expected benefits to be derived from implementation of such a program are to provide a technical basis to:

- Demonstrate compliance with applicable federal, state, and local waste storage requirements.
- Better control corrosion and thereby maximize DST service life.
- Reduce waste volumes by avoiding unnecessary chemical additions.

- Evaluate the consequences of off normal conditions and the urgency with which these conditions must be corrected.

It is expected that the above benefits will result in overall annual reduced operations costs through avoidance of off normal conditions and the initiation of corrective actions only when necessary.

1.2 Scope

This study applies to corrosion monitoring and control of the 28 DSTs for high-level waste storage at the Hanford Site.

1.3 Background

Westinghouse Hanford Company (WHC) TWRS declared an off-normal event on August 19, 1994 for low hydroxide (below analytical detection limit) conditions discovered in DSTs 241-AY-102 and 241-AP-104. This was followed closely by the discovery of the same conditions in 241-AP-107, 241-AP-108, 241-AY-101 and 241-AN-102. These tanks are in addition to the known low hydroxide condition in 241-AN-107. A subsequent inquiry into the causes and consequences of these low hydroxide conditions demonstrated that sampling and analysis was inadequately implemented in dilute and/or low volume waste tanks [6], as discussed below.

Compliance with the corrosion control specifications [3] relies on periodic physical sampling of the tank waste followed by chemical analysis to determine pH and concentrations of hydroxide, nitrate, and nitrite. The specifications establish limits for the relative concentrations of these species. These limits are duplicated in Appendix A. A combination of infrequent sampling and a hydroxide analytical capability that was unable to verify the hydroxide limit in the waste allowed hydroxide concentrations to drop below the minimum levels specified. A mechanism for carbon dioxide consumption of hydroxide in DSTs has been identified [4].

The use of sampling and analysis to infer corrosion information revealed fundamental inadequacies in the ability to resolve tank corrosion control issues for the low hydroxide occurrences. Resolution of these occurrences has been impeded by three principal issues:

- Unsatisfactory capability to characterize the DST liner condition.
- Unsatisfactory capability to characterize the corrosivity of specific DST wastes.
- Unsatisfactory capability to detect changes in the corrosivity of the DST wastes.

These issues manifested themselves as an inability to adequately answer the following questions for the resolution of the low hydroxide conditions:

- How long has the waste been out of specification?

- What type of damage has been done to the DST liner (if any)?
- How much has the DST service life been shortened (if at all)?
- What should be done to correct the low hydroxide condition?
- How can a low hydroxide recurrence be prevented?

2.0 Trade Studies and Alternatives Evaluation

2.1 Characteristics Needing Definition

[Section Purpose: This section defines the required technical characteristics of any change to the corrosion monitoring and control system. Characteristics are performance criteria without definition of minimum performance levels.]

Section Summary: Five required characteristics of the corrosion monitoring and control system are identified. These characteristics are: (1) monitor corrosion directly; (2) detect localized corrosion; (3) rapidly detect changes in waste corrosivity; (4) evaluate existing tank liner condition; (5) provide corrective action information.

From the assessment of unsatisfactory corrosion monitoring capabilities described in Section 1.3, the following characteristics are required from any corrosion monitoring and control system selected:

- The system should monitor <u>corrosion</u> rather than secondary corrosion parameters such as pH, specific ion concentration, or temperature.

  The state of the art for evaluating corrosion from chemical characteristics is inadequate for the complex conditions found in nuclear waste tanks. At best, there has been modest success in estimating order of magnitude uniform corrosion rates, and establishing inferential "good/bad" relationships between ion concentrations and pitting corrosion and stress corrosion cracking. The laboratory studies which provide the basis for the current corrosion control specifications were predicated on concentrated wastes [5]. A more recent study conducted at Pacific Northwest National Laboratory (PNNL) has demonstrated that there is a dilute waste region within the current corrosion control specifications that promotes localized corrosion [6].

- The system should provide information on the initiation and propagation of the local corrosion mechanisms of pitting and stress corrosion cracking.

  Pitting and stress corrosion cracking are considered the most probable failure mechanisms for high-level waste storage tanks. Failure by uniform corrosion is not considered probable [1]. Appendix B provides a summary of corrosion experience for high-level waste storage tanks.

- The system should provide a relatively rapid indication of changes in waste corrosivity.

  In the evaluation of the consequences of the DST low hydroxide occurrences, there were two instances where it was impossible to readily verify adequate hydroxide concentrations ever in the use of the tank (241-AP-107 and 241-AP-108). There were also three occasions where it had been more than ten years since a sample had been taken that could readily confirm hydroxide concentrations were within specification (241-AP-104, 241-AY-101, and 241-AY-102). A recent Savannah River Site (SRS) report suggests that pits in the early stages of growth may cease growing and repassivate upon the establishment of inhibiting conditions [7]. The report recommends a five day limit to reestablish adequate inhibitor concentrations after the addition of small volumes of completely uninhibited raw water. Pits allowed to grow past this early condition can rapidly proceed to a depth where no amount of inhibitor addition to the bulk waste can stop pit propagation. The SRS report proposes that pit propagation rates can be as high as 1800 mils per year (mpy) (40 mm/yr). Five days is used as a detection goal for this evaluation.

- The system should be able to evaluate the actual condition of the tank liner.

  It is only from direct examination of the tank walls that the cumulative effects of previous years of operation be determined. This determination of cumulative effect can be used in conjunction with information on current corrosion conditions to estimate remaining tank life.

- The system should provide information useful for the correction of off-normal or unacceptable corrosion conditions and provide feedback to determine whether a correction process has been effective.

  While there may be several viable techniques for monitoring tank corrosion, the only viable means of controlling tank corrosion is to change waste chemistry. The system used to monitor corrosion should provide sufficient information on waste chemistry to suggest an appropriate chemical correction to an off-normal condition.

2.2 Constraints, Alternatives, and Initial Screening

2.2.1 Constraints

[Section purpose: Applicable constraints are determined to provide a basis for eliminating unsuitable alternatives and analyzing possible solutions. Constraints are criteria having minimum acceptable values.]

Section summary: Applicable regulatory requirements for corrosion control are identified as pass/fail criteria and a performance requirement is defined for each of the five required corrosion monitoring characteristics.

Administrative Requirements

- *Code of Federal Regulations* 40-264.195(a) requires that hazardous wastes must not be placed in a tank system if they could cause the tank or associated ancillary equipment, and containment system to rupture, leak, corrode, or otherwise fail.

- *Washington Administrative Code* 173-303-640(2)(c)(iii) requires tank integrity assessments and consideration of existing corrosion protection when performing tank system integrity assessments.

- DOE Order 5820.2A, *Radioactive Waste Management*, requires monitoring of cathodic protection systems, methods for periodically assessing waste storage system integrity, and adjustment of waste chemistry to control corrosion.

- DOE-STD-1073-93, *Configuration Management*, requires implementation of a Material Condition and Aging Management Program to control aging processes in major equipment and components. The primary aging processes in waste tank systems are corrosion related.

- DOE/RL-92-60, *Tank Waste Remediation System Functions and Requirements* contains corrosion control requirements for the Store Waste (F4.2.1.1) and Transfer Waste (F4.2.4.4) functions.

- WHC-SD-WM-OSR-005, *Single-Shell Tank Interim Operational Safety Requirements*, WHC-SD-WM-OSR-004, *Aging Waste Facility Interim Operational Safety Requirements*, and WHC-SD-WM-OSR-016, *Double-Shell Tank Interim Operational Safety Requirements*. These support documents contain interim operational safety requirement - administrative controls for corrosion control, cathodic protection, and integrity assessments. Implementation of these administrative controls necessitates corrosion control activities.

- WHC-SD-WM-PLN-068, *TWRS Life Management Program Plan*, identifies stress corrosion cracking, pitting corrosion, and uniform corrosion as the primary aging mechanisms for DSTs.

Performance Criteria

- The system should monitor <u>corrosion</u> rather than a secondary corrosion related parameter such as pH, ion concentration, or temperature.

  No quantitative performance criteria is established.

- The system should provide information on the initiation of the local corrosion mechanisms of pitting and stress corrosion cracking.

  No quantitative performance criteria is established.

- The system should provide a relatively rapid indication of changes in waste corrosive characteristics.

  Five days are established as the maximum delay in detection of a change in waste corrosiveness. This value is derived from a Savannah River Site study recommending a five day limit for correction of tank waste chemistries [7].

- The system should be able to evaluate the actual condition of the tank liner.

  Flaw detection and sizing requirements have been established based on estimated flaw sizes necessary precipitate tank failure by unstable fracture or to grow flaws by intergranular stress corrosion cracking [8, 9]. These results have been used to set flaw detection and sizing requirements for an ultrasonic inspection system as shown [10]:

Type of Flaw	Dimensions (t=orig. min. wall thickness)	Degree of Accuracy
Pit	0.7 t dia. X 0.35 t deep	±0.02 in.
Crack	t long X 0.5 t deep 12 in. long X 0.2 t deep	±0.05 in deep ±0.5 in. long

- The system should provide information on how to correct off-normal or unacceptable corrosion conditions.

  To support existing chemistry control standards [2], the system should provide quantitative information on pH and the concentrations of hydroxide, nitrite, and nitrate.

2.2.2 Alternatives

[Section Purpose: Describe alternatives such that pre-selection of an option is avoided and no feasible options have been overlooked.

Section Summary: The corrosion monitoring options of Direct, Surrogate, and Inference are introduced.

There are three basic options for corrosion monitoring in existing DSTs:

- Direct methods. These provide information about the actual tank liner. No relationship has to be assumed between the tank steel and some other material. Questions about the effects of inhomogeneity of the waste chemistry within a tank or tank material irregularities such as weld defects, heat affected zones and stress risers are resolved by actual measurement of effects on the tank. No available direct method rapidly indicates current corrosion processes, but repeated application of a direct method can establish the cumulative effects of previous corrosion processes and define trends. Direct monitoring methods are represented by the following technologies:

- Photography/visual inspection of tank wall
- Ultrasonic testing of tank wall
- X-rays/neutron based inspection of tank wall
- Direct "on-wall" Corrosion monitoring
- Leak detection of tank wall

Each of these technologies are discussed in Appendix C.

- Surrogate methods. These indirect measurements depend on the detection of corrosion through the use of a tank surrogate material that is similar to the tank steel. Surrogate techniques encompass the two broad categories of coupons and probes. Coupons are steel specimens that are immersed in the tank waste for designated exposure times and physically examined at the end of the exposure. Multiple coupons are typically exposed with increasing time periods to provide an estimate of corrosion trends over time. Probes can be used to monitor electrical signals generated by corrosion processes occurring on specimens made of the same material as the tank walls. The usefulness of a probe depends on a known or empirical relationship of probe response to corrosion type and rate. In either the case of probes or coupons, assumptions have to be made about what the presence of corrosion on the surrogate means about corrosion on the tank itself. Surrogate monitoring methods are represented by the following technologies:

  - Corrosion coupons
  - Artifacts
  - Corrosion probes

  Each of these technologies are discussed in Appendix C.

- Inference (or Indirect) methods. These methods utilize the measurement of a secondary parameter related to corrosion rather than a corrosion measurement itself. Examples of these are chemical analyses, redox potential, and pH. The use of inference methods requires the assumption that the measured parameter is the primary controlling factor in the corrosion process. Inference methods are even further removed from actual tank corrosion than surrogate methods but often can identify specific chemical species or corrosion control variables that can be adjusted to change corrosion condition. Sample size and location are inherent issues associated with all monitoring techniques. Inference monitoring methods are represented by the following technologies:

- Redox potential
- Chemical analysis
- pH
- Conductivity
- Optical methods

Each of these technologies are discussed in Appendix C.

The three general corrosion monitoring techniques of Direct, Surrogate, and Inference can potentially be used individually or in combination with each other. There are seven combinations of these techniques available:

Single Method Techniques
- Direct Only
- Surrogate Only
- Inference Only

Multiple Method techniques
- Direct/Surrogate
- Direct/Inference
- Surrogate/Inference
- Direct/Surrogate/Inference

2.2.3 Initial Screening

[Section Purpose: Initial screening is used to eliminate non-viable alternatives from further consideration. Each alternative is compared to each constraint. Alternatives that do not satisfy every constraint are eliminated from further consideration. Alternatives meeting all constraints receive additional consideration.]

Section Summary: The combination corrosion monitoring technique of Direct/Surrogate/Inference is determined as the only alternative meeting all constraints. This combination is passed on for further analysis to determine which technology best provides the required information for each of Direct, Surrogate, and Inference.

Table 1 below summarizes a comparison of the corrosion monitoring techniques of Appendix C against the required characteristics of Section 2.1. In general, the shaded regions represent strengths of a corrosion monitoring category for a specific desired information type. It is apparent that complete resolution of corrosion issues will require representation from each of the monitoring categories. No single available technique of Direct, Surrogate, or Inference monitoring can acquire all of the information required to address the issues raised during the low hydroxide occurrences. Each individual category may be considered as necessary but not sufficient for characterization of tank corrosion. Only the Direct/Surrogate/Inference option can satisfy all of the information minimum constraints. Subsequent discussion will evaluate the "best" technologies within these categories.

2.3 Criteria Development

[This section defines selection criteria required to further evaluate viable alternatives. Selection criteria provide standards against which an alternative is judged.]

Section Summary: Selection criteria are defined for subsequent use in evaluating alternatives

The following selection criteria were defined for use in an industry survey described in Section 2.4. The discussion provided for each criterion is excerpted from the explanatory material accompanying the survey.

Feasibility - Is it feasible to use the technique at the location indicated. For example, the feasibility of using visual methods on the bottom of the exterior of the primary tank is nearly 0. The only locations that are at all possible are in the air channels. Therefore this could be 0 to 1 or 50 depending on whether the bottom tank bottom is considered in its entirety or whether just the channel regions are considered.

Status - What is the operational status of the technique? Is it in development or operational? Has it been used in radioactive, remote systems? Status is a non-numeric consideration which is not summarized in the survey response tables.

Accuracy - Ideally there would be objective data. In many cases the response (0-100) will be subjective.

Error - Both Type I and Type II errors are listed.

In evaluating data, one assumes a *null* hypothesis such as the calculated average corrosion rate of x mpy is correct. Then a desired probability of its being correct is assigned, for example 95%, that is there is a 5% probability of it being wrong. [The evaluation assumed a limit of 0.05 or 5%.] If the data are tested and the null hypothesis is correct, this is a positive result. If the null hypothesis is correct but rejected as false, a Type I error or a False Negative is produced.

Table 1. Capability of corrosion monitoring techniques to provide desired information.

Function	Evaluate Liner Condition		Evaluate Waste Corrosivity		Rapid detection of change in waste		Identify a control parameter	
Type of Corrosion	Uniform	Local	Uniform	Local	Uniform	Local	Uniform	Local
Direct Visual NDE X-ray, neutron Wall monitoring Leak detection								
Surrogate Coupons Artifacts Probes ER LPR EIS EN								
Inference Redox Chemical pH Conductivity Optical								

Shaded regions represent the general area of capability for a monitoring category.

If the original hypothesis is actually be wrong and is rejected as a negative, the conclusion is correct. But if the hypothesis is accepted, this is a Type II error or a False Positive.

Attributes - In this section, what is the likelihood of using the technique to provide early warning of tank failure. Is the technique **Reliable**, will it work properly when put into operation, is it **Available** when needed, and can it be easily **Maintained**? Are the data of a type that can be used to see **trends** - numerical data are better, but relative data such as yes/no may be of use. Similarly, can the information be **archived**? Presumably the latter answer is always yes, but it is necessary to consider the retrievability and application of the data when retrieved.

Selection criteria - can either be relative or "absolute" responses. **Cost** could be listed in dollars, $5000 per device, or low (0) to high (100). **Success**, is meant to assess whether it be successfully applied by the average trained operator. This may well tie into **ease of use** though ease may also mean it is a one-person operation or requires a crew of several to use it properly. **Schedule** evaluates whether it is available now (0) or will there be a significant delay to obtain one (100)?

2.4 Alternative Evaluation

[Section Purpose: Alternative are evaluated against one another on the basis of the selection criteria.]

Section Summary: The results of an industry survey of corrosion monitoring technologies are presented.

The selection of the appropriate monitoring technology could have been performed by Hanford staff. However, it was deemed worthwhile to survey persons recognized to have expertise in the various methods to find whether there were major concerns about any one method or whether features that would be either beneficial or detrimental to any monitoring technique were being overlooked. The survey form and explanation were prepared. The form contained three identical sections, one each for stress corrosion cracking, pitting, and uniform corrosion. A summary of the response statistics is provided as Table 2. The results of the survey are tabulated in Tables 3 through 8.

Table 2. Summary of survey response statistics

	Totals	%			
Surveys sent	48	100.0%			
Surveys returned	14	29.2%			
Response, text format	1	2.1%			
Unable to respond	13	27.1%			
No response	19	39.6%			
Addressee unknown	1	2.1%			
	Hanford	Other DOE	Vendors	Other Technical	Other Interested
Number sent to:	14	7	6	16	5
Number returned	7	3	1	4	0
% returned	50.0%	42.9%	16.7%	25.0%	0.0%

Table 3. Tabulated survey results for uniform corrosion

MONITORING	FEASIBILITY IP	EP	IB	EB	IS	STATUS	ACCURACY	ERROR Type I	Type II	ATTRIBUTES warn	RAM	trend	archive	cost	SELECTION CRITERIA success	ease of use	schedule	score
Coupons	91	94	87	89	94		85	40	23	57	75	69	87	60	75	78	40	1218
Resistance	84	na	82	na	93		83	33	17	82	75	82	83	46	79	80	28	1099
Linear Polarization	85	na	83	na	na		80	32	17	81	74	80	85	51	75	76	25	991
Leak Detection	55	68	55	68	33		60	59	23	22	68	33	53	33	79	89	14	956
NDE	48	82	24	22	79		71	44	29	68	61	74	83	82	66	57	44	934
Artifacts	66	63	66	63	70		54	38	34	29	39	33	60	48	69	54	38	906
Electrochemical Noise	76	na	74	na	na		51	34	39	74	56	83	83	62	58	68	40	849
Analysis	90	na	77	na	na		62	44	36	62	65	61	71	68	66	65	34	838
Electrochemical Impedance	71	na	68	na	na		67	41	26	74	66	74	79	57	52	61	51	836
pH	84	na	77	na	na		59	35	34	52	54	59	59	47	60	55	34	810
Visual Inspection	34	54	4	15	54		33	32	23	25	50	46	72	33	58	79	27	809
Redox/Potential	54	na	48	na	na		50	46	44	56	53	70	71	36	56	57	37	752
Conductivity	72	na	59	na	na		54	47	47	50	54	58	59	44	51	59	30	747
Corrosion Monitoring, walls	44	36	9	9	36		32	50	50	36	24	40	44	53	42	37	63	573
Optical	40	na	27	na	na		31	39	45	38	36	42	46	55	39	36	56	541
X-ray, neutrons	21	33	11	8	29		36	50	49	44	32	53	62	94	37	17	96	495

FEASIBILITY Terms (location from which examination/analysis occurs): IP-interior surface, primary tank wall; EP-external surface, primary tank wall; IB-interior surface, bottom of the primary tank; EB-external surface, bottom of the primary tank; IS-internal surface, secondary tank wall. na - not applicable.
All numerical values are based on a scale of 0 - 100. STATUS is non-numeric and not summarized here.

Table 4. Tabulated survey results for pitting corrosion

MONITORING	FEASIBILITY IP	EP	IB	EB	IS	STATUS	ACCURACY	ERROR Type I	Type II	ATTRIBUTES warn	RAM	trend	archive	cost	SELECTION CRITERIA success	ease of use	schedule	score
Coupons	85	86	81	64	85		73	40	29	49	70	55	82	50	59	70	46	1090
Leak Detection	58	79	50	80	49		75	41	21	29	78	33	57	31	81	90	12	1051
Visual Inspection	46	70	6	17	68		60	41	50	41	52	65	77	48	61	71	28	868
NDE	37	74	12	16	73		64	40	43	57	53	78	86	84	50	50	45	837
Artifacts	59	59	59	55	55		56	48	48	14	25	21	65	46	61	68	31	826
Electrochemical Noise	69	na	67	na	na		56	34	43	78	57	82	86	68	44	52	41	805
Analysis	76	na	70	na	na		61	49	42	59	62	58	77	61	56	66	32	802
pH	71	na	68	na	na		52	53	53	46	50	55	66	39	44	56	31	734
Conductivity	60	na	56	na	na		49	57	57	42	51	52	67	36	45	61	25	709
Redox/Potential	47	na	36	na	na		44	54	54	52	49	60	70	32	51	66	36	698
Linear Polarization	44	na	42	na	na		29	46	54	41	59	56	74	43	44	53	31	669
Resistance	38	na	35	na	27		18	50	53	21	47	32	58	31	40	64	23	622
Corrosion Monitoring, walls	17	25	7	4	14		41	43	42	46	43	47	65	49	50	48	69	601
X-ray, neutrons	16	29	9	9	24		51	33	35	56	38	65	78	93	35	17	93	572
Electrochemical Impedance	33	na	30	na	na		18	40	53	30	40	51	54	42	30	40	53	538
Optical	32	na	26	na	na		23	57	57	34	30	34	38	55	35	40	24	499

FEASIBILITY Terms (location from which examination/analysis occurs): IP-interior surface, primary tank wall; EP-external surface, primary tank wall; IB-interior surface, bottom of the primary tank; EB-external surface, bottom of the primary tank; IS-internal surface, secondary tank wall. na - not applicable.
All numerical values are based on a scale of 0 - 100. STATUS is non-numeric and not summarized here.

Table 5. Tabulated survey results for stress corrosion cracking

	FEASIBILITY					STATUS	ACCURACY	ERROR		ATTRIBUTES					SELECTION CRITERIA				
MONITORING	IP	EP	IB	EB	IS			Type I	Type II	warn	RAM	trend	archive	cost	success	ease of use	schedule		score
Leak Detection	55	84	45	76	64		70	42	28	39	79	50	64	28	78	89	10		1085
Coupons	72	71	68	59	71		76	38	27	41	65	54	84	58	56	63	51		1006
NDE	42	78	16	23	82		72	40	38	63	61	78	86	85	59	43	45		894
Visual Inspection	44	62	5	17	71		60	49	43	43	66	55	77	38	66	76	30		880
Electrochemical Noise	69	na	66	na	na		59	30	44	78	54	84	84	65	44	52	40		811
Analysis	85	na	72	na	na		57	51	49	65	70	60	76	66	66	63	35		811
Artifacts	55	49	55	41	49		54	41	41	16	27	20	60	40	57	64	36		788
pH	79	na	68	na	na		49	48	48	55	58	57	63	46	56	42	35		751
Conductivity	68	na	55	na	na		42	57	57	43	51	46	63	36	54	57	30		699
Redox/Potential	38	na	27	na	na		45	63	62	54	55	56	70	31	60	53	26		676
Linear Polarization	33	na	31	na	na		28	43	43	41	54	50	59	31	41	49	37		631
Corrosion Monitoring, walls	12	15	2	3	38		47	42	40	55	41	62	62	43	56	53	89		631
Resistance	27	na	26	na	23		27	50	50	34	49	44	53	24	43	59	43		616
X-ray, neutrons	16	29	9	9	27		55	29	29	60	35	52	78	91	39	16	94		581
Electrochemical Impedance	31	na	29	na	na		30	54	48	34	43	47	53	42	30	40	69		524
Optical	39	na	26	na	na		23	57	57	37	33	42	38	55	46	40	44		510

FEASIBILITY Terms (location from which examination/analysis occurs): IP-interior surface, primary tank wall; EP-external surface, primary tank wall; IB-interior surface, bottom of the primary tank; EB-external surface, bottom of the primary tank; IS-internal surface, secondary tank wall. na - not applicable. All numerical values are based on a scale of 0 - 100. STATUS is non-numeric and not summarized here.

Table 6. Summary ranking by corrosion mechanism

	Type	Uniform	Pitting	SCC
Coupons	Surrogate	1	1	2
Resistance	Surrogate	2	12	13
LPR	Surrogate	3	11	11
Leak Detection	Direct	4	2	1
NDE	Direct	5	4	3
Artifacts	Surrogate	6	5	7
EN	Surrogate	7	6	5
Chemical Analysis	Inference	8	7	6
EIS	Surrogate	9	15	15
pH	Inference	10	8	8
Visual	Direct	11	3	4
Redox	Inference	12	10	10
Conductivity	Inference	13	9	9
Wall Monitoring	direct	14	13	12
Optical	Inference	15	16	16
X-ray, neutrons	Direct	16	14	14

Table 7. Summary ranking by monitoring category

	Uniform	Pitting	SCC
Direct	Leak Detection NDE Visual Wall Monitoring X-ray, neutrons	Leak Detection Visual NDE Wall Monitoring X-ray, neutrons	Leak Detection NDE Visual Wall Monitoring X-ray, neutrons
Surrogate	Coupons Resistance LPR Artifacts EN EIS	Coupons Artifacts EN LPR Resistance EIS	Coupons EN Artifacts LPR Resistance EIS
Inferential	Analysis pH Redox Conductivity Optical	Analysis pH Conductivity Redox Optical	Analysis pH Conductivity Redox Optical

Table 8. Summary Ranking by data objectives.

Function	Evaluate Liner Condition		Evaluate Waste Corrosivity		Rapid detection of change in waste		Identify a control parameter	
Type of Corrosion	Uniform	Local	Uniform	Local	Uniform	Local	Uniform	Local
Direct								
Visual	3	2/3						
NDE	2	3/2						
X-ray, neutron	5	5						
Wall monitoring	4	4						
Leak detection	1	1						
Surrogate								
Coupons			1	1				
Artifacts			4	2/3				
Probes								
ER			2	5	1	3		
LPR			3	4	2	2		
EIS			6	6	4	4		
EN			5	3/2	3	1		
Inference								
Redox							3	4
Chemical							1	1
pH							2	2
Conductivity							4	3
Optical							5	5

Shaded regions represent the general area of capability for a monitoring category.
Local corrosion rankings with a / indicate a difference in rankings between pitting/SCC.

2.5 Desired Characteristics Improvements

[Section Purpose: Identify the areas of desired system performance improvements.]

Section Summary: The concept of surrogate monitoring as an alarm function is introduced. The existing ultrasonic inspection plan is accepted as the direct monitoring protocol.

The implementation of a multi-technique corrosion monitoring system would use the categories of Direct, Surrogate, and Inference to their optimum if assigned the functions of Condition Evaluation, Alarm, and Corrective Action respectively. That is:

Direct monitoring: Used to evaluate liner condition.
Surrogate monitoring: Used to provide rapid detection (Alarm) of corrosive conditions.
Inference monitoring: Used to determine appropriate corrective action.

Direct monitoring by ultrasonic examination is already a part of the Integrity Assessment Program Plan [10]. An ultrasonic examination robot device is undergoing final testing prior to use in representative DST annuli. Use of this device is part of the Integrity Assessment Program which has prepared an independent examination protocol for the implementation of ultrasonic testing. This program has been extensively reviewed and is expected to provide all required information for direct monitoring without further modification. For the purposes of this study, no further direct monitoring techniques will be evaluated and no suggestion to modify the ultrasonic inspection test plan is contemplated. This a priori conclusion is supported by the results of the industry survey discussed in Sections 2.4 and 2.7. A discussion of the ultrasonic inspection test plan is provided in references 10 and 11.

2.6 Feasibility of Desired Improvements

[Section Purpose: Improvements to alternatives are proposed by evaluating refinements.

Section Summary: A summary cost evaluation is prepared for several variations of potentially acceptable alternatives to evaluate their feasibility from an economic basis.

For further comparing the different options, a brief economic assessment of the costs of various corrosion monitoring techniques has been performed. The main evaluation was done on a spreadsheet, which is summarized in Table 9.

Five scenarios for Probes, Coupons, and Chemical Sampling are evaluated. These include:

Case 1: A dedicated probe assembly installed in a tank;

Case 2: Probes installed on another piece of equipment being inserted for other reasons;

Case 3: A dedicated set of coupons;

Case 4: Coupons inserted on another piece of equipment being inserted for other reasons;

Case 5: Chemical sampling with the data used to estimate corrosion rates.

Case 1 - Dedicated Probes

All probe types, Noise, Resistance, or Polarization, were assumed to be equal in design, installation, monitoring, and removal costs. The following assumptions were made:

- One dedicated probe assembly in each tank.
- Corrosion program covers all costs of design, fabrication, installation, removal at failure, and monitoring.
- Costs include:
  - $20K to design and fabricate probe tree.
  - $30K to install in tank.
  - 2 hours per week per tank to retrieve data on a routine basis, at $100/hr.
  - $5K per tank for above ground instrumentation.
  - $75K per tank every 5 years to pull failed equipment.
  - $10K per tank every 5 years to examine failed electrodes.

Case 2 - Piggyback Probes

Probes similar to Case 1 are installed but the probe assemblies are "Piggybacked" on equipment already scheduled for installation by other projects.

- Costs include:

  - $1K for engineering and procurement per array, 3 arrays per tank.
  - Monitoring costs as with Case 1.
  - Above ground instrumentation as with Case 1.
  - $10K per tank every 5 years to examine failed electrodes.

Table 9. Cost assessment

Case 1: Probe Assembly - per Tank						
Description	Frequency	Start up Cost $	Operating Cost $ea.	End Cost $	Annual Cost $	Total $
System Life, years	5					
Monitoring Equip.		5,000			1,000	5,000
Design/Fabrication		20,000			4,000	20,000
Installation		30,000			6,000	30,000
Data Collection/wk	2		100		10,400	52,000
Removal				75,000	15,000	75,000
Inspection				10,000	2,000	10,000
TOTAL		55,000			38,400	192,000

In no case has the cost of money been considered.

Case 2: Piggyback Probe - per Tank						
Description	Frequency	Start up Cost $ each	Operating Cost $ea.	End Cost $	Annual Cost $	Total $
System Life, years	5					
Monitoring Equip.		5,000			1,000	5,000
Design/Fabrication probe assemblies/tk	3	1,000			600	3,000
Installation		0			0	0
Data Collection/wk	2		100		10,400	52,000
Removal				0	0	0
Inspection				10,000	2,000	10,000
TOTAL		6,000			12,000	70,000

Case 3: Coupon Rack - per Tank						
Description	Frequency	Start up Cost $ each	Operating Cost $ea.	End Cost $	Annual Cost $	Total $
System Life, years	5					
Monitoring Equip.		0			0	0
Design/Fabrication		20,000			4,000	20,000
Installation		30,000			6,000	30,000
Data Collection/wk	0		0		0	0
Removal	2			75,000	30,000	150,000
Inspection	2			30,000	12,000	60,000
TOTAL		50,000			52,000	260,000

Table 9. Cost assessment

Case 4: Piggyback Coupons - per Tank						
Description	Frequency	Start up Cost $ each	Operating Cost $ea.	End Cost $	Annual Cost $	Total $
System Life, years	5					
Monitoring Equip.		0			0	0
Design/Fabrication		5,000			1,000	5,000
Installation		0			0	0
Data Collection/wk	0		0		0	0
Removal	2			75,000	30,000	150,000
Inspection	2			30,000	12,000	60,000
TOTAL		5,000			43,000	215,000

Case 5: Chemical Sampling - per Tank						
Description	Frequency	Start up Cost $	Operating Cost $ea.	End Cost $	Annual Cost $	Total $
System Life, years	5					
Samples, per year	2		60,000		120,000	600,000
TOTAL	10				120,000	600,000

Case 3 — Dedicated Coupons

Assume one dedicated coupon array per tank. Inspection with replacement every 2½ years.

- Costs include:
  - $20K to design and fabricate coupon tree.
  - Installation costs are assumed to be equivalent to Case 1.
  - No weekly monitoring costs.
  - No above ground instrumentation costs.
  - $75K for coupon removal (once per 2½ years).
  - $30K per inspection (once per 2½ years).

Case 4 — Piggyback Coupons

Installation of coupons by mounting on other equipment is much easier than installing probes because there are no requirements for signal cables. Therefore the costs are more simply stated. To remove coupons on schedule, the corrosion monitoring program will bear the removal cost burden.

- Costs include:
  - $5K for design and fabrication.
  - $75K for removal (once per 2½ years).
  - $30K for inspection (once per 2½ years).

Case 5 — Chemical Sampling

The cost consists primarily of sampling and analysis and is estimated, for 2 samples per tank per year, at $60K per sample. The cost of evaluating the data is small (after chemical analysis), several man-hours per year.

Summary of Economic Assessment

From the five year life cycle cost, the use of sampling chemical analysis is by far the most expensive. In Section 2.4, it is also characterized as one of the least effective means of evaluating corrosion.

A piggybacked array of coupons is among the least costly alternatives and is considered, in the long-term, an effective means of monitoring corrosion. Coupons are not effective for providing a rapid indication of changes in waste corrosiveness.

The most effective, and among the least expensive, technique is the use of probes. Further, looking at cost alone, a five year probe program costs about the same as a two year sampling program and provides more information.

2.7 Define Preferred Alternative
[Section Purpose: Describe the final recommended change to the system

Section Summary: A multi-technique corrosion monitoring system is recommended, utilizing ultrasonic and visual examinations for direct evaluation of tank liner condition, probes for rapid detection (alarm) of corrosive conditions, and waste sampling and analysis for determination of corrective action. The probes would incorporate electrochemical noise and linear polarization resistance techniques. When removed from the waste tank, the probe electrodes would be physically examined as corrosion coupons. The probes would be used in addition to a modified regimen of waste sampling and the existing schedule for ultrasonic examination of the tank liners. Supporting information would be obtained by examination of in-tank equipment as it is removed.

The following discussion relates to the summary rankings by data objectives shown in Table 8. In the final corrosion monitoring system, each of the 4 primary data objectives must be represented for both uniform and local corrosion. The survey results indicate, as previously proposed in Section 2, that a complete corrosion monitoring system should include representation from all three primary data sources (direct, surrogate, and inference).

Direct Monitoring

Leak Detection, NDE, and Visual examination rank as the top three techniques of the five evaluated for Direct Monitoring. Leak Detection and Visual Examination are techniques already in use for the DST system. NDE by means of ultrasonic examination is in the final stages of acceptance testing prior to implementation. A program plan for ultrasonic examination of a representative sample of DSTs has been completed [10]. No modification of the use of these three techniques is believed to be necessary to support an enhanced corrosion monitoring program. Moreover, Table 6 indicates that tank wall monitoring and X-ray examination are poorly regarded techniques in comparison to all others. These will not be considered further.

Surrogate Monitoring

Coupons, artifacts, and ER probes are the three most highly ranked techniques for surrogate evaluation of uniform corrosion. Coupons, artifacts and EN probes are the three most highly ranked techniques for surrogate evaluation of local corrosion (pitting and SCC). For rapid detection of changes in the corrosive characteristics of the waste, probes are the only viable option, with ER, LPR, and EN probes ranked most highly for evaluation of both uniform and localized corrosion. ER and LPR probes are only applicable to the monitoring of uniform corrosion. EN probes have been demonstrated to detect uniform corrosion, pitting, and stress corrosion cracking [12, 13]. Since uniform corrosion is not considered a probable tank failure mechanism and uniform corrosion data can be obtained from coupons, LPR probes, and EN probes, resistance probes will not be considered further. EIS was ranked lowest as a monitoring technique and will not be considered further.

The survey results indicate that some program using coupons and artifacts should be used to evaluate waste corrosivity. This technology is well established and the results readily interpretable. Information from coupon studies are not considered timely for detection of changing waste conditions. Coupons and artifacts must be exposed to the waste for extended periods and physically examined to obtain corrosion data. LPR and EN probes are the highest ranked techniques for obtaining timely information on changing waste conditions. These two techniques have a benefit that they can be operated utilizing the same probe configuration and electronic equipment. In general, no additional equipment is required to operate an LPR evaluation if the equipment for an EN evaluation is available.

The survey results suggest that a combination of corrosion coupons and LPR/EN probes will be adequate to monitor corrosion and detect changes in corrosive conditions.

Inference Monitoring

Chemical sampling with analysis for corrosive species and pH are the two most highly ranked inferential techniques in the survey. These two techniques are already in use for corrosion monitoring and control in the DST system. As discussed in Section 1, there have been deficiencies in the implementation of these techniques, and they cannot provide some of the required information for complete corrosion control. However chemical sampling is the only means of identifying a specific chemical deficiency. Redox, conductivity, and optical techniques are not well enough developed to provide such ion specific information. Chemical sampling with pH evaluation should continue to be used as a corrective action tool.

A complete system of corrosion monitoring should be implemented using Direct, Surrogate, and Inferential techniques. Direct monitoring should be used to evaluate DST primary liner condition utilizing the program currently in place. No change in the current implementation of the direct monitoring techniques of ultrasonic examination, visual examination, and leak detection is recommended.

Surrogate methods should be utilized to provide a direct evaluation of corrosion and timely detection of changes in corrosion conditions. One or more probe assemblies with capability for LPR/EN analyses and coupon based assessment should be installed into each DST. The EN and LPR assessments would be used as alarm systems for changes in corrosion conditions and for continuous monitoring of corrosion. The coupon system would be evaluated as necessary to correlate probe response to the well established coupon based evaluation of corrosion. It is proposed that the electrodes used in the LPR/EN probe array (3 electrodes per array) be weighed and measured to provide quantitative uniform corrosion rate data when examined. The surface condition of the electrodes can be examined for pitting attack, and the stressed electrode required for the EN detection of SCC can be examined to confirm the presence or absence of cracking. These electrodes could be replaced individually as examination frequency dictates, or the entire probe assembly could be replaced.

The inferential corrosion monitoring technique of physical sampling and chemical analyses should continue to be used on a corrective action basis. With implementation of a rapid response surrogate corrosion monitoring technique, the frequency of physical sampling would be reduced to an "as necessary" basis when the surrogate indicated an off normal condition. This approach to providing a multi-technique corrosion monitoring system is intended to provide enhanced corrosion information for the DST system, while minimizing the expense of sampling and analysis.

3.0 References

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Appendix A - DST Corrosion Control Limits

From OSD-T-151-0007 [Reference 1]

7.2 UNDERGROUND STORAGE TANKS SPECIFICATION

7.2.1 TANK COMPOSITION

7.2.1.A Temperatures ($T \le 212°F$)

Variable	Specification Limit
For $NO_3^- \le 1.0M$:	
OH^-	$0.010M \le OH^- \le 5.0M$
NO_2^-	$0.011M \le NO_2^- \le 5.5M$
(for solutions below 167°F, the OH^- limit is 8.0M)	
For $1.0M < NO_3^- \le 3.0M$:	
OH^-	$0.1\ (NO_3^-$ Concentration$) \le OH^- < 10M$
$OH^- + NO_2^-$	$\ge 0.4\ (NO_3^-$ Concentration$)$
For $NO_3^- > 3.0M$:	
OH^-	$0.3M \le OH^- < 10M$
$OH^- + NO_2^-$	$\ge 1.2M$
NO_3^-	$\le 5.5M$

7.2.1.B For High Operating Temperatures ($T > 212°F$ for AY and AZ tanks) - Section 7.2.1.A temperature limits apply with the exception that OH^- concentration must be <4M.

&.2.1.C For Tanks 102-AP, 104-AP and 106-AP the following limits may apply:

Nitrite (NO_2^-)	$NO_2^- < 0.005M$
Hydroxide (OH^-)	$0.001M < OH^- < 0.02M$

Providing the following conditions are met:

1) Only "Hanford Facility Wastes" (phosphate and/or sulfate decontamination wastes) may be added to the tanks.
2) All liquid added to the tanks must be <0.005M NO_2^-.
3) Temperature < 122°F.

If these conditions aren't met, the requirements of 7.2.1.A apply.

B. REQUIREMENTS

1. Maintain a material balance for each tank of nitrate, nitrite, and hydroxide concentrations.
2. Update the material balance for each tank and VERIFY material balances against limits.
3. Update the material balance for each tank using sample results and verify against limits.

Appendix B - Tank Corrosion Processes

Research and failure analysis from more than 50 years of operation at the various Department of Energy (DOE) nuclear waste storage sites has indicated that waste tank wall material can become susceptible to pitting corrosion, crevice corrosion, stress corrosion cracking, and unacceptable rates of uniform corrosion as a result of changes in tank operating conditions. The most relevant corrosion related failure mechanisms and the historical basis for concern over these corrosion failures are examined below.

Pitting and Crevice Corrosion

Pitting and crevice corrosion of the waste tanks should be considered in the vapor space, the liquid and sludge regions, and the interfaces between these phases. Available literature indicates that carbon steels in the vapor phase are susceptible to pitting corrosion under dilute waste conditions [1-9]. The chemical composition of the condensed vapor phase on tank walls and equipment in the vapor space is representative of a dilute waste composition. This condition is created when vapor from the waste (carried upwards from the surface by boiling, chemical processes, or air lift) condenses and coats the exposed tank surfaces. Water vapor condensation will dilute and wash dissolved solids back into the liquid phase. The resulting wetted surfaces, equilibrated with air and with the pH modified by airborne carbon dioxide, will be representative of a dilute waste chemistry with pH controlled by the carbonate/bicarbonate buffer (pH $\leq$ 10).

Pitting rates in the range of 2-37 mpy have been observed in Hanford tests, indicating that 0.25 in. Single Shell Tank (SST) wall penetration could take place in as short a time as seven years [2]. However, this evaluation is based on corrosion studies of six months or less. Vapor phase pitting rates have also been shown to rapidly decrease with time [9]. Consequently, short term pitting data may result in an overestimation of the pitting rate and an underestimation of time for wall penetration.

The literature does not show any waste-related crevice corrosion data for the vapor phase, however due to the similarity of mechanisms of pitting and crevice corrosion, crevice corrosion could also be a problem. Potential sites for crevices in waste tanks would be at chunks of attached salt crusts, regions adjacent to the bituminous coatings melted down between the concrete and steel shell (in SSTs), and at the upper wall/ceiling junction.

Studies at SRS have shown that at the vapor-liquid interface caustic solutions, the pH will drop naturally over a period of a few months to pH $\approx$ 10 due to chemical reaction of the hydroxide with atmospheric carbon dioxide [1]. The shift in pH makes this interface region vulnerable to pitting corrosion and possibly crevice corrosion. Recently, SRS personnel have studied the nitrite inhibition of liquid/vapor pitting corrosion, but these studies have not yet determined the pitting corrosion rate [4]. There is a shortage of corrosion rate data for pitting under these conditions; consequently, there are inadequate data for assessing the time for wall penetration by this mechanism.

Corrosion testing within Hanford Site waste tanks has also detected pitting corrosion in the liquid phase [3,8]. Pitting corrosion rates commonly observed were approximately 6 mpy, but there was one poorly substantiated case of 32 mpy. Ondrejcin (1977) estimated the pitting corrosion rate in the SRS evaporator coils to be 1800 mpy if the waste became dilute [2]. At this rate, tank wall penetration could take place within two months. These rates indicate that liquid phase pitting corrosion is an important failure mechanism. Detailed knowledge of the tank chemistry is necessary to predict which tanks would be vulnerable.

The saltcake environment has also been studied [7]. The saltcake is most pertinent to the SSTs, but is similar to the crusts in DSTs. The metal/salt interface resembles a crevice corrosion environment. No pitting or crevice corrosion was observed in these tests, but the hydroxide concentration was not allowed to decrease with time by reaction with carbon dioxide from the air to create the vulnerable condition. Therefore, pitting and/or crevice corrosion at the liquid/solid interface is speculative at this time.

Pitting of carbon steel in contact with liquid wastes containing nitrates can be prevented by adding inhibitors. Nitrite and hydroxide are two inhibitors that will control pitting of carbon steel if present in sufficient concentrations in the waste. Pitting is not generally expected in solutions containing hydroxide at pH > 10. In solutions of pH < 10, pitting can be prevented by the addition of nitrite as demonstrated by the experiments carried out at SRS [4].

Stress Corrosion Cracking

To date, no stress corrosion cracking (SCC) has been reported in waste tank vapor space. However, stressed carbon steels in elevated temperature, high nitrate, low hydroxide (pH ≤ 10) solutions should be susceptible to SCC in the vapor phase when the temperature is ≥ 60°C [10]. Within the DST vapor spaces, there is a low probability that SCC will occur because neither dead weight or residual stresses are high. However, residual stresses are likely to be high in non-stress relieved hanging components; here SCC has a much higher probability of occurrence both in the vapor space and the liquid phase. Because tank vapor chemistry is likely outside the safe-operating specifications recommended by Ondrejcin and Kirch, the potential for SCC cannot be ignored [11, 12]. Even when the bulk tank chemistry is within the Ondrejcin/Kirch specification, the vapor/liquid interface composition may drift into a pH and concentration regime where SCC becomes possible. Three scenarios can be hypothesized: (1) a low hydroxide concentration, from reaction with carbon dioxide, with a high nitrate concentration, (2) a low hydroxide concentration, from reaction with carbon dioxide, and low nitrate and nitrite concentrations due to dilution from condensation, and (3) low hydroxide, nitrate, and nitrite concentrations from raw flush water additions.

Laboratory studies and failure analyses have confirmed SCC to be the dominant failure mode in the liquid phase of the SRS tanks that were not stress relieved [13-16]. Payer also observed SCC in his synthetic salt cake tests [7]. Thus, SCC is the most established failure mechanism for SRS waste tanks. Due to similarities between the failed SRS tanks and the Hanford site SST's, SCC is assumed to be the principle cause of failures in Hanford Site SST's.

The DST's at the Hanford Site may also be susceptible to SCC on the wet side of the tank bottom knuckles due to hydraulic-induced stresses [17]. However, a more extensive investigation into the effects of plate fabrication, welding, heat treatment, and final loading would be required to determine which tanks are most susceptible to future failure by SCC.

Uniform Corrosion

Historical Hanford Site data indicate a maximum uniform corrosion rate of 1.6 mpy at the liquid/vapor interface. A number of other studies at the Hanford Site and SRS in a wide variety of environments, including hypothetical vapor/liquid conditions, indicate that the uniform corrosion rates are < 1 mpy [7-9]. Uniform corrosion, though an actively occurring degradation mechanism, is considered an improbable failure mechanism.

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Appendix C - Discussion of Individual Corrosion Monitoring Techniques

Direct Monitoring Methods

For the purposes of this study, direct monitoring methods were divided into five techniques as follows:

- Photography/visual inspection of tank wall
- Ultrasonic testing of tank wall
- X-rays/neutron based inspection of tank wall
- Direct "on-wall" Corrosion monitoring
- Leak detection of tank wall

Photography or visual inspections of tank walls

Visual inspection typically uses cameras to observe areas of interest. The most frequently used technique has been still photos. In recent years, the use of video cameras has become popular. Commonly the cameras are inserted at the end of a robotic arm and the area is then scanned.

Typical deficiencies of in-tank photography include the inability to obtain high resolution close-up views and the use of 2-dimensional photography. Both lead to uncertainties about what is actually being viewed. Because of these uncertainties, the rate of uniform corrosion on a tank wall cannot be accurately measured. Some relative measure of its progress can be garnered from the comparison of multiple examinations over time. Additionally, only unacceptably gross degrees of pitting and stress corrosion cracking can be determined by in-tank photography. With currently available equipment, visual inspection is essentially a leak detection method.

Ultrasonic testing (UT)

Ultrasonic testing was the only "sound" based method of non-destructive examination considered. Because of the potentially noisy environment, no consideration was given to techniques such as acoustic emission which "listen" to the noise generated by the process (generally cracking, since other forms of localized corrosion, such as pitting, are "silent").

Because the effectiveness of UT depends on the transmission of a high frequency sound pulse and the collection of its echo, the extent to which UT can detect, and measure, cracks, pits, and the extent of uniform corrosion depends on the frequency of the sound used, the alloy, and the location, that is, whether the surface is flat, sharply curved, or contains a weld. Typically however, the size that can be detected is of the order of several tenths of the wall thickness. To be able to detect changes in the feature, pit or crack, the feature has to be even larger. Depending on the feature examined, it may be necessary for it to be "fast" growing, or sufficiently numerous, so that the measurement error will not hide the information.

X-ray and Neutron Techniques

X-ray and neutron techniques are normally not used except for the inspection of newly constructed tanks. The subject was mentioned here in the hope that experts in the field would consider them as feasible. The proposed basis is discussed below.

For DSTs x-rays would not be used, rather the gamma radiation that is produced by the waste may be a source. If it is assumed that the waste is homogeneous, at least over a short range, then the radiation density striking the inner tank surface will be constant over some distance around a point. If this is the case, then thinning of the wall due to uniform corrosion or pitting would allow relatively more radiation to penetrate and the variation could be detected. The unknowns include the effects of adherent corrosion products (would they be equivalent to uncorroded metal and therefore hide the pit and crack) and the presence of liquid waste in pits and cracks.

The second option would be to use a fast neutron source in the annular region of the tank. Fast neutrons would penetrate the steel, with the majority being thermalized and absorbed in the aqueous waste. Some would be reflected back toward the annulus. These neutrons would be absorbed by the steel with more returning to a detector in the thin spots.

Neither of these methods are currently operational and the development costs are unknown, but probably significant.

Direct "on-wall" corrosion monitoring

Direct "on-wall" corrosion monitoring is defined as any method that could use the walls as the sensing element of a corrosion monitor. One representation of this technique is a proprietary method of instrumenting a tank wall with a uniform array of sensing pins from which a "map" of impedance changes between pins would be prepared. As the tank wall corrodes, the impedance between pins would change. From this change, a corrosion mechanism would be inferred.

Leak detection

Leak detection as a corrosion monitoring technique is in a unique position. If a leak is detected, the status of the tank is known - it has failed. It may not be possible to determine the mechanism or actual failure point. If the tank does not leak, no information can be derived from the knowledge - it is not possible to predict when a leak will occur.

Surrogate Monitoring Methods

For the purposes of this study, surrogate monitoring methods were divided into five techniques as follows:

- Corrosion Coupons

- Artifacts
- Corrosion Probes

Corrosion coupons

The use of coupons is the most traditional form of corrosion monitoring. Typically the coupons are made of the same steel as the tank. Relatively small coupons are ideal for uniform corrosion measurements though all past experience has shown that for current waste compositions, uniform corrosion is of little consequence and is well within the design specification.

Detection of pitting with coupons can be problematical. If pitting is not common, insertion of a few square centimeters of coupon surface may not provide sufficient area, compared to the tank which contains on the order of 10^7 cm^2. That is, the probability of pit formation may not be sufficiently great for a pit to form on the coupon.

Stress corrosion cracking specimens typically have to be a special design such as C-rings or U-bends. Past work has shown that plates containing welds as the only source of stress have to be a meter or two in each dimension in order to have sufficient propensity to crack even in the most aggressive waste simulants. On the other hand, U-bend specimens have been shown to crack in waste solutions similar to, though outside, the current composition specifications [3].

Artifacts

The use of artifacts, or, components removed from the tank is also an available technique. The major difficulty with artifacts appears to be obtaining funding to examine them and the lack of a baseline condition from which to compare the after exposure condition. They also tend to be bulky and highly contaminated and not easily examined; coupons are also contaminated but are small enough to be readily cleaned. A further disadvantage is that the steel composition and heat treatment is often significantly different than that of the tank.

Corrosion Probes

Corrosion probes have slowly evolved over the past 50 years. Only four technologies, electrical resistance, linear polarization resistance, electrical impedance spectroscopy, and electrochemical noise are discussed here. Other techniques did not appear to be feasible.

The earliest corrosion probes were the electrical resistance, ER, type probes that are essentially miniaturized, monitored, corrosion coupons. They operate on the basis that as the metal of the coupon is thinned (wire, tube, or sheet), the resistance of the coupon increases. For uniform corrosion only, the resistance is directly proportional to the thickness of metal remaining. Knowing the initial conditions extent of corrosion can be calculated.

Electrical resistance probes are subject to errors due to localized corrosion, but when operated within their stated bounds (general corrosion) are effective. Past experience and the literature show that for current waste compositions, uniform corrosion is not of concern and is well within the design specification [4].

Linear polarization resistance (LPR) probes were first described about 40 years ago. They do not work well in environments where a single anodic (corrosion) reaction is activation controlled. In Hanford type wastes, there is an excellent chance that the corrosion products are highly insoluble and therefore the rate is concentration limited. Insufficient information is available to know the operating limits. The technique is not suitable for detecting pitting or SCC. The LPR probes are generally satisfactory for determination of uniform corrosion rates.

Electrochemical Impedance Spectroscopy (EIS) utilizes a small amplitude AC signal applied to an electrochemical cell. The cell's transfer function is measured over a range of frequencies to evaluate the impedance of the electrochemical interface. This impedance can in some cases be related to the corrosion process at the interface. Because of the probable formation of adherent corrosion product films on surrogate tank steel, it would appear that EIS would be applicable.

The use of electrochemical noise (EN) for the monitoring and detection of localized corrosion processes has received considerable attention over the last several years. The technique involves the monitoring of the instantaneous fluctuations in corrosion current and corrosion potential between nominally identical electrodes during corrosion processes. The technique is unique from most electrochemical corrosion monitoring techniques in that it does not depend on externally applied currents or voltages to generate corrosion information. Thus, uncertainties in data due to unknown effects of applying an outside signal to a specimen are removed.

Any corrosion process is the sum of a series of micro-electrochemical corrosion events. These events can be measured as fluctuations in corrosion (or coupling) current and corrosion potential between electrodes. When recorded over time, different localized corrosion phenomenon present different "fingerprints" of corrosion potential and corrosion coupling current transients. These fingerprints allow for distinction between different types of corrosion events. By recording transients in electrochemical current noise and electrochemical potential noise over time, a qualitative, real-time record of the type and extent of localized and general corrosion events can be collected. The time based record can be converted to frequency based records for further analysis if necessary.

Inference Methods

For the purposes of this study, inference methods were divided into five methods as follows:

- Redox potential
- Chemical analysis
- pH
- Conductivity
- Optical methods

Redox Potential

The solution composition together with the corrosion reaction will define the redox potential. If the corrosion behavior of the steel in the waste is known as a function of the corrosion potential of the steel, and it can be assumed that the solution will force the system potential to the redox potential, then knowing the corrosion potential implies the corrosion behavior. If the value of the potential is in the acceptable range for the steel, then the assumption can be made that the steel corrosion rate is of an acceptable value.

Chemical Analysis

During the past thirty years, several research projects have been carried out at both Hanford and Savannah River which investigated the relationships between waste chemistry and waste corrosivity to carbon steel. These projects developed recommended waste chemistry specifications which minimize tank steel uniform corrosion rates, pitting, or cracking. Effectively, waste maintained to those specifications is expected to be "safe" to store in carbon steel containers. The uncertainty lies in the fact that the simulated waste solutions were made to order and not necessarily analyzed after the fact. Consequently, the specified hydroxide levels may not be what would actually be measured in the simulant. This uncertainty needs to be cleared before making any major decisions on control methodology based on chemistry. Additional information is also needed on whether there are conditions in which variations in nitrate and nitrite concentrations, while within the specification, may still be corrosive.

pH

For waste tank monitoring purposes, bulk pH acts as a measure of hydroxide in solution. Because of the complexity of the wastes, which contain large quantities of phosphates and carbonates as well as other species that impact pH, there is no simple relation between pH and the "amount" of hydroxide. However bulk pH is an indicator of the amount of hydroxide the metal "sees" and could be sufficient information if the relationship between bulk pH, localized pH, and corrosion rate is defined.

Conductivity

The influence of conductivity in DST wastes is not known. In dilute solutions, conductivity plays an important role in controlling the corrosion rate. It is possible that in DST waste, the conductivity is sufficiently high that it is no longer a factor. A question arises in the strongly concentrated solutions however, of whether the concentrations are so high that there is little free water and a conductivity decrease results in a concomitant drop in corrosion rate.

Optical Methods

Optical methods are actually expected to be a variation on some analytical method whether by absorption of species on a "glass" fiber, an in situ spectrophotometric method, or some new process based on some sensor other than corrosion monitors.

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